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Investigating the enhanced kinetics of $LiNi_{0.08}Mn_{1.92}O_4$ cathode material by regulating calcination temperature for long life lithium-ion battery

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ABSTRACT

Various $LiNi_{0.08}Mn_{1.92}O_4$ cathode materials were prepared by a solution combustion method at 500 °C for 1 h combined with two-stage calcination at 600, 650, 700, and 750 °C for 3 h, respectively. Systematic characterization and test approaches were carried out to investigate the effect of calcination temperature on the crystal structure, morphology, electrochemical performance and kinetics properties of the as-obtained $LiNi_{0.08}Mn_{1.92}O_4$ samples. As a result, all the $LiNi_{0.08}Mn_{1.92}O_4$ samples show the intrinsic spinel phase with a good crystallinity. The particles size increases with the increased calcination temperature. Especially, the $LiNi_{0.08}Mn_{1.92}O_4$ sample prepared at 700 °C (LNMO-700) has a great Li^+ ion diffusion coefficient and a low apparent activation energy, resulting in an enhanced kinetics. Owing to these merits, the optimized LNMO-700 cathode material exhibits a high initial discharge capacity of 105.0 mAh g^{-1} and improved retention of 68.6% after 1000 cycles at 1 C, whilst delivers a good rate capability of 95.7 mAh g^{-1} at a high current rate of 5 C.

1. Introduction

Lithium-ion batteries dominate the energy supply market and are widely used in electric vehicles, hybrid electric vehicles and other equipment because of its advantages such as high specific capacity, high operating voltage, small self-discharge, environmentally friendly and memory-less effect [1–3]. Now, one of the most actively used cathode active materials in lithium-ion batteries is spinel $LiMn_2O_4$, in which Mn atoms occupy only half of the 16d octahedral space and Li occupy only one eighth of the 8a tetrahedral gaps. Lithium ions are diffused along the 8a-16c-8a path during charge/discharge process, which promotes fast redox reaction [4]. However, for the commercialization of the $LiMn_2O_4$ cathode material, there stll exists some problems such as poor cycling performance and inferior rate capbility, especially at high temperature 55 °C. These reasons for the rapid capacity fading of the $LiMn_2O_4$ are mainly the Jahn-Teller distortion, the Mn dissolution, the oxygen deficiency and the decomposition of the electrolyte under at high voltage [5–7].

In order to address this problem, element doping is one of the effective methods. The previous considerable work demonstrated that the cation-doping can partially replace the positions of Mn^{3+} or Li^+, so as to effectively improve the structure stability of spinel $LiMn_2O_4$ crystals. Common doping cations including Al^{3+}, Cr^{3+}, Co^{3+}, Mg^{2+}, Ni^{2+}, and so on [8–12]. The Ni-doping has aroused widespread concern of researchers due to its abundant resources, low price, environment-friendly and stable physicochemical properties. The chemical bond of Ni-O (1029 kJ/mol) would be stronger than that of Mn-O (946 kJ/mol), which can lead to the lattice parameter decreased with an increase in the Ni substitution and enhance the stability of octahedral sites in the spinel structure by inhibiting the Jahn-Teller distortion [12,13]. Therefore, the Ni-doping can effectively improve the cycling performance and rate performance of the $LiMn_2O_4$ cathode material [14–16].

It is noticeable that the synthesis methods especially calcination temperature has an important influence on the electrochemical performances of spinel $LiMn_2O_4$. Kebede et al. [15] had reported that the $LiNi_xMn_{2-x}O_4$ (x = 0.1, 0.2) were synthesized using the solution-combustion technique. The product was prepared at 500 °C for 10 min and then calcined at 700 °C for 10 h. The $LiNi_xMn_{2-x}O_4$ (x = 0.1, 0.2)

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showed capacity retention ratio of 99% after 100 cycles at 0.2 C with an initial capacities of 116.4 mAh g^{-1} and 110.5 mAh g^{-1}, respectively. Wang et al. [16] prepared the $LiNi_xMn_{2-x}O_4$ (x = 0, 0.05, 0.10) via a sol-gel method pre-annealed at temperature of 450 °C for 6 h and then calcined at 800 °C for 10 h. The capacity of the $LiNi_{0.05}Mn_{1.95}O_4$ electrode fades from 102 to 89.7 mAh g^{-1}, about 87.9% capacity retention, after 300 cycles at the current density of 300 mAh g^{-1}. Wu et al. [17] prepared the $LiMn_{2-x}Ni_xO_4$ (x = 0–0.06) by a spray-drying method. The as-prepared precursor powders were sintered at 500 °C for 6 h in dry air, and then reannealed at 750 °C for 24 h. The initial discharge specific capacities of the $LiMn_{2-x}Ni_xO_4$ (x = 0.01, 0.02, 0.04, and 0.06) were 118, 116, 106, 102 mAh g^{-1} at 0.1 C, respectively. Raju K et al. [18] introduced the synthesis of the $LiNi_{0.2}Mn_{1.8}O_4$ via a microwave-assisted solid-state reaction at preheated at 500 °C for about 7 min and then annealed at 900 °C for 6 h, the microwave-treated $LiNi_{0.2}Mn_{1.8}O_4$ samples was subjected to microwave irradiation at 600 W for 20 min. The diffusion coefficients of the pristine $LiNi_{0.2}Mn_{1.8}O_4$ and the microwave-treated $LiNi_{0.2}Mn_{1.8}O_4$ were 2.8×10^{-12} and $5.1 \times 10^{-12}\ cm^2\ s^{-1}$, respectively. Although great progress has been made to improve the electrochemical performance through these strategies, the preparation methods to synthesize spinel $LiNi_xMn_{2-x}O_4$ are time-consuming and high sintering temperature that are detrimental to the quality of the final product. Additionally, different calcination temperatures derived spinel $LiNi_xMn_{2-x}O_4$ cathode materials have respective unique structure, hence showing different kinetics properties. Because the rate capability and long cycling performance of the $LiNi_xMn_{2-x}O_4$ cathode is closely associated with its kinetics such as Li^+ ion diffusion coefficient and activation energy. Therefore, introducing an acceptable strategy for the facile synthesis of the $LiNi_xMn_{2-x}O_4$ cathode material is a challenging task, whilst the relationship of kinetic process and electrochemical performance should be investigated synthetically.

In this work, the $LiNi_{0.08}Mn_{1.92}O_4$ cathode materials were prepared by a solution combustion method following by the two-stage calcination. To further understand the reaction mechanism of the material at different temperatures, the Li^+ ion diffusion coefficient and apparent activation energy of the material were calculated using cyclic voltammetric (CV) and electrochemical impedance spectroscopy (EIS) tests. Crystal structure, morphology and electrochemical properties of the $LiNi_{0.08}Mn_{1.92}O_4$ cathodes were also investigated in detail.

2. Experimental

2.1. Preparation of materials

$LiNi_{0.08}Mn_{1.92}O_4$ materials were prepared by a solution combustion method using $LiNO_3$ as a lithium resource, $Mn(CH_3COO)_2{\cdot}4H_2O$ as a manganese resource and $Ni(CH_3COO)_2{\cdot}4H_2O$ as a dopant, respectively. Specifically, the raw materials with a stoichiometric ratio of Li:Mn:Ni = 1:1.92:0.08 were firstly mixed in a crucible and then HNO_3 (AR, KESHI) solution as an auxiliary oxidant with a concentration of 6 mol/L was also added into the crucible. Secondly, the crucible together the reactive materials was preheated at 105 °C in oven to form an uniformly solution [19]. Subsequently, the mixed solution was calcined at 500 °C for 1 h in a muffle furnace using the acetate ions in the raw material as a fuel, and then further calcined at 600, 650, 700 and 750 °C for 3 h, respectively. Finally, four $LiNi_{0.08}Mn_{1.92}O_4$ (denoted as LNMO-x, the x represents calcination temperatures of 600, 650, 700, and 750 °C, respectively) materials were obtained after naturally cooling to ambient temperature.

2.2. Characterization of materials

X-ray diffraction (XRD) patterns were collected on a D8 ADVANCE instrument with Cu Kα radiation from 10° to 70° and at a scan rate of 4°/min (40 kV tube voltage and 40 mA tube current). The phase and crystallinity of the samples were analyzed by XRD data and the unit cell parameters were calculated through the Jade 5.0 software. The particle morphologies of the samples were characterized by a scanning electron microscope (SEM, NOVA NANOSEM 450). The distribution of elemental species was analyzed by energy dispersive spectrometer (EDS). X-ray photoelectron spectroscopy (XPS) was performed on PHI5000 Versaprobe-II X-ray photoelectron spectrometer. The contents of nickel and manganese of the samples were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Teledyne Leeman Labs Prodigy ICP-OES). Transmission electron microscope (TEM, JEM-2100) was performed to further observe the morphology and identify the structure.

2.3. Electrochemical tests of materials

The electrochemical performances were carried out in CR2032 coin-type cells using metallic lithium foil as the counter and reference electrode, the polypropylene microporous film (Celgard 2320) as separator. The cathode electrode was prepared by 80 wt% $LiNi_{0.08}Mn_{1.92}O_4$ active material, 10 wt% carbon, and 10 wt% PVDF dissolved in n-methyl-2-pyrrol-idone (NMP) by ball-mill mixing the active material. The slurry-like mixture is uniformly coated on the aluminum foil with a spatula and dried in an oven at 80 °C for 4 h to obtain the cathode film. Then the film was cut into disks with 16 mm diameter after pressure rolling, the average mass loading was about 2.0 mg cm^{-2}. All as-prepared cathode sheets were further dried at 120 °C overnight in vacuum. The electrolyte was composed of 1 M $LiPF_6$ in a 1:1:1 mixture (volume ratio) of ethylene carbonate (EC), dimethyl carbonate (DMC) and Ethyl methyl carbonate (EMC). All button cells were assembled in a glove box filled with high purity argon gas. The galvanostatic charge-discharge test was performed on the LAND battery test system CT2001A (Wuhan Jinnuo Electronics Co, Ltd) at a current density of 1 C (corresponding to the theoretical capacity of 148 mAh g^{-1}) between 3.0 and 4.5 V (vs. Li^+/Li) at room temperature. Cyclic voltammogram (CV) was tested on an electrochemical workstation (IM6ex, ZAHNER-elektrik GmbH & Co. KG, Kronach, Germany) with a scanning rate of 0.1 mV s^{-1} in the voltage range of 3.6–4.5 V. Electrochemical impedance spectroscopy (EIS) measurements were also determined, which conducted with AC amplitude of 5 mV over the frequency range from 1.0 Hz to 100 kHz. All the electrochemical performances were performed at ambient temperature.

3. Results and discussion

3.1. Structural and morphological characterization

Fig. 1 shows the XRD patterns of various LNMO-x samples. It can be seen that eight characteristic diffraction peaks of spinel $LiMn_2O_4$ are detected obviously, indicating that all samples conform to the cubic spinel structure with a space group of Fd3m (JCPSD No. 35-0782) wherein lithium occupies at 8a tetrahedral sites, manganese and Ni ions occupy the16d sites and oxygen at 32e sites [20]. Table 1 describes the comparation of lattice parameters for all LNMO-x materials. Both the lattice constant and unit cell volume presents an increasing trend with the increased calcination temperature. This result is well consistent with the previous study by Chung et al. [21] and Ma et al. [22]. As they pointed out that the increased lattice parameters are ascribed to the loss of oxygen from the lattice at high temperature. Because the elevated temperature could generate oxygen deficiency, thereby giving rise to an effective increase in the Mn^{3+} content, in comparison to Mn^{4+} content, eventually causing an increase in the *a* value [23]. Particularly, the FWHM values of (400) peak show a decreasing trend as the elevated calcination temperature (Table 1), indicating an increase in crystallinity from LNMO-600 to LNMO-750 samples.

The SEM characterization was performed to observe the influence of different calcination temperatures on the morphology of the