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$LiNi_{0.5}Mn_{1.5}O_4$ nano-submicro cubes as high-performance 5 V cathode materials for lithium-ion batteries

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ABSTRACT

High-voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ is considered the most promising cathode materials for large-scale lithium-ion batteries to meet the fast increasing high energy and power density requirements. However, its commercial applications are restricted due to rigorous capacity fading, particularly at high temperatures. Herein, we propose novel highly uniform nano/submicro $LiNi_{0.5}Mn_{1.5}O_4$ cubes for the first time using cubic $MnCO_3$ precursors, which are prepared via a facile co-precipitation route. The as-synthesized $LiNi_{0.5}Mn_{1.5}O_4$ demonstrates excellent cycle stability and superior rate capability. Specifically, the materials retain a nearly 100% capacity retention after 100 cycles at 25 °C. Moreover, under the elevated temperature of 55 °C, it can deliver a discharge capacity of 131.7 mAh g^{-1} with the specific energy of 605.1 Wh Kg^{-1} and even over 98.4% of primal discharge capacity can be maintained for up to 100 cycles.

1. Introduction

The rapid increasing demand of lithium ion batteries for portable electronic devices, electric vehicles (EVs), and hybrid electric vehicles (HEVs) requires the cathode materials with higher energy and power density, lower cost, higher thermal stability and longer lifetime [1–4]. Recently, high-voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials are considered as prospective candidates to meet such requirements owing to high working potential (~4.7 V), large specific capacity of 147 mAh g^{-1}, and fast three dimensional Li^+ migration channel [5–13]. The high working potential at around 4.7 V, making its energy density (650 Wh/kg) higher than that of conventional $LiMn_2O_4$ (410–530 Wh/kg) and $LiFePO_4$ (520 Wh/kg) cathode materials [14–18]. These fascinating characteristics, along with the environmental friendliness, have made this cathode a potential preference for the next-generation of high-performance batteries. On the other hand, its commercial applications are hampered by severe capacity fade due to Mn^{2+} dissolution into the electrolyte, particularly at elevated temperatures and still a huge challenge to attain concurrently superior rate capacity and cyclability for $LiNi_{0.5}Mn_{1.5}O_4$ because of intricate performance-influencing factors [19–23]. Because the deterioration in cell performance results from the electrode materials, rational cathode architecture design offers a more direct, easy, practical, and potentially satisfied approach to overcome these limitations [6,7].

Recently, the nano-submicro architecture holds the crux to achieve simultaneously superior rate capacity and cyclability because the nano-sized subunits can markedly shorten the chemical diffusion distance of Li and the submicro-sized assemblies can guarantee structural stability, leading to enhanced electrochemical performances [24–26]. In our previous reports, nano-submicro architecture electrode materials have exhibited excellent rate capability and improved cycle performance [27–30]. Therefore, nano-submicro electrode material can be anticipated to effectively enhance the cycling stability and simultaneously improve the rate capability. Unfortunately, nano/submicro cube-like architecture of $LiNi_{0.5}Mn_{1.5}O_4$ has not been reported until now.

Herein we report a facile co-precipitation method, coupled with lithiation reaction, to synthesize novel nano/submicro $LiNi_{0.5}Mn_{1.5}O_4$ cubes for the first time. The co-precipitation reaction represents a convenient, facile and fast chemical approach, in which $MnCO_3$ cube precursors were first synthesized, after which lithiation reaction was implemented to obtain

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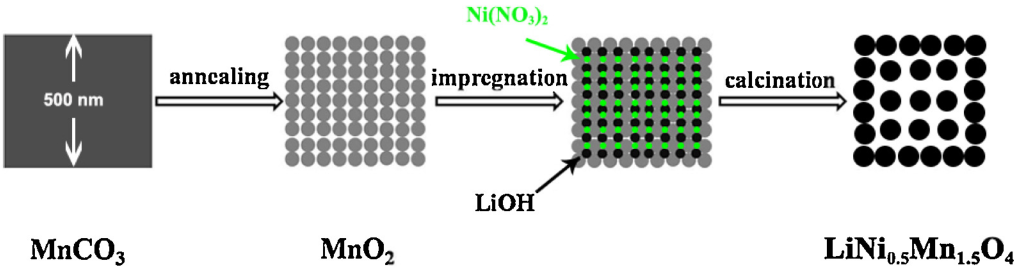

Fig. 1. Graphic representation of the synthesis of cubic $LiNi_{0.5}Mn_{1.5}O_4$.

$LiNi_{0.5}Mn_{1.5}O_4$ at 750 °C. The obtained submicron $LiNi_{0.5}Mn_{1.5}O_4$ cubes are about 500 nm in size, and consist of interconnected nano-sized subunits. These cathode materials exhibit excellent cycling stability and superior rate capability, retaining 99.5% capacity retentions for up to 100 cycles at 1C under the temperature of 25 °C. These samples deliver discharge specific capacity of 116.0 mAh g^{-1} at 5C rate and 25 °C, corresponding to capacity retention of 98.1% after 100 cycles and coulombic efficiencies are almost 100%. Furthermore, under the elevated temperature of 55 °C, it can deliver a discharge capacity of 131.7 mAh g^{-1} with the high specific energy of 605.1 Wh Kg^{-1} and even over 98.4% of primal discharge capacity can be maintained for up to 100 cycles. With the increase in current density there was a slight decrease in the discharge capacity. The values of discharge capacities are 121.4 to 117.3, 114.4, 111.3, 108.1, and 89.5 mAh g^{-1} at current densities of 1, 2, 3, 4, 5, and 10C, respectively. After measuring the device at a higher current density, it was switched to 1C again and the LIB can still deliver a discharge capacity of 118.7 mAh g^{-1}.

2. Experimental

2.1. Preparation of $LiNi_{0.5}Mn_{1.5}O_4$

Firstly, the submicron cubic $MnCO_3$ precursors were fabricated through the method reported by our group [28]. Specifically, 0.1 mmol $MnSO_4$ was added in 7 mL de-ionized (DI) water. The $MnSO_4$ solution was stirred using a magnetic stirrer and an amount of 35 mL ethanol was added to the solution and a complete dispersion was obtained after few minutes. Afterwards, a solution of 1 mmol NH_4HCO_3 dissolved in 7 mL deionized water was added to the above solution. The magnetic stirring was kept on for about 15 minutes. Later on centrifuge was utilized to obtain the $MnCO_3$ cubes. The mixture was washed three times using DI water and ethanol to eliminate any possible contaminations. In order to obtain MnO_2 cubes the obtained product was annealed at 400 °C. The obtained MnO_2 cubes were dispersed in ethanol by using appropriate stoichiometric amount of $Ni(NO_3)_2{\cdot}6H_2O$ and $LiOH{\cdot}H_2O$. In order to dry the product it was kept at room temperature until completely dried out. At last, a manual grounding of the obtained mixture was performed for about 5 minutes and annealed at different temperatures for 12 h.

2.2. Characterization

The phase purity and crystallographic analysis of the obtained products were studied with the help of PANalytical X-pert diffractometer (PANalytical, Netherlands) with Cu Ka radiation. The structure and morphological features of the product were analyzed using Hitachi field emission scanning electron microscopy (FESEMS, Hitachi S-4800). The crystalline nature of the product was studied using Transmission electron microscopy (TEM) (FEI Tecnai G2 F20, 200 kV).

2.3. Electrochemical measurements

The Electrochemical measurements were carried out in accordance with our previous report [28]. The cell was fabricated in a glove-box where the environment was well controlled. In order to make cathode, the as-prepared materials, carbon black and polyvinylidene fluoride (PVDF) were mixed thoroughly and used in a ratio of 80:10:10 wt%, respectively. To make slurry, the mixture was well dissolved in N-methyl-2-pyrrolidone (NMP) solution. Afterwards, the obtained slurry was coated on an Aluminum foil using doctor-blade method. The foil was then dried overnight in an oven at 120 °C. The Charge-discharge measurements were performed on a CT2001A Land battery testing system. The measurements were carried out at various current rates between 3.5–5.0 V.

3. Results and discussion

Fig. 1 schematically illustrates a morphology-inheritance avenue to prepare nano-submicro $LiNi_{0.5}Mn_{1.5}O_4$ cubes. Firstly, the cubic submicron $MnCO_3$ precursors were synthesized by a simple and fast co-precipitation method. Subsequent annealing of $MnCO_3$ precursors yielded MnO_2 caused by CO_2 release from carbonate decomposition. Then, stoichiometric amounts of $Ni(NO_3)_2{\cdot}6H_2O$ and $LiOH{\cdot}H_2O$ were implanted into the MnO_2 cubes by impregnation and calcination, leading to the $LiNi_{0.5}Mn_{1.5}O_4$ cubes.

The formation of submicron $MnCO_3$ and MnO_2 precursor cubes were demonstrated by SEM (Fig. S1) and XRD (Fig. S2), consistent with the previous report [28]. Fig. 2 demonstrates the XRD graphs of the finishing product $LiNi_{0.5}Mn_{1.5}O_4$ which was obtained from the solid state reaction at different temperatures. All the patterns display sharp diffraction peaks at similar positions. The sharp diffraction peaks can be indexed and are in agreement with the

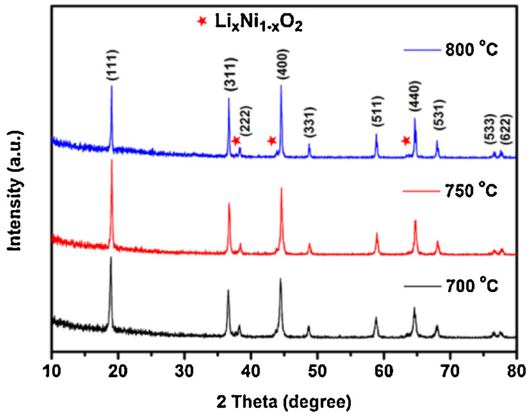

Fig. 2. X-ray diffraction curves of $LiNi_{0.5}Mn_{1.5}O_4$ prepared at different temperatures.