Abstract

A novel and simple solid state synthesis of layered LiNi0.5Mn0.5O2 directly from a mixture of LiOH, NiO and MnO2 prepared by ball milling is reported. The mixtures of precursors were heated at temperatures from 400 to 1000 °C in air to synthesize the compound. The heat treatment process and the crystal structure of the synthesized material were investigated by TG/DTA and X-ray diffraction (XRD) methods. The well-crystallized LiNi0.5Mn0.5O2 powder of single phase was prepared at 1000 °C. Morphology of the synthesized material was investigated using field emission scanning electron microscopy (FESEM). X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV) measurements were carried out on the synthesized LiNi0.5Mn0.5O2 powder suggesting that the oxidation states of Ni and Mn in LiNi0.5Mn0.5O2 be +2 and +4, respectively. Galvanostatic charge–discharge behavior of the Li/LiNi0.5Mn0.5O2 cell in the voltage range 2.5–4.3 V at a current rate of 0.1 mA cm−2 exhibited a stable discharge capacity of ~120 mAh g−1 with a very small capacity fading for 10 cycles.

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1. Introduction

Layered lithium nickel manganese oxides have recently been reported as promising positive electrode materials for advanced lithium-ion batteries due to their potential for very high capacity, relative safety and affordability [1–4]. In LiNi0.5Mn0.5O2, the nickel- and manganese-ions have a valence state of +2 and +4, respectively, as suggested by a first-principles study [5], and later confirmed by X-ray photoelectron spectroscopy (XPS) [6,7] and X-ray absorption near-edge fine structure (XANES) results [8]. This compound has a rhombohedral layered structure with space group R3m, but about 8–10% Ni and Li ions interchange their sites in the layered structure, which is often referred to cation mixing and observed in this compound synthesized at high temperature [1,9].

Though this material may have a good future in the use for lithium-ion batteries, it is not easy to prepare electrochemically active LiNi0.5Mn0.5O2. Until recently, a mixed hydroxide method [2,3], which gives one-to-one solid solutions of Ni(OH)2 and Mn(OH)2, is developed to be the most commonly used method to synthesize this material. Recently, a new method has been developed to synthesize this layered LiNi0.5Mn0.5O2 by heating a mixture of nickel acetate, manganese acetate and lithium acetate prepared in a solution [6,7,10]. However, no paper reported to ever try to synthesize this material through solid state reaction directly from mixture of metal hydroxides or metal oxides with physical mixing.

In this work, a simplified synthesis route for layered LiNi0.5Mn0.5O2 is developed. We report preparation of layered LiNi0.5Mn0.5O2 compound directly from a mixture of LiOH, NiO and MnO2 through ball milling technique. The synthesis conditions, the crystal structure and electrochemical properties of this compound are investigated in this paper.

2. Experimental

LiOH (99%, Alfa Aesar), NiO (99%, Alfa Aesar) and MnO2 (99.9%, Alfa Aesar) were used as the starting materials. A one-to-one mixture of NiO and MnO2 were loaded into a container and ball-milled for 2 h to get a well mixed nickel and manganese oxides with a homogeneous distribution. A stoichiometric amount of LiOH was then added into the container and another 2 h ball milling was performed on the mixture. The ball milled mixture was cold-pressed into pellets. Six pellets were prepared and heated in air respectively at 400, 600, 700, 800, 900 and 1000 °C for 12 h, and then slowly cooled to room temperature.
The thermogravimetric analysis and differential thermal analysis (TG/DTA) were performed on the final mixture using a Shimadzu DTG-60H at a scan rate of 10 °C min⁻¹ in the temperature range between 30 and 800 °C. The structure and crystallinity of the synthesized powders at different temperatures were investigated by a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα radiation. The data were collected in the 2θ range of 10–80° at a scan rate of 2° per min. The morphology of the synthesized powder was investigated by a field emission scanning electron microscope (FESEM, HITACHI S6100). X-ray photoelectron spectroscopy (XPS) of the synthesized powder was performed with a Kratos AXIS Hs spectrometer with a Mono Al X-ray source (1486.6 eV). The collected spectra were analyzed using XPSPEAK41 fitting software. The energy scale was adjusted based on the graphite peak in the C 1s spectrum at 284.6 eV.

Electrochemical measurements were carried out using a Solartron 1287 two terminal cell test system with a Lab-made Swagelok cell. The working electrode consisted of 80% LiNi₀.₅Mn₀.₅O₂, 10% acetylene black and 10% PTFE binder, while a lithium foil was used as both counter and reference electrodes. One molar LiPF₆ in ethyl carbonate/dimethyl carbonate solution (EC/DEC, 1/1 vol%) Ozark Fluorine Specialties, Inc.) was used as the electrolyte. Cyclic voltammetric measurements were carried out at a sweep rate of 0.1 mV s⁻¹ in the potential range 2.5–4.3 V at a current rate of 0.1 mA cm⁻². Galvanostatic charge/discharge cycling experiments were performed in the LiPF₆ in ethyl carbonate/dimethyl carbonate solution (EC/DEC, 1/1 vol% Ozark Fluorine Specialties, Inc.) while a lithium foil was used as both counter and reference electrodes. One molar

3. Results and discussion

TG/DTA curves obtained for the precursor of the final mixture prepared by ball milling are shown in Fig. 1. It can be seen that there are three obvious endothermic peaks on the DTA curve at the peak temperatures of 80, 228 and 466 °C, respectively. At the same temperatures of the first two endothermic reactions, two significant weight loss stages were clearly observed. The first endothermic peak occurring at 80 °C is ascribed to the removal of hydroxyl. The second endothermic peak occurring at 228 °C is ascribed to the removal of hydroxyl. The third endothermic peak occurring at 466 °C, accompanying a slight weight loss, should correspond to the formation of the LiNi₀.₅Mn₀.₅O₂ compound. The slight weight loss stops till 600 °C, which means the formation of the LiNi₀.₅Mn₀.₅O₂ compound is finished at 600 °C. Further heating from 600 to 800 °C did not induce any phase change.

Fig. 2 presents the XRD spectra of all the synthesized powders obtained by heating the final mixture at 400, 600, 700, 800, 900 and 1000 °C. It can be seen that the LiNi₀.₅Mn₀.₅O₂ compound has not been formed until heated above 600 °C, which agrees the above TG/DTA analysis. However, the newly formed LiNi₀.₅Mn₀.₅O₂ at low temperature shows low crystallinity even by heating to 800 °C. XRD spectra through Fig. 2b to d show relatively broad peaks indicating extremely fine crystallite size and low crystallinity. The XRD peaks start to become sharp and intensity of peaks starts to increase remarkably when heating temperature is above 800 °C. Well crystallized LiNi₀.₅Mn₀.₅O₂ was prepared by heating the mixture at 1000 °C (Fig. 2f). All diffraction peaks were indexed based on the α-NaFeO₂ structure (R₃m). Further, the existence of doublets at (0 0 6), (1 0 2), (1 0 8) and (1 1 0) clearly confirms the layered crystal structure of the as synthesized powder at 1000 °C. The lattice parameters of the synthesized powder at 1000 °C were determined to be a = 2.895 Å and c = 14.308 Å by using the least square fits. Both the diffraction peaks and lattice parameters of the synthesized LiNi₀.₅Mn₀.₅O₂ are in good agreement with those reported in literature [7,9,11]. It was found that the ratio of the integrated intensities of (0 0 3) to (1 0 4) peaks (I₀₀₃/I₁₀₄) is only slightly lower than unity thereby suggesting only a small amount of cation mixing existing in the material. Since the value of I₀₀₃/I₁₀₄ depends on the degree of the displacement between ions located at the 3(a) and 3(b) sites in a space group of R₃m, this value was a measure to estimate reactivity of lithium insertion materials for a series of LiNiO₂ families. According to Ohzuku and Makimura [9], a low value of I₀₀₃/I₁₀₄ is an indicator of poor electrochemical reactivity due to high concentration of inactive rock-salt domains in a layered solid matrix.

The morphology of the synthesized LiNi₀.₅Mn₀.₅O₂ observed using FESEM is shown in Fig. 3. It can be seen that individual particles are of submicron size between 100 and 200 nm and some of them aggregate to form big particles. Such morphology is quite similar to that of the powder synthesized using the mixed hydroxide method [3,9].

For a layered LiNi₀.₅Mn₀.₅O₂, the oxidation states of Ni and Mn are +2 and +4, respectively [5]. To determine the oxidation states of Ni and Mn in the material prepared by our ball milling
method, XPS measurements were carried out on the synthesized LiNi_{0.5}Mn_{0.5}O_{2} powder. The XPS spectra of Ni 2p_{3/2} and Mn 2p_{3/2} in LiNi_{0.5}Mn_{0.5}O_{2} are shown in Fig. 4. The XPS spectrum of Ni 2p_{3/2} shows the characteristic peak at 854.5 eV, which is similar to the binding energy of Ni^{2+} in NiO [12]. A satellite peak with the binding energy at 860.5 eV was also observed, which is due to the multiple splitting in the energy levels of the nickel oxides [6,7]. The XPS spectrum of Mn 2p_{3/2} shows the characteristic peak at 642.1 eV, which is similar to the binding energy of Mn^{4+} in \( \lambda \)-MnO_{2} [4]. There is also a satellite peak with the binding energy at 653.6 eV was observed for Mn 2p_{3/2} in the LiNi_{0.5}Mn_{0.5}O_{2}. The above data are in good agreement with the results reported in the literature [4,6,7]. Therefore, it can be concluded that the oxidation states of Ni and Mn in this compound are +2 and +4, respectively.

Two continuous cyclic voltammograms (CV) of the Li/LiNi_{0.5}Mn_{0.5}O_{2} cell are shown in Fig. 5. Two major peaks at 4.0 and 3.6 V for anodic scan and cathodic scan, respectively, were observed, representing lithium deintercalation and intercalation processes. It is noted that no redox-reaction peaks are observed near 3 V in the CV, indicating that Mn ions are electrochemically inactive and present +4 oxidation state in the sample. The current increase above 4.8 V is due to the oxidation of the electrolyte. Therefore, the observed peaks near 4 V are attributed to the redox reaction of Ni^{2+}/Ni^{4+} as discussed by Lu et al. and Kang et al [3,4]. The CV results also suggest that Ni and Mn ions in the LiNi_{0.5}Mn_{0.5}O_{2} are present as Ni^{2+} and Mn^{4+}, respectively, which is consistent with the XPS results.

In order to examine the electrochemical reactivity and stability of LiNi_{0.5}Mn_{0.5}O_{2}, 10 cycles charge/discharge were carried out at low-rate. Fig. 6a shows the charge/discharge curves for the 10 initial cycles between 3 and 4.3 V at a current rate of 0.1 mA cm\(^{-2}\). On starting the charge process, the voltage of the cell suddenly increased to ~3.9 V and then slowly increased up to 4.3 V, which is similar to the voltage profile of LiCoO_{2}. Similar voltage profile was also observed by other research groups [1–4]. From starting the discharge process, the voltage of the cell quickly dropped to about 4 V, which indicates a big polarization due to the resistance of the cell. Kang et al. [4] reported that LiNi_{0.5}Mn_{0.5}O_{2} showed high impedance, which means a relatively slow Li diffusion in this material. That is why a slow rate for charge/discharge is often used in LiNi_{0.5}Mn_{0.5}O_{2} cathode. It can be seen that the voltage profiles of the first charge/discharge cycle showed a slight difference with subse-
Fig. 6. (a) Charge/discharge curves of Li/LiNi$_{0.5}$Mn$_{0.5}$O$_2$ cell operated in voltage range 2.5–4.3 V at a current rate of 0.1 mA cm$^{-2}$. (b) Capacity vs. cycle number of Li/LiNi$_{0.5}$Mn$_{0.5}$O$_2$ cell for 10 cycles.

quent ones. The first charge capacity is about 150 mAh g$^{-1}$ based on LiNi$_{0.5}$Mn$_{0.5}$O$_2$ sample weight, and the first discharge capacity is about 122 mAh g$^{-1}$, exhibiting a capacity loss of about 28 mAh g$^{-1}$ during the first charge/discharge cycle. For subsequent cycles, a reversible capacity of about 120 mAh g$^{-1}$ was maintained with about 98% of charge–discharge coulombic efficiency. As shown in Fig. 6b, the Li/LiNi$_{0.5}$Mn$_{0.5}$O$_2$ cell shows good cycle performance between 3 and 4.3 V at the current rate of 0.1 mA cm$^{-2}$ with a very small capacity fading rate about 0.2% per cycle during 10 cycles. According to literature [4,7], a reversible capacity of $\sim$120–130 mAh g$^{-1}$ was obtainable in the voltage range 2.5–4.2 (or 4.3) V from the high temperature synthesized LiNi$_{0.5}$Mn$_{0.5}$O$_2$. Our results are in good agreement with those reported the literatures.

4. Summary

Layered LiNi$_{0.5}$Mn$_{0.5}$O$_2$ cathode material can be directly synthesized from a mixture of LiOH, NiO and MnO$_2$ prepared by a ball milling method. The XRD results confirm the layered structure of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ synthesized at 1000°C. XPS and CV results suggest that the oxidation states of Ni and Mn in LiNi$_{0.5}$Mn$_{0.5}$O$_2$ to be +2 and +4, respectively. The synthesized material exhibits good cycle performance in the voltage range 2.5–4.3 V with a reversible capacity of 120 mAh g$^{-1}$ for 10 cycles.

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References