Preparation of lithium nickel manganese oxide cathode material for 5V-class high-voltage batteries by a microwave heating method

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Lithium nickel manganese oxide cathode material, LiNi_{0.5}Mn_{1.5}O_{4}, was prepared by an improved microwave heating method. Prepared cathode materials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), and charge-discharge measurements. XRD results indicated that single-phase LiNi_{0.5}Mn_{1.5}O_{4} powders were obtained under the optimized preparation conditions. SEM investigation demonstrated that the powders had an octahedron shape and a particle size of about 200–300 nm. The obtained LiNi_{0.5}Mn_{1.5}O_{4} exhibited good electrochemical performance and delivered an initial discharge capacity of 145 mAh g⁻¹ at a current density of 20 mAg⁻¹.

Key-words : Lithium-ion secondary batteries, Cathode material, Lithium nickel manganese oxide, Microwave heating method

Lithium-ion batteries have become the primary power source for most portable electronic devices. The faster technologies are developed, the greater the worldwide demand for higher performance batteries. The transition to new applications, such as electrical and hybrid electric vehicles, will require going beyond what the present state of batteries can achieve in terms of density. One possible solution for realizing high-energy density is the use of cathode materials with high voltage output, such as lithium nickel manganese oxide, LiNi_{0.5}Mn_{1.5}O_{4}. LiNi_{0.5}Mn_{1.5}O_{4} is considered one of the most promising cathode materials for lithium-ion batteries due to its acceptable thermal stability, environmental friendliness, and most importantly, its high discharge plateau of about 4.7 V.

Recently, many methods have been reported for preparing LiNi_{0.5}Mn_{1.5}O_{4}, including solid-state reaction, sol–gel technique, molten-salt synthesis, hydrothermal treatment, spray pyrolysis, and precipitation. We developed a unique synthetic method using microwaves that is promising for the preparation of cathode materials. In this technique, unlike in other heating methods, the microwaves produce higher temperatures inside the product than on its surface. Also, because the material is heated throughout its volume, high uniformity of warming is possible, as well as more precise temperature regulation. This method can quickly achieve a uniform reaction at the level of the atom and molecule in order to synthesize multicomponent materials and correctly controlled metal oxide. A few studies on the preparation of LiNi_{0.5}Mn_{1.5}O_{4} using microwave irradiation have been reported. However, in these reports, an elaborate synthesis process was necessary for the precursor materials before microwave irradiation. In addition, the electrochemical performance of prepared LiNi_{0.5}Mn_{1.5}O_{4} cathode material was insufficient. In this study, we report an improved microwave heating method for preparation of LiNi_{0.5}Mn_{1.5}O_{4}, using a simplified precursor process.

All chemical reagents used in this study were analytical grade. LiNi_{0.5}Mn_{1.5}O_{4} precursor was prepared by dissolving lithium nitrate, nickel (II) nitrate hexahydrate and manganese (II) nitrate hexahydrate with a molar ratio of Li:Ni:Mn = 0.1:0.05:0.15 in distilled water to form a mixed aqueous solution. The solution was then heated in a microwave under various conditions, such as an irradiation time from 3–15 min with air or oxygen flow. Microwave irradiation was supplied by a microwave oven operating at 2.45 GHz under a maximum power of 700 W. The obtained sample was ground in an agate mortar and left to dry before various characterization tests were performed.

The crystalline structures and phase composition of the prepared samples were determined by X-ray diffraction analysis (XRD; D8 Discover, Bruker AXS) using Cu Kα radiation at 40 kV. Fourier transform infrared spectroscopy (FT-IR; IRAffinity-1, Shimadzu) was used to investigate the chemical bonding of the samples. The particle size and morphologies of the samples were measured using a field-emission-type scanning electron microscope (FE-SEM; S-4800, Hitachi).

The prepared LiNi_{0.5}Mn_{1.5}O_{4}, acetylene black (AB), and polytetrafluoroethylene (PTFE), were mixed with a weight ratio of 70:20:10. The material was then rolled to form a thin sheet and cut into 12-mm diameter discs to make the cathode. A coin-type cell was assembled in an argon atmosphere with the LiNi_{0.5}Mn_{1.5}O_{4} cathode, a lithium metal anode, and a 1M LiPF₆ electrolyte in a 1:1 solvent mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC). The charge–discharge measurements of the cell were evaluated at a constant discharge current density of 20 mAg⁻¹ with a charge–discharge voltage limit of 3.0–4.9 V at 25°C.

Figure 1 shows the XRD patterns of the samples prepared by the microwave heating method for 3, 9, and 15 min. Every sample looks more or less like a single-phase spinel structure. The results confirmed that spinel LiNi_{0.5}Mn_{1.5}O_{4} powder can be
directly prepared by a simpler microwave heating method than has been previously reported. With an increase in heating time to 15 min, the samples showed rather sharper diffractions. Heating time in excess of 15 min did not show any changes in the data. It was thus assumed that the ideal microwave heating time with 700 W of power was 15 min.

It has been reported that preparation temperature and atmosphere are key factors to obtaining LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with a high electrochemical performance. Samples were prepared with the flow of O$_2$ in the microwave heating process. Figure 2 shows the surface temperatures of samples prepared without [Fig. 2(a)] and with [Fig. 2(b)] the flow of O$_2$. Sample (a) rose to temperatures of 900°C and then dropped gradually. In sample (b), surface temperature rose to about 700°C in less than a minute. The flow of O$_2$ not only enriched the atmosphere with the required O$_2$ for the reaction, but also played a role in cooling the material and maintaining it at the idle temperature of 700°C proven best for this material in other papers.

Figure 3 shows the XRD patterns of both samples prepared without [Fig. 3(a)] and with [Fig. 3(b)] the flow of O$_2$, compared to LiNi$_{0.5}$Mn$_{1.5}$O$_4$ prepared by a conventional heating method using an electric furnace [Fig. 3(c)]. Samples (a) and (b) both show the proper peaks and are really close to the peaks heights of sample (c). As mentioned above, every sample looks more or less like a single-phase spinel structure. This implied that the microwave heating method was reliable and produced almost the same results as that of a conventional heating method.

Figure 4 contains SEM photographs of the samples prepared by the microwave heating method without [Fig. 4(a)] and with [Fig. 4(b)] the flow of O$_2$. Both samples were composed of small particles whose morphologies were almost the same as the spinel reported in another paper. Sample (a) had smaller particles about 50–300 nm in diameter, while sample (b), which maintained temperatures of 700°C, was composed of somewhat larger particles with an octahedron shape, growing to about 200–300 nm in diameter. The surface of the particles in sample (b) appeared to become smooth, which indicated an improvement of the intrinsic structure of the particles.

A charge and discharge test was applied to all 3 products, as shown in Fig. 5. Samples (b) and (c) both showed a one-plateau curve with a high potential at the 4.7 V region. However, the sample (a) product had two plateaus in the discharge curve, one with a high potential at the 4.7 V region, and the other in the 4V region. The plateau at 4.7 V has been ascribed to the two-step...
voltage of 4.6 V and a capacity of 120 mAh g\(^{-1}\), and (c) LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) prepared by the conventional heating method.

In conclusion, LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) was prepared by a simplified microwave heating method. The prepared LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) can be classified as the typical cubic spinel structure with a simple phase. Also, applying a flow of O\(_2\) during the microwave heating improved the crystallinity and morphology of the structure in the LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) sample, resulting in significant improvement of electrochemical properties by extending the output potential at the 4.7 V region, and producing a total capacity of 145 mAh g\(^{-1}\).

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