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, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, 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 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders were obtained under the optimized preparation conditions. SEM investigation demonstrated that the powders had an octahedron shape and a particles size of about 200–300 nm. The obtained $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited good electrochemical performance and delivered an initial discharge capacity of 145 mAh g^{-1} at a current density of 20 mA g^{-1} .

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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, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.¹⁾ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 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.^{2)–5)}

Recently, many methods have been reported for preparing $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, including solid-state reaction, sol–gel technique, molten-salt synthesis, hydrothermal treatment, spray pyrolysis, and precipitation.^{6)–16)} We developed a unique synthetic method using microwaves that is promising for the preparation of cathode materials.^{17),18)} 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 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using microwave irradiation have been reported.^{18)–20)} However, in these reports, an elaborate synthesis process was necessary for the precursor materials before microwave irradiation. In addition, the electrochemical performance of prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material was insufficient. In this study, we report an improved microwave heating method for

preparation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, using a simplified precursor process.

All chemical reagents used in this study were analytical grade. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ precursor was prepared by dissolving lithium nitrate, nickel (II) nitrate hexahydrate and manganese (II) nitrate hexahydrate with a molar ratio of $\text{Li}:\text{Ni}:\text{Mn} = 0.1:0.05:0.15$ 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 $\text{Cu K}\alpha$ 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 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, 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 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode, a lithium metal anode, and a 1M LiPF_6 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 mA g^{-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 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder can be

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Fig. 1. XRD patterns of the samples prepared for (a) 3 min; (b) 9 min; and (c) 15 min using the simplified precursor and the microwave heating method.

Fig. 2. Surface temperatures of the samples prepared (a) without the flow of O_2 and (b) with the flow of O_2 in microwave heating process.

directly prepared by a simpler microwave heating method than has been previously reported.¹⁸⁾ 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.²¹⁾ 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.^{21),22)}

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

Fig. 3. XRD patterns of samples prepared (a) without the flow of O_2 , (b) with the flow of O_2 and (c) $LiNi_{0.5}Mn_{1.5}O_4$ prepared by the conventional heating method using an electric furnace.

Fig. 4. SEM photographs of the samples prepared by the microwave heating method (a) without the flow of O_2 , and (b) with the flow of O_2 .

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.¹⁶⁾ 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 4 V region. The plateau at 4.7 V has been ascribed to the two-step

Fig. 5. Initial discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared by the microwave heating method (a) without the flow of O_2 , (b) with the flow of O_2 , and (c) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared by the conventional heating method.

Fig. 6. FT-IR spectra of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared by the microwave heating method (a) without the flow of O_2 , (b) with the flow of O_2 , and (c) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared by the conventional heating method.

($\text{Ni}^{4+}/\text{Ni}^{3+}$, $\text{Ni}^{3+}/\text{Ni}^{2+}$) redox reactions, and the plateau at 4V to the presence of a residual amount of Mn^{3+} in the spinel.²³⁾ Both samples (a) and (b) showed similar results in terms of output voltage of 4.7 V and a capacity of 145 mAh g^{-1} , which is about 97.5% of the theoretical capacity. Sample (c) had an output voltage of 4.6 V and a capacity of 120 mAh g^{-1} . Details of its electrochemical properties and reaction mechanism are still under investigation and will be reported in the near future.

Figure 6 shows FT-IR spectra of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared by the microwave heating method without (a) and with (b) the flow of O_2 , and (c) shows the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared by a conventional heating method. The spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has two space groups, referring to the $\text{P4}_3\text{32}$ group representing Mn and Ni ion ordering in the 12d and 4a sites, and the $\text{Fd}\bar{3}\text{m}$ group indicating the random occupation of Mn and Ni ions in the 16d sites of the octahedral.²⁴⁾ FT-IR spectroscopy was applied to differentiate the ordered vs. disordered structures of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples in the frequency range from $400\text{--}700 \text{ cm}^{-1}$.²⁴⁾ The vibration bands of Mn–O and Ni–O were located at 621 and 588 cm^{-1} , respectively, and the characteristic bands from $400\text{--}530 \text{ cm}^{-1}$ appeared in the $\text{P4}_3\text{32}$ phase.^{22),24)} Samples (b) and (c) showed similar peaks in this area, which proves that they had the $\text{P4}_3\text{32}$

phase ordering the cation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Sample (a) showed the same base peaks in the $400\text{--}700 \text{ cm}^{-1}$ region; however, those peaks were much smaller. The smaller peaks indicated that the sample had undeveloped crystals making its structure disordered.

In conclusion, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was prepared by a simplified microwave heating method. The prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 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 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 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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