

LiNi_{0.4}Mn_{1.6}O₄ Cathode For Rechargeable Lithium Batteries with 5 V

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Spinel Mn oxide has been investigated as cheap cathode material of rechargeable lithium batteries. However, its discharge and charge cycleability was not good enough for practical cells. Many excellent efforts have been done to improve it. In such studies, some researchers have found that LiMe_xMn_{2-x}O₄ exhibits 5 V operation voltage. This high voltage cathode may improve an energy density of rechargeable lithium batteries. However, this high voltage may lead to a decomposition of nonaqueous electrolytes used in rechargeable lithium batteries. This decomposition should occur on a cathode material surface. Therefore, the performance of these 5 V cathode materials should depend on their particle nature, such as size, surface area, and shape. In this study, two different starting materials were adopted to prepare LiNi_{0.4}Mn_{1.6}O₄ particles with different particle sizes.

MnO₂ (Aldrich) and Mn₃O₄ (Nanotek Co.) were used as Mn sources. LiOH·H₂O was used as Li source. NiO was used as Ni source. The Mn, Ni, and Li sources were mixed with an atomic ratio of 1:0.4:1.6 and then heated at 750 (MnO₂) or 1000 (Mn₃O₄) °C for 24 h under air atmosphere. Two prepared samples were analyzed with x-ray diffraction method to investigate their crystal structures. Figure 1 shows the x-ray diffraction patterns of two LiNi_{0.4}Mn_{1.6}O₄. Both samples have a spinel structure. From two patterns, it can be said that both samples have the same crystal structure. On the other hand, the crystal shapes were completely different each other. Figure 2 shows the scanning electron micrographs of two LiNi_{0.4}Mn_{1.6}O₄ samples. The particle size of LiNi_{0.4}Mn_{1.6}O₄ prepared from Mn₃O₄ was ten times smaller than that prepared from MnO₂. In this way, LiNi_{0.4}Mn_{1.6}O₄ particles with two different sizes were prepared by using different Mn sources.

Figure 3 shows the discharge and charge curves of two LiNi_{0.4}Mn_{1.6}O₄ particles in a mixed solvent of ethylene carbonate and ethyl methyl carbonate (1:1 in volume) containing 1.0 mol dm⁻³ LiPF₆. The discharge and charge rates were 0.1 C. In both discharge and charge curves, two voltage regions were observed. This indicates that a substitution of Mn ions by Ni ions results in an appearance of 5 V voltage region. The 5 V and 4 V voltage regions for LiNi_{0.4}Mn_{1.6}O₄ particles prepared from Mn₃O₄ were 100 mA h g⁻¹ and 30 mA h g⁻¹, respectively. Those for LiNi_{0.4}Mn_{1.6}O₄ particles prepared from MnO₂ were 70 mA h g⁻¹ and 50 mA h g⁻¹, respectively. This result might be explained from a kinetic problem. In order to investigate this point, the discharge and charge curves for LiNi_{0.4}Mn_{1.6}O₄ particles prepared from MnO₂ was measured at 0.05 C rate and shown in Figure 3 (dotted curves). However, the discharge and charge curves were not so different from those measured at 0.1 C. This result indicates that the difference in capacities at 5 V and 4 V regions is not due to a kinetic problem. Therefore, it may be proposed that the difference in discharge and charge curves is caused by a thermodynamic reason that is related to structural change. In order to investigate the structural change occurring on both LiNi_{0.4}Mn_{1.6}O₄ particles was measured with x-ray diffraction method. In the range from x=0 to x=1 in

Li_{1-x}Ni_{0.4}Mn_{1.6}O₄, any extra peaks were not observed. All x-ray diffraction patterns were basically assigned to spinel structure. The shift of peaks was only observed during the discharge and charge processes. This peak shift was reversible, indicating that ideal insertion and extraction of Li⁺ ions took place on both Li_{1-x}Ni_{0.4}Mn_{1.6}O₄ particles. In conclusion, the appearance of 5 V region is not only determined from chemical composition of cathode material, but also influenced by particle size.

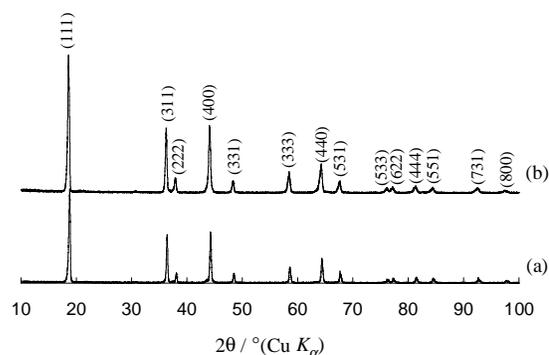


Figure 1 X-ray diffraction patterns of LiNi_{0.4}Mn_{1.6}O₄ prepared from (a) Mn₃O₄ and (b) MnO₂.

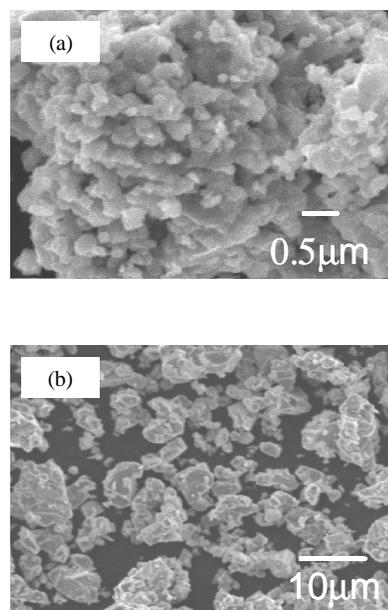


Figure 2 Scanning electron micrographs of LiNi_{0.4}Mn_{1.6}O₄ prepared from (a) Mn₃O₄ and (b) MnO₂.

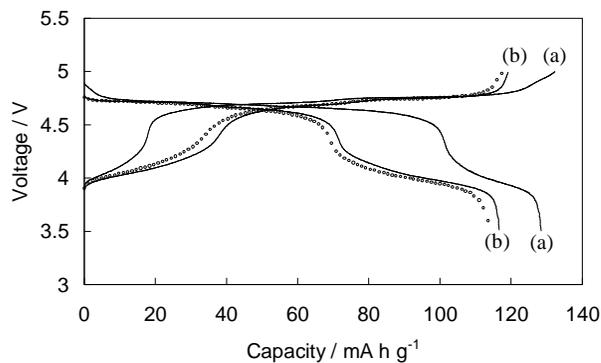


Figure 3 Discharge and charge curves of LiNi_{0.4}Mn_{1.6}O₄ prepared from (a) Mn₃O₄ and (b) MnO₂ at 0.1 C, dotted curves at 0.05 C