

# Electrochemical Properties of $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ by Microwave-assisted Sol-gel Method

Yong Joon Park\* and Seuk Buom Kim

*Department of Advanced Materials Engineering, Kyonggi University, San94-6, Yiui-dong, Yeongtong-gu, Suwon, Gyeonggi 443-760, Republic of Korea*

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$\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  cathode materials have been synthesized by a microwave-assisted sol-gel method. The structure and electrochemical properties of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  were studied by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and charge-discharge cyclers. The powder prepared by microwave assisted sol-gel method showed good crystallinity and well-defined facet shapes. The  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode delivered a high discharge capacity of  $230 \text{ mAhg}^{-1}$  at the specific current of  $40 \text{ mA g}^{-1}$  (0.2 C rate) in the voltage range of 2.0–4.8 V. About 60 % of the discharge capacity measured at 0.2 C rate ( $140 \text{ mAhg}^{-1}$ ) was maintained at a 6 C ( $1200 \text{ mA g}^{-1}$ ) rate. The cyclic property was also stable and it did not deteriorated at a high C rate.

**Keywords:** Cathode, Lithium battery, Microwave, Electrochemical property, Sol-gel

## 1. INTRODUCTION

A microwave synthesis method was developed to prepare cathode materials for lithium batteries[1-7]. In the microwave irradiation field, uniform and rapid heating can be achieved within several minutes, since the microwave energy is absorbed directly by the bulk of the heated object and the reaction time can be decreased. With these considerations, a microwave-assisted sol-gel method has been used to synthesize  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  cathodes. The synthesis of  $\text{LiMn}_2\text{O}_4$ [1,2],  $\text{LiCoO}_2$ [3],  $\text{LiNiO}_2$ [4],  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ [5],  $\text{LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$  (M=Cr, Co)[6] and  $\text{LiFePO}_4$ [7] have been tried by a microwave or microwave-assisted method. However (to the best of the author's knowledge) the synthesis of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  and the derivative systems by microwave-assisted method have not been noted. Mn based layered oxides such as  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  for lithium-ion batteries are under intense investigation due to a higher specific capacity than commercial cathode material such as  $\text{LiCoO}_2$ [8-10]. The substitution of some portion of transition metal ion by a lithium ion on transition metal layer leads to a high discharge capacity. In addition, Mn based layered oxides have low cost, safety, and environmental compatibility. In this study, the structural and electrochemical properties of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  synthesized by microwave-assisted sol-gel method were investigated using X-ray diffractometry (XRD), scanning electron microscopy (SEM) and a charge-discharge cycling system. The thermal stability of the electrode was also measured by differential scanning calorimeter (DSC) analysis.

## 2. EXPERIMENT

$\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  was prepared by a microwave-assisted sol-gel method from manganese acetate tetrahydrate  $[\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}]$ , nickel(II) nitrate hexahydrate

$[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , lithium nitrate  $[\text{LiNO}_3]$  and lithium acetate dihydrate  $[\text{CH}_3\text{CO}_2\text{Li} \cdot 2\text{H}_2\text{O}]$ . The starting materials were dissolved in distilled water and mixed with 5 wt% high surface area carbon black to enhance the heating rate[7]. The solution was heated to  $100^\circ\text{C}$  until it formed a viscous gel. The gel was placed in the microwave oven and heat treated for 20 minutes with a microwave power of 650 W. The obtained powder was ground and heated at  $900^\circ\text{C}$  in air for 5 hours in the furnace. Then, it was quenched to room temperature. Powder images were observed by scanning electron microscopy (SEM 535M, Philips). The surface area of the powder was determined by Brunauer-Emmett-Teller (BET) analysis using a surface area and porosity analyzer.

For the preparation of positive electrode, 0.4 g of polyvinyl difluoride (Aldrich) was dissolved in about 12.5 g of N-methyl-2-pyrrolidone for 1 hour and then 4 g of sample powder and 0.6 g of Super P black (MMM Carbon Co.) were added. After 24 hours of ball mill process, viscous slurry was coated on an aluminum foil using a doctor blade and dried at  $90^\circ\text{C}$  in an oven. The thickness of the cathode film was about  $30 \mu\text{m}$ . The electrochemical cell was assembled in a dry box using the above positive electrode, lithium, porous polyethylene film, and 1M  $\text{LiPF}_6$  solution in a 1:1 volume ratio of ethylene carbonate/dimethyl carbonate. Cells were subjected to galvanostatic cycling using a WonATech charge-discharge system before and after storage.

XRD patterns of the cathode were obtained using a Philips X-ray diffractometer in the  $2\theta$  range of  $15^\circ$  to  $70^\circ$  with monochromatized Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). DSC samples of the cathode were prepared by the following treatment before the test. The cells containing sample electrodes were charged to 4.6 V or 4.8 V at the current density of  $40 \text{ mA g}^{-1}$ , and were held at that potential until the current density reached to  $4 \text{ mA g}^{-1}$ . Then these cells were disassembled in a dry box to remove the charged positive electrodes. 4.5 mg of the positive electrode and  $3 \mu\text{l}$  of fresh electrolyte were sealed in a high-pressure DSC pan. The heating rate and temperature range of the DSC tests were  $5^\circ\text{C}/\text{min}$  and  $25\text{-}300^\circ\text{C}$ , respectively.

\* Author to whom corresponding should be addressed: electronic mail: yjpark2006@kyonggi.ac.kr

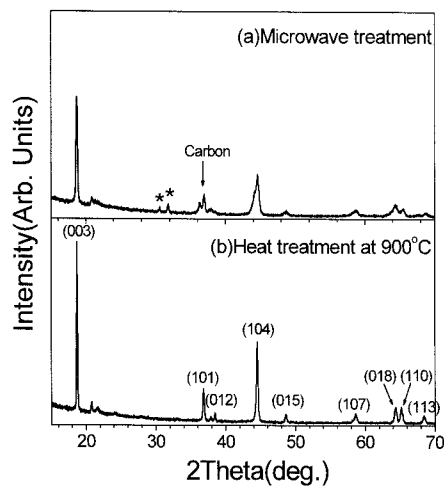


Fig. 1. XRD pattern of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  prepared by microwave-assisted sol-gel method. (a) Only microwave treatment (b) After heat treatment at  $900^\circ\text{C}$ .

### 3. RESULTS AND DISCUSSION

Figure 1 shows the XRD diffraction pattern of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder prepared by microwave-assisted sol-gel method. The powder obtained by only microwave treatment for 20 min. is displaying O3 layered structure (Fig. 1(a)). However, the diffraction pattern attributable to O3 phase was so broad, the carbon and other unidentified phase (marked by \*) were also detected. In preparation, 5 wt% of carbon black was added in the precursor gel, because carbon is known to exhibit an extremely high heating rate when subjected to microwave irradiation. This was effective in increasing the heating rate. However, the oxidation of carbon black during microwave heat treatment can create a reductive atmosphere, which leads to reduction of manganese or nickel ions. A microwave heating of pure precursor gel without carbon was tried, but the heating rate was too slow and the final temperature of precursor was not enough to burn out organic materials. Therefore, another heat treatment at  $900^\circ\text{C}$  was introduced to the powder obtained by microwave treatment for preparing a stable layered structure of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ . The XRD patterns for the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder after heat treatment at  $900^\circ\text{C}$  turned clear and all impurity peaks disappeared (Fig. 1(b)). All of the diffraction peaks were assigned to the typical O3 layered structure.

Figure 2 shows the SEM images of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder after heat treatment at  $900^\circ\text{C}$ . The particles seem to be crystalline with well-defined facets that have a wide range of size distribution. The small particles were  $0.2\ \mu\text{m} \sim 0.5\ \mu\text{m}$ , but the largest was  $2\ \mu\text{m}$ . The microwave heats not from the outside but from the inside of the precursor and provides a uniform heating environment that led to good structural shape and small particle size. However, some particles agglomerated during heat treatment at  $900^\circ\text{C}$ , which created large particles. The surface area determined by Brunauer-Emmette-Teller (BET) analysis was  $1.26\ \text{m}^2/\text{g}$ .

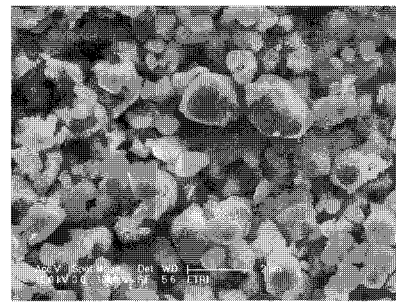


Fig. 2. Scanning electron microscopy (SEM) images of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  prepared by a microwave-assisted sol-gel method.

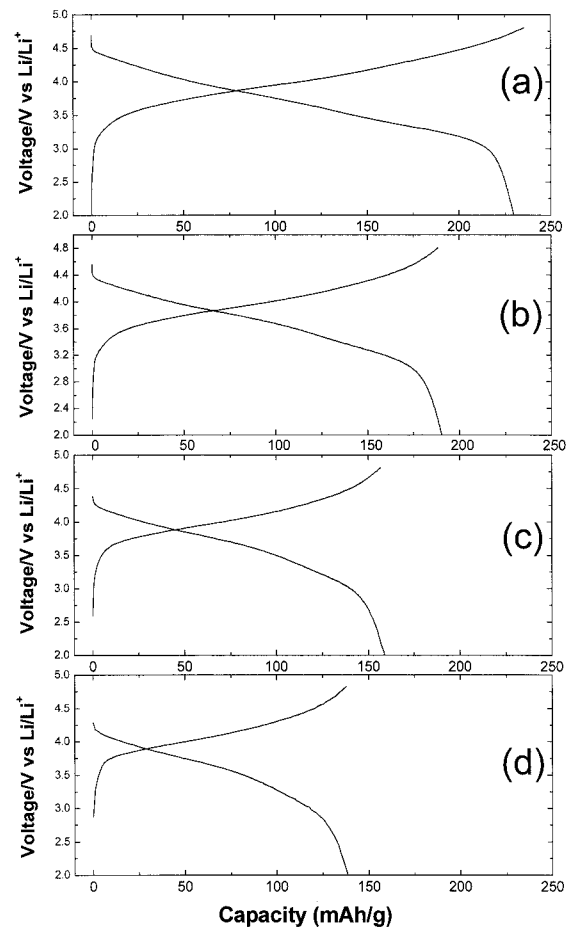


Fig. 3. Charge and discharge profile of the cell containing  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode at different current rates (0.2 C, 1 C, 3 C and 6 C rate). Voltage range 2.0–4.8 V.

The electrochemical properties of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode were measured by charge-discharge cycles. Figure 3 displays the voltage versus specific charge-discharge profiles of the cell containing the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode at different current rates (0.2 C, 1 C, 3 C and 6 C rate). The profiles were measured after initial charge process to 4.8 V at 0.2 C rate to eliminate the effect of irreversible phase change, which is observed in  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  [10]. Generally, the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode showed an irreversible long plateau at around 4.5 V in the initial charge process, which vanished

during subsequent cycling process. The origin of this plateau has been previously noted[8]. The discharge capacity of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode was  $230 \text{ mAhg}^{-1}$  at the specific current of  $40 \text{ mA/g}^{-1}$  (0.2 C rate) in the voltage range of 2.0 ~4.8 V. As expected, the capacity decreased as the specific current density increased. The discharge capacity at 1 C ( $200 \text{ mA/g}^{-1}$ ), 3 C ( $600 \text{ mA/g}^{-1}$ ), 6 C ( $1200 \text{ mA/g}^{-1}$ ) rate was about 185, 160, and  $140 \text{ mAhg}^{-1}$ . The ratio of capacity at the 6C / 0.2 C rate was about ~60 %. This rate is a relatively good performance considering the surface area of powder ( $1.26 \text{ m}^2/\text{g}$ ). We have reported the effect of surface area on rate capability of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode prepared by another method (simple combustion method)[11]. Generally, a large sample surface area makes the electrolyte accessible to a wider region of the active material and it can enhance the rate capability of the cell[12,13]. Moreover, this phenomenon will be more prominent at much faster charge/discharge rates. According to the previous work[11], the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder prepared by simple combustion method clearly showed surface area effect on rate capability. The ratio of capacity at 6 C / 0.2 C rate (capacity retention) of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder with surface area of 9.6, 7.3 and  $4.0 \text{ m}^2/\text{g}$  was ~64, ~60 and ~52 %, respectively[11], which clearly showed the rate capability was deteriorated as the surface area of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder decreased. Although the surface area was just  $1.26 \text{ m}^2/\text{g}$ , the capacity retention of the sample prepared by microwave-assisted sol-gel method was ~60 %. This is a similar value to the capacity retention of the sample prepared by a simple combustion method with surface area of  $7.3 \text{ m}^2/\text{g}$ . Although it could deliver a high rate capability, a large surface area of cathode powder may be accompanied by some disadvantages such as a degrading of the cycle life and thermal stability of the electrode. It is likely that increased interaction of the interlayer region between the active material and electrolyte can result in an increased dissolution of metal ions and surface reaction with the electrolyte, which may lead to unstable cyclic performance and thermal instability. So the powder having both high rate capability and low surface area would be better than the powder having one of them.

As mentioned earlier, 5 wt% of carbon black was added in the gelation process, so if there is remaining residual carbon after heating process, the capacity and rate capability can be improved due to an increase of electrical conductivity. The sample was heat treated at  $900 \text{ }^\circ\text{C}$  under air, so the amount of residual carbon is minimal. However, the small amount of carbon in the powder, which did not react with air yet, may positively affect the rate capability. The cyclic performance of the cell containing  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode at different current rates (0.2 C, 1 C, 3 C and 6 C rate) is shown in Fig. 4. At a low current rate of 0.2 C, the discharge capacity of the cell was saturated at about  $200 \text{ mAhg}^{-1}$  after a small capacity loss during the initial several cycles. The cyclic performance did not deteriorate at a high current rate. Over  $110 \text{ mAhg}^{-1}$  of discharge capacity was retained during 50 cycles, even at a high current density of  $1200 \text{ mA/g}^{-1}$  (6 C rate).

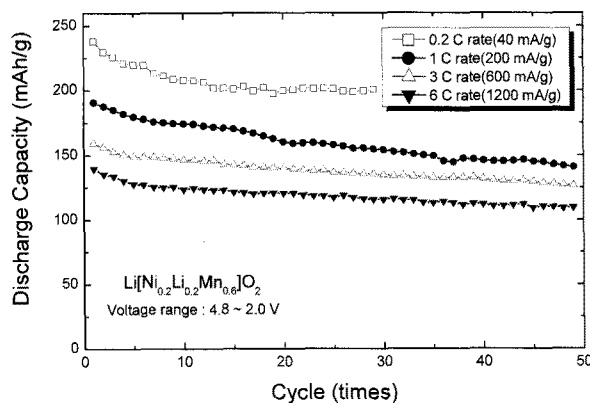


Fig. 4. Cyclic performance of the cell containing  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode at different current rates (0.2 C, 1 C, 3 C and 6 C rate). Voltage range 2.0~4.8 V.

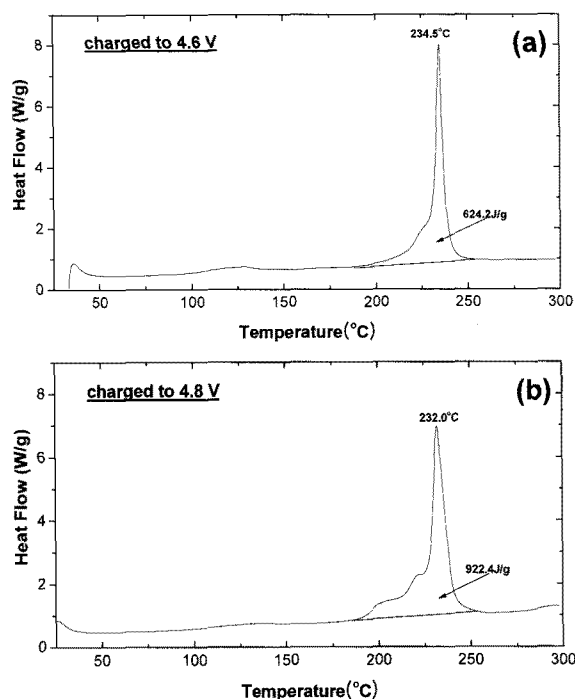


Fig. 5. Differential scanning calorimetry (DSC) profile of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode. (a) Charged to 4.6 V; (b) Charged to 4.8 V.

As shown in Fig. 5, thermal stability of a charged  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode was tested by performing differential scanning calorimetry (DSC) measurement. All samples were cycled 1 time between 2.0~4.8 V to eliminate the effect of irreversible phase change in the initial cycle, and then charged to 4.6 V and 4.8 V, respectively. The sample charged to 4.6 V started thermally reacting with the electrolyte at around  $180 \text{ }^\circ\text{C}$  and proceeded to a thermal runaway at  $\sim 234 \text{ }^\circ\text{C}$  (Fig 5(a)). The exothermic peaks produced  $\sim 642 \text{ Jg}^{-1}$  of heat. The exothermic peaks of the sample charged to 4.8 V produced a slightly higher heat ( $922 \text{ Jg}^{-1}$ ). However, the difference of the shape of the peaks was minimal except a small peak at around  $200 \text{ }^\circ\text{C}$ .

#### 4. CONCLUSION

Li[Ni<sub>0.2</sub>Li<sub>0.2</sub>Mn<sub>0.6</sub>]O<sub>2</sub> cathode powder was synthesized via the microwave assisted sol-gel process. The XRD study of the material has confirmed that an O3 layered structure formed during a microwave treatment that followed a heating process. The electrochemical test of the sample has shown that it has a high discharge capacity and stable cyclic properties. The discharge capacity of the sample electrode was ~230 mAhg<sup>-1</sup> at the specific current of 40 mA g<sup>-1</sup> (0.2 C rate) in the voltage range of 2.0~4.8 V. It was saturated to ~200 mAhg<sup>-1</sup> after 30 cycles. The discharge capacity decreased to ~140 mAhg<sup>-1</sup> at 6 C (1200 mA g<sup>-1</sup>) rate, but the cyclic performance did not deteriorate at a high C rate.

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