

Structural and Electrochemical Characteristics of $\text{Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ Synthesized using Sol-Gel Method

Ki Soo Park, Myung Hun Cho, Sung Jang Jin, Chi Hoon Song and Kee Suk Nahm[†]

School of Chemical Engineering and Technology, College of Engineering,
Chonbuk National University, Chonju 561-756, Korea
(Received 29 May 2003 • accepted 20 September 2004)

Abstract—Layered O2-lithium manganese oxide ($\text{O2-Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$) was prepared by ion-exchange of P2-sodium manganese oxide ($\text{P2-Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$). $\text{P2-Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ precursor was first synthesized by using a sol-gel method, and then $\text{O2-Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ was produced by an ion exchange of Li for Na in the $\text{P2-Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ precursor. Structural and electrochemical analyses suggested that good quality $\text{O2-Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ was prepared from $\text{P2-Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ synthesized at 800 °C for 10 h using glycolic acid as a chelating agent. During the cycle, the discharge profile of the synthesized samples showed two plateaus at around 4 and 3 V, respectively, with a steep slope between the two plateaus. The discharge curve at 3 V escalated with an increase in the cycle number, presenting a phase transition from a layered to a spinel like structure. The sample prepared at 800 °C for 10 h using glycolic acid delivered a discharge capacity of 187 mAh/g with small capacity fading.

Key words: Sol-Gel Method, Chelating Agent, Glycolic Acid, Adipic Acid, Layered Structure, Lithium-ion Battery

INTRODUCTION

The LiMn_2O_4 spinel and its derivatives have attracted much attention as a promising material for rechargeable lithium batteries because of their high voltage, low cost, and nontoxicity [Thackeray, 1997; Ohzuku et al., 1990; Guyomard et al., 1994]. One of most significant drawbacks of the spinel manganese oxides is a low discharge capacity due to their inherent structures [Jang et al., 1996, 1997; Franger et al., 2000]. Recently, layered LiMnO_2 has been intensively investigated as a new layered cathode material because of its reversible production of high discharge capacity. The preparation of layered LiMnO_2 has commonly been attempted by ion exchange of layered alkali bronze A_xMnO_2 ($\text{A}=\text{K}, \text{Na}$) with lithium because layered LiMnO_2 is unstable at high temperatures.

According to a phase diagram of Na_xMnO_2 developed by Parant et al. [1971] and Delmas et al. [1982], layered alkali bronzes Na_xMnO_2 can exist with many different structures, i.e., layered phases ($\alpha\text{-NaMnO}_2$ (P3), $\alpha\text{-Na}_{0.7}\text{MnO}_2$ (P2), and $\beta\text{-NaMnO}_2$ (P3)) and channel structures ($\text{Na}_{0.44}\text{MnO}_2$). Owing to this structural property, ion exchange of Li for Na in Na_xMnO_2 produces a variety of layered bronzes Li_xMnO_2 ; LiMnO_2 (O3) from NaMnO_2 and $\text{Li}_{0.7}\text{MnO}_2$ (O2) from $\text{Na}_{0.7}\text{MnO}_2$, respectively.

For layered LiMnO_2 , which normally adopts an O3 structure with the space group C2/m , the stacking of oxygen atoms follows the cubic, close packed (ccp) structure which the stable spinel structure exhibits. However, the LiMnO_2 is apt to transform into a stable spinel phase even with minor cationic rearrangements occurring during the first removal and subsequent cycling of Li, causing the degradation of electrode performance. On the other hand, layered Li_xMnO_2 with an O2 structure, which has the most symmetric hexagonal space group $\text{P6}_3/\text{mmc}$, is thermodynamically stable compared with the

O3- LiMnO_2 structure. This is why layered Li_xMnO_2 with an O2 structure is recently of great interest as a cathode material for rechargeable lithium batteries.

The synthesis of layered Li_xMnO_2 with an O2 structure has been studied by Dhan's group using a solid-state reaction [Paulsen, 1971, 1999, 2000; Lu et al., 2000, 2001]. They first prepared layered $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ (P2 structure) from stoichiometric amounts of Mn_2O_3 , Li_2CO_3 , and Na_2CO_3 using a solid state reaction, and then ion-exchanged the prepared $\text{P2-Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ in a boiling solution of 5 M lithium bromide dissolved in hexanol to form the layered O2 structure. They investigated the correlation between structure, composition, and electrochemical properties of the crystalline $\text{Na}_{0.7}[\text{Li}_x\text{Mn}_{1-x}]\text{O}_2$, and asserted that the material is a layered oxide with T2 structure [Paulsen, 2000; Lu et al., 2000, 2001]. They observed that small deviations cause less ordered samples showing T2-O2 intergrowth structures, and reported that the disordered T2 structure obtains the best electrochemical result, approximately 170 mAh/g [Paulsen, 2000]. They also investigated the effect of different Li/Na ratios on the structure and reported an optimum Li/Na ratio [Paulsen, 2000].

In this work, we report the synthesis of layered $\text{O2-Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ using a sol-gel method. A $\text{P2-Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ precursor was first synthesized by a sol-gel method, and then $\text{O2-Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ was prepared by an ion exchange of Li for Na in the $\text{P2-Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ precursor. The synthesis of $\text{P2-Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ precursor was carried out at various calcination temperatures using different chelating agents. Structural and electrochemical characterizations of the synthesized samples were performed with various analytic techniques.

EXPERIMENT

1. Synthesis of $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ Powders by a Sol-gel Method

A $\text{P2-Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ precursor was synthesized using a sol-

[†]To whom correspondence should be addressed.
E-mail: nahmks@moak.chonbuk.ac.kr

gel method as previously reported [Park et al., 2002, 2004]. Sodium acetate ($\text{CH}_3\text{CO}_2\text{Na}$, Aldrich), lithium acetate ($\text{Li}(\text{CH}_3\text{COO})\cdot 2\text{H}_2\text{O}$), and manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$) salts were employed as starting materials for the synthesis of the $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ powders. Stoichiometric amounts of sodium, lithium, and nickel acetate salts were dissolved in DI water with a cationic ratio of Na : Li : Mn = 0.7 : 1/6 : 5/6. The dissolved solution was added drop by drop into a continuously agitating aqueous chelating agent. The chelating agents used in this synthesis were adipic and glycolic acids. The molar ratio of chelating agent to total metal ions was fixed at unity. The pH of the solution was adjusted to be in the range of 2.5–3.5 for the adipic acid by adding acetic acid, and 8.5–9.5 for the glycolic acid by adding ammonium hydroxide. The prepared solution was evaporated at 70–80 °C for 5 h until a transparent sol was obtained. As water evaporated further, the sol turned into a viscous transparent gel. The resulting gel precursors were heated with a ramping rate of 1 °C/min and decomposed at 450 °C for 10 h in air to eliminate organic components. The obtained powders were calcined at the temperature range of 700–1,000 °C in a flow of air for 10 hours. After the calcination process, the powders were suddenly quenched in liquid N_2 . In this work, we named the $\text{P2-Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ precursors prepared at 700, 800, 900, and 1,000 °C as samples A, B, C, and D for adipic acid, and samples E, F, G, and H for glycolic acid.

2. Preparation of $\text{Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ Powders by a Ion Exchange

The prepared precursor powders ($\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$; 5 g) were introduced into a mixed solution of hexanol (150 ml) and lithium bromide (LiBr; 55 g). Ion exchange of Na in $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ with Li was carried out at 160 °C for 3 hours under an Ar environment in a batch reactor equipped with a reflux condenser to prepare $\text{O2-Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$. After the reaction, the solution was filtered using an aspirator under vacuum and the remaining powders were washed with methyl alcohol. The washed powders were dried at 180 °C for 10 h in a vacuum oven. In this work, samples A–I, B–I, C–I, D–I, E–I, F–I, G–I, and H–I are $\text{O2-Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ prepared from samples A, B, C, D, E, F, G, and H by ion-exchange.

3. Characterization of $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ and $\text{Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ Powders

Powder X-ray diffraction (XRD, D/Max-3A, Rigaku) measurements using $\text{Cu-K}\alpha$ radiation was performed to characterize the structural properties of the synthesized powders.

The electrochemical characterization was carried out using CR2032 coin-type cells. The test cells were assembled by the following method: the cathode was fabricated with an accurately weighed active material (20 mg) and conductive binder (13 mg). It was pressed on 25 mm² stainless steel mesh used as the current collector at 300 kg/cm² and dried at 200 °C for 5 hours in an oven. This cell was composed of a cathode and a lithium metal anode (Cyprus Foote Mineral Co.) separated by a porous polypropylene film used as the separator (Celgard 3401). The electrolyte used was a 1 M LiPF_6 -ethylene carbonate (EC)/dimethyl carbonate (DMC) (1 : 2 by volume). The cells were assembled in an argon-filled dry box and tested at room temperature. The cell was charged and discharged at a current density of 0.4 mA/cm² with cut-off voltages from 2.0 V to an upper voltage of 4.2 V (vs. Li/Li^+). After 2–3 charge-discharge cycles, the upper voltage was sequentially increased by 0.2 V until 4.8 V was reached.

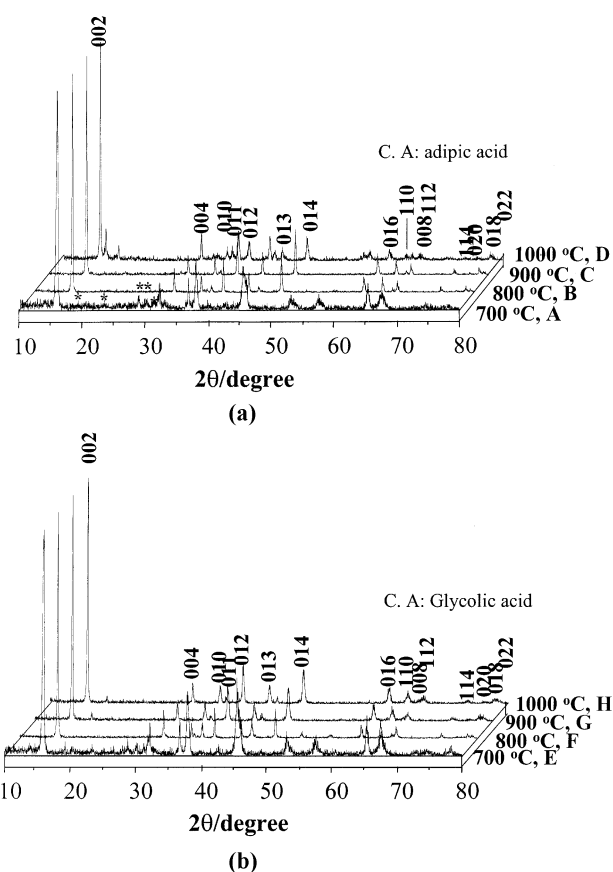


Fig. 1. XRD spectra for $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ precursors synthesized using (a) adipic and (b) glycolic acids at 700, 800, 900, and 1,000 °C, respectively.

RESULTS AND DISCUSSION

1. $\text{P2-Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ Powders

$\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ powders were synthesized at 700, 800, 900, and 1,000 °C, using adipic and glycolic acids for chelating agent. The $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ powders were synthesized with a Li composition of 1/6. Literature reports that lithium is soluble in $\text{Na}_{0.7}[\text{Li}_x\text{Mn}_{1-x}]\text{O}_2$ only in the range of $x=1/9$ – $2/9$ [Paulsen, 1999]. Fig. 1(a) and (b) show XRD patterns for $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ synthesized using adipic and glycolic acids, respectively, as a function of calcination temperatures. All the synthesized samples except the sample prepared at 700 °C are indexed as a P2 structure with a symmetric hexagonal space group structure ($P6_3/mmc$) [Paulsen, 1999]. They show a (002) peak at $2\theta=16^\circ$ as a main peak and (012) and (014) planes at $2\theta=39^\circ$ and 49° , respectively. These traits are also observed in the typical P2 layered structure. The oxygen lattice in the P2 structure is not a cubic close packed. Sandwiches of $\text{Na}_x\text{Mn}_{1-x}\text{O}_2$ are separated by 0.7 filled layers of sodium in prismatic sites. Our observed XRD spectra are very similar to the data previously reported for $\text{Na}_{0.7}\text{CoO}_2$, identifying the formation of the desired P2 structure in this experiment [Balsys et al., 1996]. The calculation of the lattice constants, a and c , for sample F by a Rietveld refinement method using the measured XRD data also identified the formation of P2 structure. The lattice constants of the sample were $a=2.371$ and $c=11.079$, which are very similar to the values reported in literature

($a=2.867$ and $c=11.154$) [Paulsen, 1999].

Samples A and E, synthesized at 700 °C, show a P3 structure. Sample E is almost equal to sample A in XRD spectra. According to previous work reporting the synthesis of Mn based cathode materials [Paulsen, 1999, 2000; Kim et al., 1998; Jeong, 1999], the structural stability of the materials increases in order from P2 to spinel to P3. In our system, it seems that the formation of P3 structure is favorable at a low temperature of 700 °C. The XRD spectra are consistent with observations made by Paulsen et al., who reported the synthesis of a P3 structure at 900 °C [Paulsen, 2000]. Besides, the spectra show some impurity related peaks, shown as asterisks at $2\theta=18$, 23, 28, and 30°. The impurities seem to originate from unreacted reactants remaining in the product. The synthetic process is mainly influenced by temperature, time, chelating agent, etc. In this work, it is likely that the synthetic reaction has been insufficiently accomplished at 700 °C for a given reaction time (10 h) and chelating agent, resulting in the emergence of impurity peaks on the XRD spectra.

Meanwhile, samples B, C, and F show the formation of good quality P2 structure without the inclusion of impurities, but the inclusion of a small amount of P3 structure is detected at $2\theta=38$, 45.6, 53, and 57° from the XRD spectra of samples B and F. This means that samples B and F are a mixed structure of P2 with P3. For sample D synthesized at 1,000 °C, however, various impurity peaks emerge at $2\theta=18^\circ$ and 37° on the XRD spectrum. This indicates that a higher temperature deteriorates the crystal structure and is not proper for the formation of good quality P2 structure.

Samples G and H also exhibit the improvement of the crystal quality, although both show an impurity peak at $2\theta=18^\circ$. Full width at half maximum (FWHM) of a main peak, (002), at $2\theta=16^\circ$ for the samples decreased with the increase of the calcinations temperature from 0.310° for 700 °C to 0.152° for 1,000 °C in case of glycolic acid. As opposed to sample D, it is interesting to note that sample H exhibits a negligible impurity peak even though both are calcined at 1,000 °C. This means that glycolic acid works as a more effective chelating agent than adipic acid in the synthesis of $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ powders, even at high temperature. Both adipic and glycolic acids have been employed as a chelating agent to synthesize lithium metal oxide cathode materials in the literature [Park et al., 2000, 2001; Sun et al., 2000]. But the effectiveness of the chelating agents has not been discussed in detail in the works. Chen et al. investigated the reactivity of chelating agents by comparing polyacrylic acid (PAA) with citric acid, which is a conventionally employed chelating agent. They reported that PAA enhances significantly the formation of a cross-linked gel since it contains a large number of carboxylic acid groups used for the formation of chelates among mixed cations. This induces more homogeneous mixing of the cations, resulting in fewer tendencies for segregation during calcination [Chen et al., 2001]. The present experimental data presents that glycolic acid seems to be more effective chelating agent for the preparation of $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ powders. We speculate that this is because glycolic acid has many more OH^- radicals per mole than adipic acid. Another possibility is that the chain length of glycolic acid is shorter than that of adipic acid. The short chain length of glycolic acid tends to enhance the synthetic reaction rate of $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ powders during the calcinations. Both these characteristics seem to suggest that glycolic acid is superior to acetic acid in synthesizing good quality

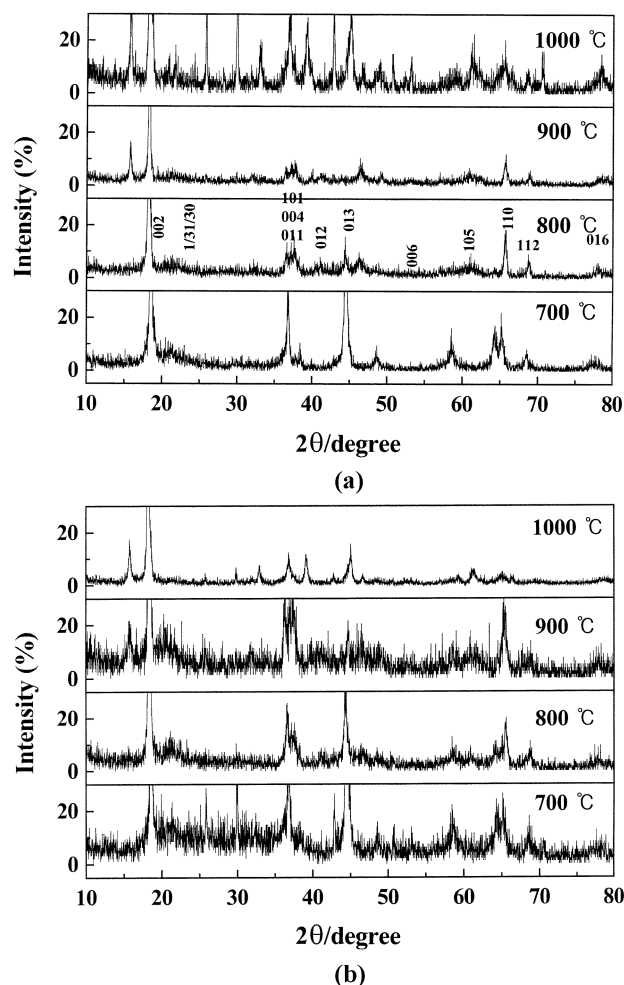


Fig. 2. XRD spectra for $\text{Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ prepared by ion-exchange of Na for Li in $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ precursors synthesized using (a) adipic and (b) glycolic acids at 700, 800, 900, and 1,000 °C, respectively.

$\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ powders.

2. O2- $\text{Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ Powders

$\text{Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ is prepared by ion exchange of Li for Na in the P2- $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ precursor. Fig. 2 shows XRD patterns of layered lithium manganese oxides prepared by ion exchange of sodium manganese bronzes synthesized as a function of calcination temperature. All the XRD patterns exhibit broad characteristic peaks with low intensities and indicate the existence of stacking faults. Paulsen et al. reported that the existence of the stacking faults in layered structures is shown as sharp 00 l and $hk0$ peaks on their diffraction patterns, as shown also in our observed XRD spectra. Furthermore, they suggested that the broad characteristic peaks with low intensities are ascribed to the effect of layer gliding in the layered structure when the structure changes from P2 to O2 during ion exchange [Paulsen et al., 2000]. In P2 structures, sodium prefers prismatic or octahedral places, whereas lithium adopts only octahedral coordination. In other words, the prismatic sites are not favorable for lithium. Oxygen stacking in the P2 structure is accumulated in an array of BAABBAABBA, etc. During the ion exchange process, the layers of the P2 structure are rearranged to create an octahedral

structure for lithium. This can be accomplished by gliding every second MnO_2 layer in one direction or, alternatively, by gliding in the other direction. Delmas et al. reported that both possibilities are proper for energetically equivalent principle and lead to the same O2 structure with space group P_3m1 [Delmas et al., 1996]. The appearance of an (002) peak at $2\theta=18^\circ$ on the XRD spectra of Fig. 2 represents the formation of an O2 structure by replacing Na in the P2 structure with Li during ion exchange. Therefore, it is assessed that ion exchange is completely terminated when the Na phase peak vanishes at $2\theta=16^\circ$ and, meanwhile, only (002) peak shows up at $2\theta=18^\circ$.

From Fig. 2(a) and (b), it is seen that the layered lithium manganese oxides prepared from sodium manganese bronzes synthesized at 700 and 800 °C attain a perfect ion exchange, regardless of chelating agents. However, those at 900 and 1,000 °C are not completely ion-exchanged. This indicates that the ion-exchange is unfavorable for sodium manganese bronzes calcinated at higher temperatures. The extent of the ion-exchange decreases with the increase of the calcinations temperature. Samples A-I and E-I show the formation of O3 structure though there are slight difference in the XRD patterns of the two samples. Many unknown impurities are also detected at $2\theta=26, 30$, and 51° from sample E-I. However, an O2 structure is observed from the other samples (B-I, C-I, D-I, F-I, G-I, and H-I). Literature [Paulsen et al., 2000] has reported that either the O3 or O2 structure has a main peak at $2\theta=18^\circ$, but the splitting direction of the peaks at $2\theta=36$ and 37° is different depending on the structures. In the case of the O3 structure, the splitting emerges behind the peaks, whereas the splitting starts before the peaks in the case of O2 structures. In addition, the peak at $2\theta=62^\circ$ that appeared in the O3 structure disappears in O2 structure and, instead, a new peak emerges at $2\theta=59^\circ$. Samples B-I and F-I seem to include a small amount of O3 structure because samples B-I and F-I are still showing low intensity peaks at $2\theta=62^\circ$ and a splitting peak at $2\theta=36^\circ$ from their XRD spectra. This means that samples B-I and F-I are a mixed structure of O2 and O3. Samples C-I, D-I, G-I, and H-I exhibit O2 structure although they were imperfectly ion-exchanged. For samples D-I and H-I (especially from D-I), however, many unknown impurity peaks are observed from the XRD spectra, indicating that the high calcination temperature of sodium manganese bronzes are also unfavorable to the formation of good quality O2 structure.

Fig. 1 shows that relatively good quality sodium bronze oxides are synthesized at 800 and 900 °C, and glycolic acid acts as a more effective chelating agent than adipic acid in the synthesis of $\text{Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ powders. However, Fig. 2 reveals that the ion-exchange is imperfectly carried out at 900 and 1,000 °C, whereas 700 °C forms O3 structure. Here, we have employed samples B-I and F-I for the electrochemical characterization of the prepared layered lithium manganese oxides.

3. Electrochemical Analysis

Fig. 3(a) and (b) show the capacity vs voltage profile for $\text{Li}/\text{Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ cells prepared by using adipic and glycolic acids, respectively. The cells were charged and discharged three times at a constant current density ($0.4 \text{ mA}/\text{cm}^2$) from 2.0 V to an upper voltage of 4.2 V. After the 3rd charge-discharge cycle, the upper voltage was increased by 0.2 V sequentially until 4.8 V was attained. While charging and discharging the cells, it is seen that both samples B-I

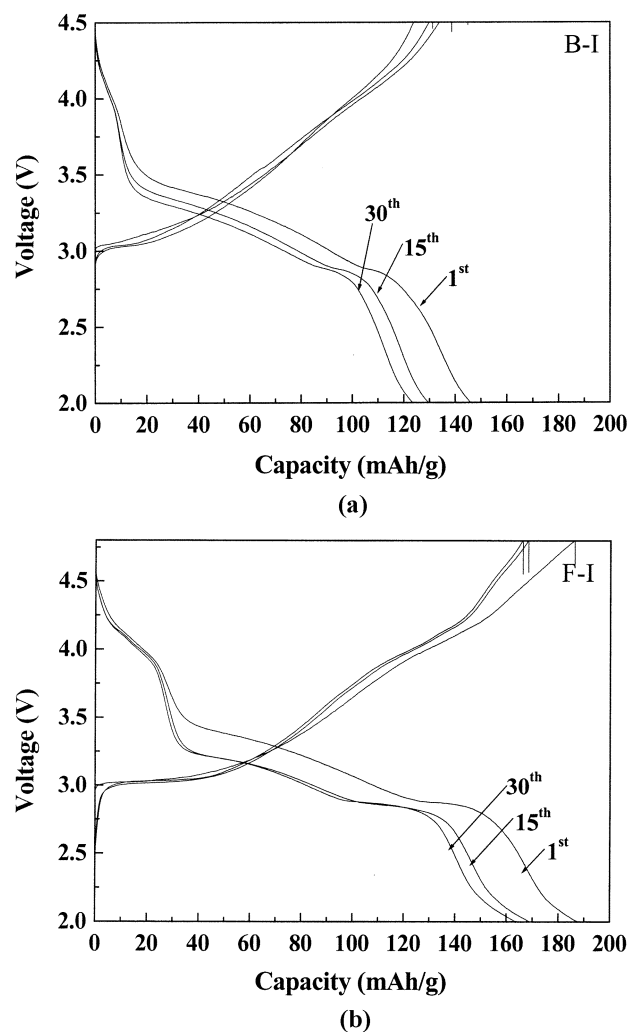


Fig. 3. Charge-discharge curves of $\text{Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ prepared using (a) adipic and (b) glycolic acids, respectively.

and F-I produce two voltage plateaus, which are usually observed in materials having a structural change from layered to spinel during cycling. Our prepared samples seem to undergo a structural transition to a spinel-like phase. Both the samples show a rapid capacity fading at the initial cycles, but the capacity fading breadth was decreased after 25 cycles. The sample F-I, especially, shows a high initial discharge capacity of 187 mAh/g and maintains the capacity of 170 mAh/g after 25 cycles. Many researchers have reported that this material attains a high discharge capacity with a low capacity fading although the structure transforms to a spinel-like phase with cycling [Armstrong et al., 1999; Quine et al., 2000]. Bruce et al. reported that the phase change of O3- LiMnO_2 from layered to spinel structure does not have a deleterious effect on the cycling performance of the material [Armstrong et al., 1999]. Quine and coworkers also reported that layered $\text{Li}_x[\text{Mn}_{1-y}\text{Ni}_y]\text{O}_2$ with the O3- NaFeO_2 structure delivers a high capacity of 220 mAh/g in the voltage 2.4-4.8 V. But they reported that the $\text{Li}_x[\text{Mn}_{1-y}\text{Ni}_y]\text{O}_2$ electrode transformed to a spinel-like structure after scores of cycling [Quine et al., 2000]. After the first cycle, samples B-I and F-I show two plateaus at around 4 and 3 V with a steep curve slope between the two plateaus. The discharge curve at the 3 V region becomes especially

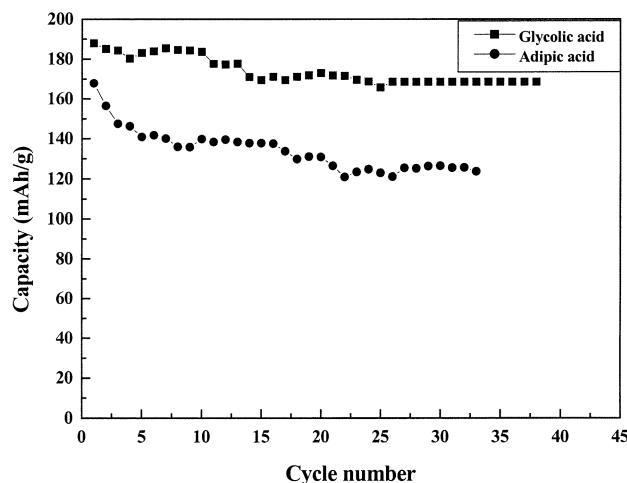


Fig. 4. Plots of specific discharge capacity versus cyclic number for $\text{Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ prepared at different chelating agents.

valid with cycling, indicating the formation of a spinel-like phase. From the electrochemical results, we speculate that our prepared cathode materials undergo a phase transformation from layered to spinel structure during the cycling, although no direct evidence was detected from the XRD patterns of the cycled electrode.

Fig. 4 shows the discharge capacity for $\text{Li}/\text{Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ cells cycled between 2.0 and 4.8 V at room temperature. Both the samples show a rapid capacity fading at the initial cycles, but the capacity fading breadth is decreased after 25 cycles. At the first cycle, the samples B-I and F-I deliver the discharge capacities of 145 and 187 mAh/g, respectively. After 30 cycles, however, the discharge capacities of samples B-I and F-I show 125 and 170 mAh/g with the capacity retention rates of 0.49 and 0.42%/cycles, respectively. The electrochemical measurements for our prepared samples again show that glycolic acid is more effective than adipic acid as a chelating agent to prepare the layered lithium manganese oxides.

XRD spectra of the samples in Fig. 2 show that both the samples B-I and F-I experienced perfect ion-exchange and mainly produced O2 structure with small amount of O3 structure. Background noise levels of the XRD patterns in Fig. 2(b) were higher than those in Fig. 2(a). However, FWHM values of the main (002) peak for samples B-I and F-I were 0.237 and 0.196°, respectively, indicating that better crystal quality is obtained in glycolic acid than in adipic acid. The intensity ratios of other peaks ((010), (004), (011), and (110) peaks) to the main peak ((002) peak) were much higher in glycolic acid than in adipic acid. This indicates that O2 structure is prevalent in sample F-I. It was reported that the obvious splitting of XRD peaks appeared at $2\theta=65$ and 66° corresponds to the production of high discharge capacity with low capacity fading in the electrochemical characterization [Paulsen et al., 2000]. The degree of the peak splitting was much apparent in glycolic acid than in adipic acid. Consequently, we speculate that the use of glycolic acid as a chelating agent in the preparation of the layered lithium manganese oxide is proper to get better crystal and electrochemical properties.

CONCLUSION

We have synthesized layered $\text{O2-Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ by ion ex-

change from $\text{P2-Na}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ prepared at different calcination temperatures and with different chelating agents. The optimum $\text{O2-Li}_{0.7}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ was synthesized at 800°C using glycolic acid. During the cycle, the discharge profile of the samples showed two plateaus at around 4 and 3 V, respectively, with a steep slope between the two plateaus. Our prepared samples seemed to undergo a structural transition from layered to spinel like phase. The sample prepared at 800°C for 10 h using glycolic acid showed a high discharge capacity with low capacity fading. At the first cycle, the discharge capacities of the samples prepared at 800°C for 10 h using adipic acid and glycolic acid were 145 and 187 mAh/g, respectively, and they reached 125 and 170 mAh/g with capacity retention rates of 0.49 and 0.42%/cycles, respectively, after 30 cycles.

ACKNOWLEDGMENT

This work was supported by the Ministry of Science and Technology (2004).

REFERENCES

- Armstrong, A. R., Robertson, A. D. and Bruce, P. G., "Structural Transformation on Cycling Layered $\text{Li}(\text{Mn}_{1-x}\text{Co}_x)\text{O}_2$ Cathode Materials," *Electrochimica Acta*, **45**, 285 (1999).
- Balsys, J. and Davis, R. L., "Refinement of the Structure of $\text{Na}_{0.7}\text{CoO}_2$ using Neutron Powder Diffraction," *Solid State Ionics*, **93**, 279 (1996).
- Chen, D. H. and He, X. R., "Structural and Electrochemical Properties of $\text{O2-Li}_x\text{MnO}_2$," *Mat. R. Bull.*, **36**, 1369 (2001).
- Delmas, C., Braconnier, J. J. and Hagenmuller, P., "A New Variety of LiCoO_2 with an Unusual Oxygen Packing Obtained by Exchange Reaction," *Mater. Res. Bull.*, **17**, 117 (1982).
- Delmas, C., Braconnier, J. J., Maazaz, A. and Hagenmuller, P., " A_xMnO_2 Prepared by Ion Exchange of Layered Alkali Bronze," *Rev. Chim. Miner.*, **19**, 343 (1982).
- Franger, S., Bach, S., Pereira-Ramos, J. P. and Baffier, N., "Chemistry and Electrochemistry of Low-Temperature Manganese Oxides as Lithium Intercalation Compounds," *J. Electrochem. Soc.*, **147**, 3226 (2000).
- Guyomard, D. and Tarascon, J. M., "The Carbon/ $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ System," *Solid State Ionics*, **69**, 222 (1994).
- Jang, D. H. and Oh, S. M., "Electrolyte Effects on Spinel Dissolution and Cathodic Capacity Losses in 4 V $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ Rechargeable Cells," *J. Electrochem. Soc.*, **144**, 3342 (1997).
- Jang, D. H., Shin, U. J. and Oh, S. M., "Dissolution of Spinel Oxides and Capacity Losses in 4 V $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ Cells," *J. Electrochem. Soc.*, **143**, 2204 (1996).
- Jeong, Y. U. and Manthiram, A., "Synthesis and Lithium Intercalation Properties of $\text{Na}_{0.5x}\text{Li}_x\text{MnO}_2$ and $\text{Na}_{0.5x}\text{MnO}_2$ Cathodes," *Electrochem. Solid-State Lett.*, **2**, 421 (1999).
- Kim, J. and Manthiram, A., "Nanocomposite Manganese Oxides for Rechargeable Lithium Batteries," *Electrochem. Solid-State Lett.*, **1**, 207 (1998).
- Lu, Z. and Dahn, J. R., "Intercalation of Water in P2, T2 and O2 Structure $\text{A}_x[\text{Co}_x\text{Ni}_{1/3-x}\text{Mn}_{2/3}]\text{O}_2$," *Chem Mater.*, **13**, 1252 (2001).
- Lu, Z. and Dahn, J. R., "Effects of Stacking Fault Defects on the X-ray Diffraction Patterns of T2, O2, and O6 Structure $\text{Li}_{2/3}[\text{Co}_x\text{Ni}_{1/3-x}]$

- $\text{Mn}_{2/3}\text{O}_2$,” *Chem Mater.*, **13**, 2078 (2001).
- Lu, Z., Donaberger, R. A. and Dahn, J. R., “Superlattice Ordering of Mn, Ni, and Co in Layered Alkali Transition Metal Oxides with P2, P3, and O3 Structures,” *Chem. Mater.*, **12**, 3583 (2000).
- Ohuzuk, T., Kitagawa, M. and Hirai, T., “Electrochemistry of Manganese Dioxide in Lithium Nonaqueous Cell (III) X-Ray Diffractonal Study on the Reduction of Spinel-Related Manganese Dioxide,” *J. Electrochem. Soc.*, **137**, 769 (1990).
- Parant, J. P., Olazcuaga, R., Devalette, M., Fouassier, C. and Hagenmuller, P., “Sur Quelques Nouvelles Phases de Formule Na_xMnO_2 ($x \leq 1$)” *J. Solid State Chem.*, **3**, 1 (1971).
- Park, K. S., Cho, M. H., Jin, S. J., Song, C. H. and Nahm, K. S., “The Effect of Ni Doping on the Performance of O3-Lithium Manganese Oxide Material,” *Korean J. Chem. Eng.*, **21**, 983 (2004).
- Park, S. H., Park, K. S., Cho, M. H., Sun, Y. K., Nahm, K. S., Lee, Y. S. and Yoshio, M., “The Effect of Oxygen Flow Rate and Anion Doping on the Performance of the LiNiO_2 Electrode for Lithium Secondary Batteries,” *Korean J. Chem. Eng.*, **19**, 791 (2004).
- Park, S. H., Park, K. S., Moon, S. S., Sun, Y. K. and Nahm, K. S., “Synthesis and Electrochemical Characterization of $\text{Li}_{1.02}\text{Mg}_{0.1}\text{Mn}_{1.9}\text{O}_{3.99-\text{S}_{0.01}}$ using Solgel Method,” *J. Power Sources*, **92**, 244 (2001).
- Paulsen, J. M. and Dahn, J. R., “O₂-Type $\text{Li}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$: A New Layered Cathode Material for Rechargeable Lithium Batteries II. Structure, Composition, and Properties,” *J. Electrochem. Soc.*, **147**, 2478 (2000).
- Paulsen, J. M. and Dahn, J. R., “Studies of the Layered Manganese Bronzes, $\text{Na}_{2/3}[\text{Mn}_{1-x}\text{M}_x]\text{O}_2$ with M=Co, Ni, Li, and $\text{Li}_{2/3}[\text{Mn}_{1-x}\text{M}_x]\text{O}_2$ Prepared by Ion-exchange,” *Solid State Ionics*, **126**, 3 (1999).
- Paulsen, J. M., Larcher, D. and Dahn, J. R., “O2 Structure $\text{Li}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$: A New Layered Cathode Material for Rechargeable Lithium Batteries III. Ion Exchange,” *J. Electrochem. Soc.*, **147**, 2862 (2000).
- Paulsen, J. M., Thomas, C. L. and Dahn, J. R., “Layered Li-Mn-Oxide with the O2 Structure: A Cathode Material for Li-Ion Cells which Does Not Convert to Spinel,” *J. Electrochem. Soc.*, **146**, 3560 (1999).
- Paulsen, J. M., Thomas, C. L. and Dahn, J. R., “O2 Structure $\text{Li}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$: A New Layered Cathode Material for Rechargeable Lithium Batteries. I. Electrochemical Properties,” *J. Electrochem. Soc.*, **147**, 861 (2000).
- Quine, T. E., Duncan, M. J., Armstrong, A. R., Robertson, A. D. and Bruce, P. G., “Layered $\text{Li}_x\text{Mn}_{1-y}\text{Ni}_y\text{O}_2$ Intercalation Electrodes,” *J. Mater. Chem.*, **10**, 2838 (2000).
- Sun, Y. K., Jeon, Y. S. and Lee, H. J., “Overcoming Jahn-Teller Distortion for Spinel Mn Phase,” *Electrochem. Solid-State Lett.*, **3**, 7 (2000).
- Thackeray, M. M., “Manganese Oxides for Lithium Batteries,” *Prog. Solid State Chem.*, **25**, 1 (1997).