Orthorhombic $LiMnO_2$ as a High Capacity Cathode for Lithium-Ion Battery Synthesized by Hydrothermal Route at 170 °C

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An orthorhombic $LiMnO_2$ having a high capacity was hydrothermally synthesized at 170 °C from Mn_3O_4 obtained through autoxidation route. The $LiMnO_2$/Li cell demonstrated the initial reversible capacities of about 210 mAh (g-oxide)$^{-1}$ at 30 °C. After several initial cycling, the cell showed stabilized cycling behavior (175 mAh g^{-1} at the 30th cycle). We believe that orthorhombic $LiMnO_2$ prepared by a new hydrothermal condition is an excellent candidate for the cathode of coming generation of high capacity material to be applied for lithium-ion secondary battery.

The trivalent manganese compound $LiMnO_2$ offers a theoretical capacity twice of $LiMn_2O_4$ and is expected to work as a 3 V class cathode material for lithium-ion secondary battery. An orthorhombic unit cell of $LiMnO_2$ was firstly assigned by Johnston[1] as early as 1956, and the detailed structural information was given by Hoppe.[2] The orthorhombic $LiMnO_2$ (hereafter referred to as *o*-$LiMnO_2$) has been commonly synthesized by high temperature solid state reactions, that is, reaction between LiOH and $MnCO_3$ at 750 °C,[2] decomposition of $LiMn_2O_4$ above 940 °C,[3] and calcination of LiOH and γ-MnOOH mixture at 1000 °C.[4] It was not until 1992 that low temperature *o*-$LiMnO_2$ was synthesized at a temperature as low as 450 °C.[4]

Low-temperature synthesis is necessary to obtain a high capacity in *o*-$LiMnO_2$, according to Gummow et al.[5] Efforts to make further lowering of the synthesis temperature have been made by several research groups.[6–8] In the cases, increased initial capacities are seen, but obvious capacity fadings were also accompanied during extended cyclings, although those are less severe than in $LiMn_2O_4$ spinels.

Electrochemical behaviors of *o*-$LiMnO_2$ materials are significantly dependent on the crystalline size.[9–11] The materials with grain size below about 1 µm in diameter showed more enhanced electrochemical performances. Increased capacities in initial several cyclings were also observed in disordered form of *o*-$LiMnO_2$ material.[9] However, its capacity fading was quite large.

Croguennec et al.[9] have suggested that, in general, an well-ordered *o*-$LiMnO_2$ did not show any good cycling performances. However, Jang et al.[12] have recently reported that highly ordered *o*-$LiMnO_2$ prepared by 900 °C calcination of freeze dried precursor maintains a good cyclability during extended cycling. Though the *o*-$LiMnO_2$ showed good electrochemical properties, its powder preparation condition (high firing temperature and very low oxygen partial pressure) is too complicated. This point prompted us to consider a mild preparation route to synthesize the oxide powder, namely, hydrothermal treatment, which is a kind of promising technique for synthesis of lithium transition metal oxide cathodes. It was reported earlier that *o*-$LiMnO_2$ could be prepared by hydrothermal reaction between MnO_2 or Mn_2O_3 and LiOH at a high temperature of 600 °C under a high pressure of 100 MPa.[13] *o*-$LiMnO_2$ has been synthesized from γ-MnOOH by hydrothermal method.[14,15] Nonetheless, the charge–discharge cyclings at a long term have not been performed yet. Here, *o*-$LiMnO_2$ was firstly synthesized from Mn_3O_4 by hydrothermal route at 170 °C, which demonstrated > 200 mAh g^{-1} reversibly.

Mn_3O_4 was synthesized through a mild autoxidation route.[16] Manganese acetate tetrahydrate ($(CH_3COO)_2Mn{\cdot}4H_2O$, R.G. of Kanto Chemicals) was dissolved in distilled water. Then, the manganese solutions were mixed with potassium hydroxide solution, and the solution mixture was stirred at 80 °C for 1 day with flowing O_2 gas, and finally dark brown powders of Mn_3O_4 precipitated on the bottom of reactor. The precipitates were continuously washed with deionized water until pH reaches neutral and dried at 80 °C in air. The prepared Mn_3O_4 powder was hydrothermally treated with 40 mL of $LiOH{\cdot}H_2O$ (R.G. of Wako Chemicals) aqueous solution with various Li concentrations at 170 °C for 4 days in an autoclave. A teflon beaker was used to avoid any reaction with the vessel. After hydrothermal reaction, the precipitates were washed with deionized water, and the products were dried to remove water at 120 °C in air.

For electrochemical testing, cathodes were fabricated by mixing the prepared *o*-$LiMnO_2$ powder, graphite, acetylene black and polyvinylidene fluoride (80:5:10:5) in NMP. The slurry was pasted on nickel ex-met (1 cm^2), and the electrode was dried at 80 °C for 1 day, and then dried again at 120 °C for 4 days in vacuum state. The cell consisted of the oxide cathode as a working electrode and lithium foil as a counter electrode was assembled in Ar-filled glove box. The cells were charged and discharged between 2.0 and 4.3 V_{Li/Li^+} at current densities of 0.05 mA cm^{-2} at 30 °C.

XRD pattern of Mn_3O_4 prepared through oxidation of $Mn(OH)_2$ in flowing oxygen is shown in Figure 1-(a). During hydrothermal reaction in LiOH aqueous solution, the Mn_3O_4

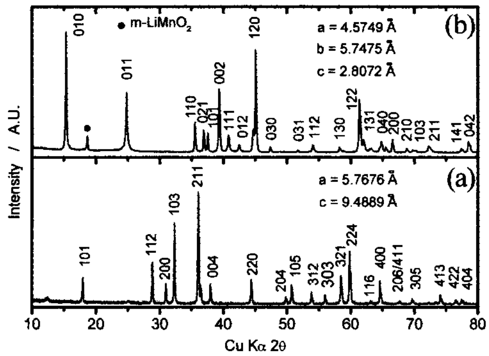

Figure 1. XRD patterns of (a) Mn_3O_4 prepared by autoxidation route in flowing oxygen at 80 °C (b) *o*-$LiMnO_2$ by hydrothermal reaction with as-prepared Mn_3O_4 and LiOH aqueous solution at 170 °C in autoclave.

phase was gradually changed to *o*-LiMnO$_2$ phase. The XRD pattern presented in Figure 1-(b) is very similar to that prepared from freeze dried precursor.[12] The doublet (122) and (131) peaks in Figure 1-(b) are not so clear compared to those reported by Croguennec et.al..[11] Those observations mean that the crystallites of the product obtained by hydrothermal treatment are very fine, and the narrow full width of half maximum (FWHM) of the (011) peak (0.18° 2θ) depicts that the *o*-LiMnO$_2$ oxide has a well-ordered orthorhombic crystallinity. SEM observation gave the confirmation that the observed average crystalline size is 0.1–1 μm in diameter. Furthermore, the calculated lattice parameters of Mn$_3$O$_4$ and *o*-LiMnO$_2$ shown in Figure 1 agree well with other literatures.[2,12,17]

Figure 2 shows the initial charge–discharge curves and cycling performances of *o*-LiMnO$_2$ oxide prepared by hydrothermal treatment at 170 °C. As can be seen in Figure 2-(a), the o-LiMnO$_2$ phase was progressively transformed to spinel phase in the first charge step, which was confirmed by XRD. This phenomenon accords well with the in-situ XRD studies.[18] The outset of 4 V in the charge process is similar to that of LiMn$_2$O$_4$. About 0.75 mole of Li ion was extracted from the parent *o*-LiMnO$_2$ structure in the charge process. Therefore, the *o*-LiMnO$_2$ can be electrochemically transformed to spinel like LiMn$_2$O$_4$ phase, when more than 0.5 mole of Li ion is deintercalated, forming spinel like Li$_{0.5}$MnO$_2$ phase. According to Croguennec et al.,[19] this *o*-LiMnO$_2$ oxide electrode may not show any good cyclability because of the higher ordering of crystal structure, as described above. As can be seen in Figure 2-(b), the highly crystalline material delivered about 210 mAh g^{-1} in the initial charge and discharge process, and the capacity increased to 222 mAh g^{-1} with accompanying cycle-induced spinel phase. The average efficiency between charge and discharge capacity was more than 98%, and the discharge capacity was more than 175 mAh g^{-1} over 30 cycles. It is notable that battery performance of the *o*-LiMnO$_2$ oxide electrode synthesized by hydrothermal reaction between Mn$_3$O$_4$ and LiOH aqueous solution is superior to that of *o*-LiMnO$_2$ prepared at over 900 °C in the reduction atmosphere from freeze dried precursor.[12] From these results, it was found that the hydrothermal approach has advantages to synthesize an highly ordered crystalline oxide electrode material at a temperature as low as 170 °C under a mild condition as well as to obtain much more enhanced battery performance than other powders prepared by other synthetic routes. We are going to develop the physical and electrochemical properties, and report elsewhere in near future.

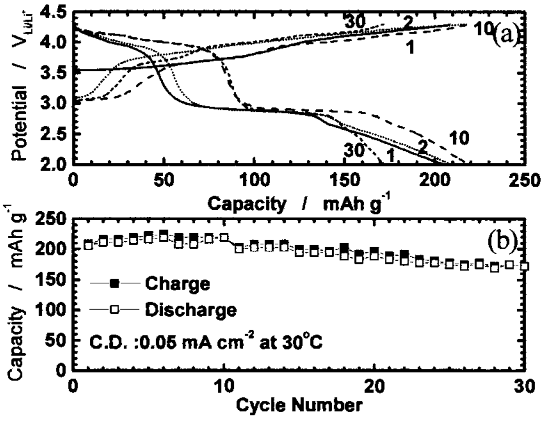

Figure 2. (a) Charge and discharge curves and (b) cyclability of *o*-LiMnO$_2$ synthesized by hydrothermal treatment at 170 °C. The operation temperature of the cell was 30 °C.

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