Layered lithium manganese oxide with disordered layer stacking for cathode material

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Introduction

Layered $LiMnO_2$ attracts much attention as a cathode material in lithium batteries, because of its low cost, low toxicity, and high theoretical capacity. However it is not structurally stable during charge-discharge cycling. For example, a layered material $LiMnO_2$ synthesized from layered $NaMnO_2$ via ion-exchange gradually transformed to the more stable spinel phase accompanied by capacity fading [1]. Structural similarity between the layered $LiMnO_2$ and spinel $LiMn_2O_4$ is considered to be a reason for the transformation. Both of them have ccp stacking of oxygen atoms; therefore, partial movement of Mn modifies the layered structure into the spinel one. Although, layered $LiMnO_2$ with hcp stacking was proposed to prevent the phase transformation [2], such oxides have not been synthesized so far.

We synthesized a new layered Li_xMnO_2 having good resistance to the transformation to spinel phase. Layered K_xMnO_2 was delaminated into individual MnO_2 nanosheets [3], which were restacked again by flocculation. The obtained layered Li_xMnO_2 has disordered staking, i.e., a heavy stacking fault of MnO_2 layers and showed excellent potential as a cathode material [4].

Experimental

Layered $K_{0.45}MnO_2$ was synthesized from K_2CO_3 and Mn_2O_3 as a starting material by solid-state reaction. The K^+ ions were exchanged for protons by stirring the $K_{0.45}MnO_2$ in hydrochloric acid. The resultant $H_{0.13}MnO_2{\cdot}0.7H_2O$ was mixed with tetrabutylammonium hydroxide solution, and the mixture was agitated to produce MnO_2 nanosheets. The $Li_{0.36}MnO_2$ with turbostratic structure was finally prepared by restacking the nanosheets. The colloidal suspension of the nanosheets was added to a LiOH solution to be flocculated.

Results and discussion

The flocculated product was analyzed to have a composition of $Li_{0.36}MnO_2{\cdot}1.15H_2O$. Figure 1 shows its powder X-ray diffraction pattern. The two pronounced reflections at $2\theta = 12.3$ ° and 25.1 ° can be indexed as 001 and 002 of basal series indicating a lamellar structure with a basal spacing of 7.2 Å. On the other hand, the broad bands around 36.5 ° and 65.6 ° are indexable as intrasheet reflections of 10 and 11 for the hexagonal cell with $a = 2.8$ Å. The absence of general *hkl* reflections and the asymmetric profiles of the 10 and 11 reflections with a tail toward a higher angle indicate that the nanosheets were restacked without regular sheet-to-sheet registry.

The basal spacing of 7.2 Å, which is a typical value for monolayer-hydrate layered materials, suggested that water molecules were incorporated between the MnO_2 layers. Therefore, the sample was heated at 150 °C in vacuum in order to remove the intercalated water molecules before the electrochemical measurement. The dehydration decreased the interlayer spacing to 5.0 Å.

Charge-discharge curves of the cell, Li / Li_xMnO_2, are shown in Fig. 2. It showed a very high initial charge capacity of 266 $mAh{\cdot}g^{-1}$. The voltage profiles were smooth in shape and clearly distinguished from that of spinel $LiMn_2O_4$ having two potential plateaus at 3 V and 4 V. The cycling did not bring about a change in the smooth profile, and a high capacity of ca. 200 $mAh{\cdot}g^{-1}$ remained after 7 cycles, indicating that the layered structure was hardly transformed to spinel one. The disordered stacking of oxygen atoms in the present material, which is largely different from the ccp stacking in spinel structure, is considered to prevent the transformation to spinel phase during the cycling.

References

[1] A. R. Armstrong and P. G. Bruce, *Nature* **381** 499 (1996).
[2] J. M. Paulsen, C. L. Thomas, and J. R. Dahn, *J. Electrochem. Soc.* **146** 3560 (1999).
[3] Y. Omomo, T. Sasaki, L. Wang, and M. Watanabe, *J. Am. Chem. Soc.* **125** 3568 (2003).
[4] L. Wang, K. Takada, A. Kajiyama, M. Onoda, Y. Michiue, L Zhang, M. Watanabe, and T. Sasaki, *Chem. Mater.* **15**, 4508 (2003).

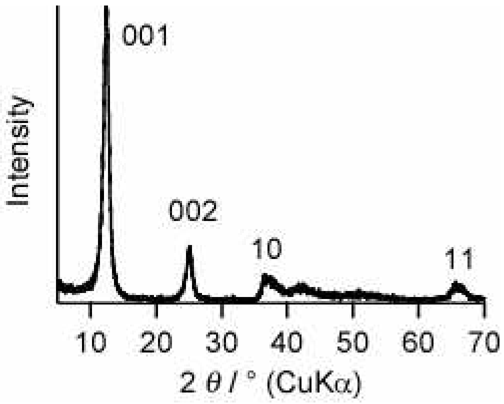

Fig. 1 Powder XRD pattern of $Li_{0.36}MnO_2{\cdot}0.7H_2O$

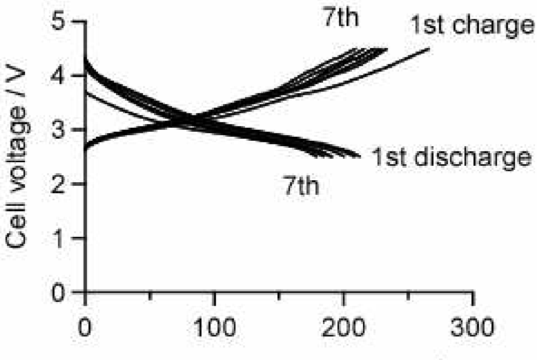

Fig. 2 Charge-discharge curves of the cell, Li / Li_xMnO_2