Activation mechanism of Li₂MnO₃ cathode for lithium ion battery

She-huang Wu^{*}, Jian-Liang Chen, and Wei Kong Pang Department of Materials Engineering, Tatung University, 40, Sec. 3, Chungshan N. Rd., Taipei 104, Taiwan

In the past, layered Li_2MnO_3 or $Li[Li_{1/3}Mn_{2/3}]O_2$ with C2/m space group is generally considered as a electrochemically inactive material due to difficulty of oxidation from Mn⁴⁺, however, recent studies reveal that the inert Li₂MnO₃ can be activated chemically by ion exchange method^{1, 2}, or electrochemically by charging it up to potential higher than 4.6 V (vs. Li)³. Though the electrochemical activation mechanism of Li2MnO3 has been studied for years, it still remains unclear. Robertson et al. reported that Li⁺ removal is accompanied with oxygen loss (net Li_2O loss), but further Li^+ removal involves proton exchange in the activation process¹. On the contrary, Amalraj et al. suggested that the oxidation and generation of O2 from Li2MnO3 electrode exist during activating³. Nevertheless, information about the products/active form of lithium manganese oxide and the following charge-discharge properties are lacking.

In this study, layered Li_2MnO_3 compounds are synthesized via Pechini method. Customized cells with Li counter electrode are fabricated to study in-situ phase evolution and activation mechanism of Li_2MnO_3 when cycling between 2.0 and 4.8 V (vs. Li) using highresolution synchrotron radiation diffraction. The in-situ results (as shown in Fig. 1) reveal that gamma- or orthorhombic-MnO₂ is detected and assumed to be the product of electrochemical activation of Li_2MnO_3 . In addition, the properties of the as-synthesized Li_2MnO_3 are investigated with conventional XRD, SEM, TEM, and galvanostatic cycling (as shown in Fig. 2). The correlation between activation mechanism, the properties, and electrochemical performance is established and discussed in this work.



Fig. 1 In-situ synchrotron radiation diffraction patterns of a customized cell using Li_2MnO_3 cathode and Li anode during initial charging of first cycle.



Fig. 2 Initial charge-discharge curves of Li_2MnO_3 cathode at current density of 14 mA/g when cycling between 2.0 and 4.8 V.

References:

1. A. D. Robertson and P. G. Bruce, *Chem. Mater.*, **15**, 1984 (2003).

2. J. Lim, J. Moon, J. Gim, S. Kim, K. Kim, J. Song, J. Kang, W. B. Im and J. Kim, *J. Mater Chem.*, **22**, 11772 (2012).

3. S. Francis Amalraj, B. Markovsky, D. Sharon, M. Talianker, E. Zinigrad, R. Persky, O. Haik, J. Grinblat, J. Lampert, M. Schulz-Dobrick, A. Garsuch, L. Burlaka and D. Aurbach, *Electrochim. Acta*, **78**, 32 (2012).