Cycle performance and degradation mechanism of full-cell with $LiNi_{0.5}Mn_{1.5}O_4$ paired to various carbon materials depends on crystalline structure in lithium ion battery.

Min-Je Jeon [a], Kwang-Sun Ryu* [a]
[a] *Department of Chemistry, University of Ulsan, Mugeo-dong, Nam-gu, Ulsan, Korea*

E-mail: mk2zero@naver.com

The positive electrode material $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) with 5V class spinel structure is a promising candidate for a high energy density in lithium ion batteries. LNMO spinel has an advantage not only high voltage operation but also good rate capability due to 3D spinel crystalline structure. However, the high operating potential brings about oxidation of electrolyte and also Mn dissolution problem is still remained similar to what has been encountered in other manganese based spinel materials when paired graphite. It also has reported severe capacity fading in LNMO/graphite full cell system. Basically LNMO contains only Mn^{4+} oxidation state and it is stable, which doesn't react to the electrolyte. Otherwise during cycling, non-negligible amount of Ni and Mn dissolutions are proceeding during cycling in LNMO/graphite full cell system. Especially, the 3.7~4.1V range in voltage profile during cycling represents Mn^{4+}/Mn^{3+} redox couple and Mn^{3+} ion can be dissolved into an electrolyte and it caused severe degradation of cycle performance.

In this study, to suppress degradation of cycle performance, various type of carbons which has different crystalline structure are paired with LNMO. Specifically, we review the electrochemical performances such as cycle performance, 60°C high temperature storage test, cyclic voltammetry, and AC-impedance technique in LNMO/various carbon full cell system. In addition, surface of LNMO and aged carbon electrodes are analyzed by scanning electron microscopy(SEM), transmission electron microscopy/energy dispersive spectroscopy(TEM/EDS) line mapping, X-ray photoelectron spectroscopy(XPS), furrier transfer Raman spectroscopy (FT-RAMAN), X-ray diffraction(XRD), and focused ion beam/transmission electron spectroscopy(FIB/TEM). An aged electrolyte composition is verified with gas chromatography(GC) after cycling. Finally, the perspective on and challenges for the improvement of high voltage lithium ion battery cycling in LNMO/carbon full cell system are presented for different morphology, surface condition, different Lithium ion insertion mechanism, and different reduction potential of different crystalline structure of anode materials.

References:

[1] Nicholas P.W.Pieczonka, Zhongyi Liu, Peng Lu, Keith L. Olson, John Moote, Bob R. Powell, , Jung-Hyun Kim, J. Phys. Chem. C 2013, 117, 15947−15957
[2] Boulet-Roblin, L, Sheptyakov, D, Borel, P, Tessier, C, Novak, P, Villevieille, C, JOURNAL OF MATERIALS CHEMISTRY A 2017, Volume: 5 Issue: 48 pp: 25574-25582,
[3] Lu, DS, Yuan, LB, Chen, ZX, Zeng, RH, Cai, YP, JOURNAL OF ALLOYS AND COMPOUNDS, 2018, Volume: 730 pp: 509-515
[4] Asl, N. M., Kim, J.-H., Pieczonka, N. P. W., Liu, Z.; Kim, Y. Electrochem.Commun. 2013, Volume: 32, pp:1−4.
[5] J. Libich, J. Vondrák, M. Sedlaříková, International Conference on Renewable Energies and Power Quality (ICREPQ'13), Vol.1, No.11, March 2013
[6] Haiyan L., Ying L., Jingying X., Quansheng Z., Liqin Y. Journal of Alloys and Compounds 639 (2015) pp: 346–351