Diffusion-induced surface control by $LiNbO_3$ nano-coating layer on $LiNi_{0.5}Mn_{1.5}O_4$ cathode material for lithium ion batteries

Wonchang Choi [a,b] , Hyeongwoo Kim [a,c]

[a] *Center for Energy Convergence Research, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea*
[b] *Division of Energy & Environment Technology, KIST School, Korea University of Science and Technology, Seoul Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-79, Republic of Korea*
[c] *Department of Materials science and Engineering, Korea University, 17, Anam-dong, Seongbuk-gu, Seoul 136-701, Republic of Korea*

E-mail: *wonchangchoi@kist.re.kr*

5-V class spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is one of the attractive candidate for cathode material of high-power lithium ion batteries. Furthermore, the high power capability becomes more significantly considered with development of large-scale electric devices such as hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs). However, the high-voltage LNMO has suffered from capacity fading by electrode degradations, although it also has advantages from the "high-voltage" property. Most of all, the electrode degradations are mainly triggered by electrolyte decomposition and Mn dissolution. For the modification, the surface coating method is well-kwon as an effective way to relieve the surface degradation of LNMO particles. Herein, we synthesized the $LiNbO_3$ nano-coating layer on the LNMO particles as a surface modification using the sol-gel assisted single calcination process. In our process, thin, homogeneous coating layer is formed after the calcination at 900 ^oC with direct reaction between Nb-citrate and $Ni_{0.25}Mn_{0.75}(OH)_2$ by aid of the diffusion of excess amount of LiOH as a lithium source. Interestingly, we found the partial diffusion of Nb^{5+} ions at the particle surface and it makes Mn^{3+}-rich domains. Those Mn^{3+} domains results the enhanced kinetic of Li^+ diffusion at the high rate condition. For instance, the discharge capacity of the 1 wt.% $LiNbO_3$-coated LNMO showed above 100 mA h g^{-1} even at 10 C. Besides, thermal stability of the cathode material is also enhanced by coating layer which suppressed severe Mn dissolution from HF attack at 60 ^oC, and Nb^{5+} diffused into the surface domain strengthened cubic lattice by strong Nb-O bond. Consequently, our $LiNbO_3$ coating process provides both protection layer from electrolyte degradation and the high rate capability from Nb^{5+} diffusion.