Surface Doping for Improved Thermal Properties of Ni-rich Layered Cathode for Lithium Ion Batteries

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Ni-rich layered cathode, $LiNi_xCo_yMn_zO_2$ (NCM, x > 0.6, x + y + z = 1) has been considered as promising cathode materials for EVs because of its high capacity resulted from high Ni content. However, the essential limitation of using Ni-rich NCM is rapid capacity fading during cycling due to material degradation especially at high temperature. Structural instability is increased with increasing Ni portion, which will lead poor cycle performance of Ni-rich NCM. Thermal stability is also decreased by high nickel content because of weak Ni-O bonding in framework. Ni dissolution from cathode surface by undesirable side reaction between electrode and electrolyte have been usually discussed as main reason of material degradation. To overcome these negative features, surface doping would be effective way to improve thermal properties of Ni-rich NCM materials.

In this study, Mn surface doping was designed in order to construct more stable surface structure by reinforcing metal-oxygen bond in Ni-rich NCM. To achieve effective Mn surface doping, surface of $LiNi_{0.82}Co_{0.12}Mn_{0.08}O_2$ (NCM) was coated with Mn using Mn acetate as coating source. Mn coated NCM was then heat treated. Finally Mn surface doped NCM (Mn-NCM) was prepared. Higher Mn content was obtained at surface of Mn-NCM by cross-section TEM-EDS analysis, where surface composite of Mn surface coated NCM was $LiNi_{0.71}Co_{0.10}Mn_{0.19}O_2$. TEM-EDS linear mapping indicates Ni content is increased from surface to center of NCM particle while Mn and Co contents are decreased. The depth of Mn doping depth is about 150 nm. Particle hardness was measured, and is found to improve from 51 MPa to 110 MPa as a result of Mn surface doping. High temperature (60°C) cycle performance indicates the enhanced cycle performance was obtained for Mn-NCM. Even capacity retention after 50 cycle was 31% for pristine NCM, that of Mn-NCM was maintained up to 61%. DSC curves for charged cathode show that main exothermic peak is increased from 214°C to 231°C by Mn surface doping. This result emphasizes that a surface doping is effective to improve thermal stability of NCM. The detail results will be discussed at meeting.

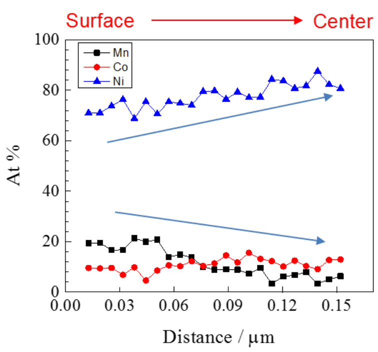

Fig. 1. Cross-sectional TEM-EDS linear mapping results for Mn-NCM

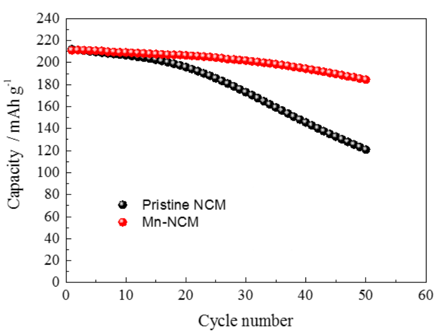

Fig. 2. Cycle performance with a current of 0.5C at a temperature of 60°C