

# Improvement of structural stability of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode against high-voltage cycling by lithium silicate modification

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A high energy density is required for the next-generation lithium ion batteries as power sources of electric vehicles. The energy density is improved by the use of positive electrode materials with high specific capacity such as high-nickel layer-structured  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  ( $x > 0.5$ ).  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  (NCM) can offer a high capacity of around 200 mAh  $\text{g}^{-1}$  by charging to potentials higher than 4.5 V (vs.  $\text{Li}/\text{Li}^+$ ) [1]. However, the reversible capacity gradually decreases with repetitive charge/discharge cycles, which is caused by structural changes, crack formation and dissolution of NCM, oxidative decomposition of electrolyte solution, etc. The cracks result in a loss of electrical contacts between NCM particles. In addition, the cracked surfaces cause further decomposition of electrolyte solution and dissolution of  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ . One effective approach to suppress the crack formation is a surface treatment of NCM [2]. In this study, we coated NCM with lithium silicate (LS), and investigated the charge/discharge properties of the LS-coated NCM (LS-NCM) positive electrode.

LS-NCM powder was prepared via a precipitation method; NCM powder was suspended in an aqueous solution of  $\text{Li}_2\text{Si}_5\text{O}_{11}$  and  $\text{LiOH}$ . Ethanol was added drop-wisely to the suspension with vigorous stirring. The precipitate was filtered, and dried at 60°C for 12 h. Then, the powder was annealed at 500°C for 8 h to obtain LS-NCM. Charge/discharge tests were performed using two-electrode cells at a rate of 0.1 C between 2.5 and 4.6 V at 30°C. The counter electrode and electrolyte solution were lithium foil and 1 M  $\text{LiPF}_6/\text{EC}+\text{DMC}$  (1:2 vol. ratio), respectively.

In the 100th cycle, 81.6% of the initial discharge capacity was obtained for the LS-NCM electrode, which was higher than that obtained for the uncoated NCM electrode (71.4%). The coulombic efficiency of LS-NCM and uncoated NCM electrodes in 100 charge/discharge cycles averaged 99.4% and 97.8%, respectively; the LS-NCM electrode maintained relatively constant coulombic efficiency over 100 cycles, while it gradually decreased in the later cycles for the uncoated NCM. Thus, the LS-coating effectively suppressed not only capacity fading, but also the irreversible decomposition of electrolyte solution. In addition, cross-sectional SEM images revealed that many cracks were formed in the uncoated NCM particles along the grain boundaries after 100 cycles, while the crack generation was significantly inhibited for the LS-NCM electrodes. Cross-sectional FIB-TEM-EDX analysis of LS-NCM showed that LS was present not only on the surface of the secondary particles, but also at the grain boundaries inside the particles. These results suggest that LS at the grain boundaries effectively enhance the structural integrity of the NCM particles.

## References:

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