Synthesis of Ni-Rich NMC Cathode Material by Redox-assisted Deposition Method for Lithium ion Batteries

Ya-Ting Tsai (蔡亞庭) Che-Ya Wu (吳哲亞) Jenq-Gong Duh (杜正恭)
Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan

ABSTRACT

This work demonstrates a novel solution-based synthesis method for NCM powder and surface modification at the same time. KMnO₄ is used as strong oxidant and the source of manganese. This is different from conventional process that metal ions in the precursors have the same valence state as product. Cobalt manganese oxyhydroxide precipitated on spherical Ni(OH)₂ uniformly by redox reaction between Co and Mn. Besides, partial amount of Ni²⁺ on the surface of Ni(OH)₂ is oxidized to Ni³⁺. This process was proved to enhance the structure stability and the rate capacity of Ni-rich cathode materials. The impurity-free LiNi₀.₉₆Co₀.₀₃Mn₀.₀₁O₂ (NMC-R) with high crystallinity is successfully fabricated. NMC-R performed low cation mixing degree and order surface structure. The material synthesized by redox-assisted deposition displays a high capacity of ~197 mAh g⁻¹ at the beginning and the capacity retention is about 93% after 100 cycles. It also provides 68 mAh g⁻¹ higher than the LiNiO₂ (LNO) sample at a high rate of 10C. In summary, a novel solvent-based preparation method for cathode material with stable structure is developed, which is very promising for practical industrial scale.

CHARACTERIZATION

The SEM images of the NMC-R show the spherical particle. According to the EDX analysis of NMC-Pre and NMC-R, the thickness of the coating layer is around 750 nm and the element distributed evenly over the particle after calcination.

ELECTROCHEMICAL PERFORMANCE

NMC-R shows higher coulombic efficiency and only declines from 197 to 183 mAh g⁻¹ with a capacity retention of 93% after 100 cycles. However, LNO suffers from serious capacity fading and the retention is only 73%. NMC-R also displays a better rate capability than LNO sample, especially at high C-rates. Smaller ΔV indicates that NMC-R has better reversibility and electronic conductivity caused by doping cobalt and manganese. From the EIS test, both Rs and Rct of NMC-R are smaller than that of LNO. The Li diffusion coefficient is significantly increased after doping and surface oxidation.

MANUFACTURING SCALE-UP

The results wasn’t optimal when the same calcination condition was adopted. With longer calcination time, the performance is improved and appears even better than before.

CONCLUSION

The nickel-rich LiNi₀.₉₆Co₀.₀₃Mn₀.₀₁O₂ cathode material is successfully prepared by redox-assisted deposition method and surface oxidation is completed simultaneously. The process is carried at milder condition without tedious steps, lots of control and expensive chemicals. It exhibits remarkable electrochemical performance with retention of 93% after 100 cycle test at 0.5C.

ACKNOWLEDGEMENTS

This research is sponsored by Ministry of Science and Technology under the contract No. MOST 108-3116-F-007-003.