Electrochemical characteristics of metal oxide coated LiCoO₂ prepared by fluidized bed spray method for the lithium secondary battery Seungsuk Oh^a, Joong Kee Lee*, Dongjin Byun^a, Byung Won Cho and Dalkeun Park Eco-Nano Research Center, KIST, Seoul 130-650 KOREA ^aDept. of Materials Science & Engineering, Korea

University, Seoul 136-701 KOREA

LiCoO₂ has been commercially employed as active material of the cathode of Li-ion cells due to its high energy density and stable capacity. The capacity of the cell depends on the electrochemical characteristics of cathode active materials. Therefore, much work should be focused on the optimization of the active materials. The modification of surface properties of the cathode materials by coating its particles with some metal oxides recognized as one of the reliable techniques. The advantage of this technique is that the side reactions on the surface with electrolyte are avoided and the structural breakage of LiCoO₂ during charge discharge cycling can be lessened [1].

In the present study, metal oxides such as Al_2O_3 and NiO were coated on the surface of LiCoO₂ particles by fluidized-bed spray method and then investigations of effects of surface modification on electrochemical characteristics were carried out for lithium secondary battery.

Used raw $LiCoO_2$ powder was a commercial product (Nippon chemical Industrial) with average particle diameter of about 5μ m. For coating solutions, the employed metal salts were Aluminum lactate and Nickel acetate tetrahydrate. These metal salts were dissolved into a mixture of distilled water and ethanol. Spray coating was based on fluidized-bed process where fluidized LiCoO₂ powder was coated by spraying coating solution and dried simultaneously inside the chamber. The LiCoO₂ powder which coated metal solution was calcined in the furnace at 300 $^{\circ}$ C for 3h and at 500 $^{\circ}$ C for 3h under O₂ atmosphere. Coated LiCoO2 was mixed with Acetylene black for conductor and a PVDF binder at weigh ratio of oxide coated LiCoO₂/ acetylene metal black /binder=85:9:6 in a solvent to prepare a slurry. The slurry was spread on Al foil by dipping method to make the positive electrode. Half cells were assembled in dry room with LiCoO₂ as the working electrode, Lithium foil as the counter electrode, 1M LiPF₆ in EC:DMC:EMC(1:1:1) as the electrolyte and polypropylene-based film as the separator. Typical charge-discharge tests were carried out using galvanostatic cycling at 0.2C rate between 3 and 4.2V.

Fig. 1 compared surface morphologies between raw $LiCoO_2$ and Al_2O_3 and NiO coated $LiCoO_2$, respectively.

Table1 shows quantitative analysis of weight percent of metal oxide coating on $LiCoO_2$ surface by ICP.

Fig. 2 shows the discharge curves of the raw $LiCoO_2$ and metal oxide coated $LiCoO_2$. The difference in discharge capacity between raw and surface modified $LiCoO_2$ was observed with cycling. Fig. 3 shows the cycling profiles of raw $LiCoO_2$ and metal oxide coated $LiCoO_2$. The discharge capacity of raw $LiCoO_2$ is 144mAg/h at first cycle, but it decreases sharply after 10cycles and then reached to 100mAh/g after 50cycles. As for Al_2O_3 and NiO coated $LiCoO_2$, the discharge capacity maintains about 90% of their initial capacity even after 50cycles.

References

[1] Z. Wang, L. Liu, L. Chen, X. Huang, J. Solid State

Ionics 148 (2000) 335.

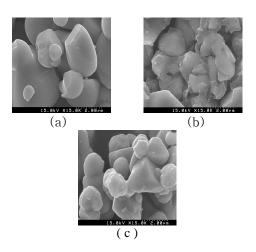


Fig. 1. Scanning electron micrographics of (a) raw $LiCoO_2$, (b) Al_2O_3 coated $LiCoO_2$, (c) NiO coated $LiCoO_2$.

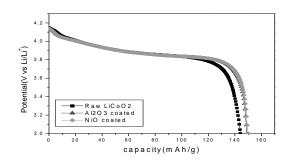


Fig. 2. Comparison of initial discharge curves between LiCoO₂ and the surface modified LiCoO₂s at 0.2 C rate.

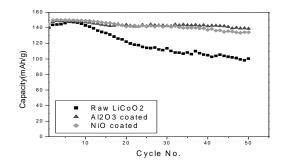


Fig. 3. The change of discharge capacities with cycles for LiCoO₂ and the surface modified LiCoO₂s

Table 1. Elemental analysis for LiCoO₂ and the surface modified LiCoO₂s

	Coating weight Percent (Wt%)	Element analysis by ICP (Wt%)	BET Surface Area (cm ² /g)
LiCoO ₂ as Received	0	0	0.2782
Al ₂ O ₃ coated LiCoO ₂	1.00	1.00	0.7302
NiO coated LiCoO ₂	1.00	1.05	0.5833