Enhanced long-term cycle life of cathode material for Lithium ion battery by AlF_3 coating

Sang-Hyuk Lee[a], Chong Seung Yoon[b], and Yang-Kook Sun[a]

[a] Department of WCU Energy Engineering, [b] Department of Materials Science and Engineering, Hanyang University, Seoul 133-791, Republic of Korea

Introduction

Nickel-rich $Li[Ni_{1-x}M_x]O_2$ (M = Co, Mn, Al, etc.) materials areconsidered to be the most promising cathode materials owing to their high specific capacity which is greater than 200 mA h g^{-1} [1.2].

However, the $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ material shows poor cycle durability especially at an elevated temperature (e.g., 55 ^oC) because the highly delithiated $Li_{1-\delta}[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ contains a high concentration of unstable Ni^{4+} ions and will easily transform to a more stable NiO on the cathode surface, which results in high interfacial resistance and eventual capacity fading [3].

Herein, a simple dry-process was developed to coat an ultrathin AlF_3 layer on a $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ cathode material based on highspeed mechanofusion without any solvent. This is suggested and investigated to overcome those issues.

Experimental

Nano-sized AlF_3 powder was synthesized using $Al(NO_3)_3 \cdot 9H_2O$ and NH_4F with a molar ratio of 1:7. An aqueous NH4F solution was added drop by drop into an aqueous $Al(NO_3)_3 \cdot 9H_2O$ solution in which the pH was adjusted to 10. The mixed solution was aged for 5 min at 25 ^oC and the solvent was evaporated. The obtained $(NH_4)_3AlF_6$ powders were heated at 400 ^oC for 5 h in continuously flowing nitrogen and AlF_3 powders were obtained.

To coat the surface of the $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$, 5 g of AlF_3 (1 wt%) was mixed thoroughly with 500 g of $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ powder via a Nobilta (NOB-130, Hosokawa Micron Co., Japan) for 5 min at a speed of 3400 rpm.

Long cycle-life tests were performed in a laminated-type full cell wrapped with an Al pouch. Mesocarbon microbeads (MCMB) were used as the anode electrode material. Cell fabrication was completed in a dry room. The cells were charged and discharged between 3.0 and 4.2 V by applying a constant 1 C rate (200 mA g^{-1}) at 25 ^oC and 55 ^oC.

Results and discussion

The pristine $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ had a clean and rough spherical surface consisting of nanoparticles, whereas the AlF_3-coated sample was completely covered by an AlF_3 layer with a thickness of 50 nm, as shown in Fig. 1.

To investigate the AlF_3 coating effect further, the cells of C/pristine and AlF_3-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ were cycled over 500 cycles at 55 ^oC and the results are shown in Fig. 2. The C/pristine $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ exhibited a rapid capacity loss, leading to a capacity retention of only 11.7%. However, C/AlF_3-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ demonstrates a greatly improved cycling performance, exhibiting a capacity retention of 55.9% due to complete encapsulation of the particle surface with an AlF_3 layer.

The improved electrochemical performance likely arose from the AlF_3 coating layer which may have retarded the transition metal dissolution from HF attack. Electrochemical impedance spectroscopy and transmission electron microscopy provided direct evidence that the AlF_3 coating layer suppressed the increase in charge transfer resistance and cathode material pulverization during cycling.

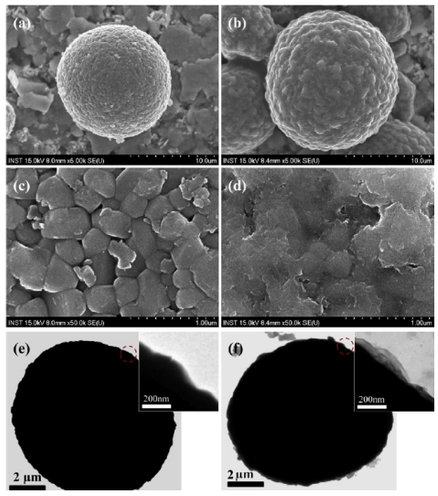

Fig. 1. SEM images of (a) the pristine $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$, (c) magnified images of (a), (b) the AlF_3-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$, and (d) magnified images of (b). TEM images of (e) the pristine $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ and (f) the AlF_3-coated Li $[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$. TEM image in inset confirms existence of the AlF_3 coating layer (50 nm) on the surface of $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ particle.

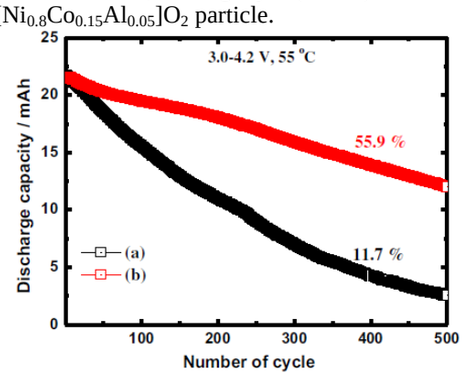

Fig. 2. Cycling performance of (a) C/pristine $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ and (b) C/AlF_3-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ cells during 500 cycles at a current density of 200 mA g^{-1}(1.0 C) at 55 ^oC.

References

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