

## Enhanced Capacity Retention and Rate Capability of Layered Li-Ni-Co-Mn-O Compound by Al Oxide Coating

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### Introduction

Extensive research has been carried out over past 10 years to find alternative cathode materials and to beat LiCoO<sub>2</sub> in lithium-ion rechargeable batteries. Recently, manganese based layer-structured materials, Li[Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>]O<sub>2</sub> and Li[Ni<sub>1/2</sub>Mn<sub>1/2</sub>]O<sub>2</sub>, have been shown to be one of the most promising alternative materials for LiCoO<sub>2</sub> since their electrochemical and safety characteristics are comparable or superior to LiCoO<sub>2</sub> [1,2].

Cho et al. [3] reported that metal oxide coating of LiCoO<sub>2</sub> effectively enhanced the cycling performances and capacity retention. Chen et al. [4] suggested that such metal oxide coating made it possible to cycle LiCoO<sub>2</sub> to 4.5 V versus Li with excellent cyclability.

To maintain high capacity, there are two kinds of way to improve the nature of active materials; i) partial substitution and ii) coating of active materials. Substitution gives rise to improvement of structural and thermal stability even in highly oxidized state. However, this method should sacrifice the original capacity of active materials because the electro-active transition metal is replaced by other elements such as Mg, Zn, Al, Zr, Ti, etc.. On the other hand, coating approach is beneficial in respect to retain the original capacity because improvements of electrochemical properties can be achieved by a very small amount of coating of electrode materials. Furthermore, the coated layer may provide a passivation layer on the surface of active materials so that it would protect the active material from HF attack into electrolyte, especially at higher voltage operation, as suggested by Sun et al. [5]. Here we would like to report the effect of Al coating on layered Li[Li<sub>0.05</sub>Ni<sub>0.4</sub>Co<sub>0.15</sub>Mn<sub>0.4</sub>]O<sub>2</sub>.

### Experimental

Li[Li<sub>0.05</sub>Ni<sub>0.4</sub>Co<sub>0.15</sub>Mn<sub>0.4</sub>]O<sub>2</sub> powders were coated by Aluminum triisopropoxide (1 wt %). For comparison, bare and coated materials were fired at 400 °C in air. The as-fired materials were examined by XRD, SEM-EDX, TEM, XPS. For electrode preparation, the prepared powders were mixed with 6 wt % of conducting carbon and 4 wt % of poly(vinylidene fluoride) binder in *N*-methyl pyrrolidinone. For electrochemical investigation, a coin-type cell (2016) consisted of the cathode, lithium foil as the anode, separator and 1 M LiPF<sub>6</sub> in EC:DEC (1:2 in volume) as the electrolyte. The cells were firstly charged, and then discharged between 3.3 V and 4.3 V with various densities at 25 °C.

### Results and discussion

After firing the bare and Al coated materials at 400 °C in air, XRD examination was carried out. There was no Al-related impurity phase in the final product. TEM observation showed that nano-dispersed particles (Al<sub>2</sub>O<sub>3</sub>) partially coated the surface of the active materials. Lattice parameters were calculated by a least square method from the XRD patterns. As shown in Table 1, there is no remarkable difference in the lattice parameters. This means that the Al elements are not incorporated in to the layered lattice, but coated on the surface of the Li[Li<sub>0.05</sub>Ni<sub>0.4</sub>Co<sub>0.15</sub>Mn<sub>0.4</sub>]O<sub>2</sub>.

Obviously, the Al coated sample delivered greater discharge capacity than uncoated sample, especially at the high discharge rate (3 C). Figure 1 shows cycling results of bare and Al coated Li[Li<sub>0.05</sub>Ni<sub>0.4</sub>Co<sub>0.15</sub>Mn<sub>0.4</sub>]O<sub>2</sub>. The higher capacity at 3 C rate was maintained during cycling. On contrast, there was a severe capacity fade at high rate for the bare sample during cycling. Details of structure and electrochemistry of Al coated Li[Li<sub>0.05</sub>Ni<sub>0.4</sub>Co<sub>0.15</sub>Mn<sub>0.4</sub>]O<sub>2</sub> will be discussed on the conference site.

### References

- [1] T. Ohzuku et al., *Chem. Lett.*, **2001**, 642.
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- [3] J. Cho et al., *J. Electrochem. Soc.*, **148**, A1110 (2001).
- [4] Z. Chen et al., *Electrochem. Solid State Lett.*, **6**, A221 (2003).
- [5] Y.-K. Sun et al., *J. Electrochem. Soc.*, **150**, A970 (2003).

Table 1. Comparison of lattice parameters of bare and Al coated Li[Li<sub>0.05</sub>Ni<sub>0.4</sub>Co<sub>0.15</sub>Mn<sub>0.4</sub>]O<sub>2</sub>. Both materials were fired at 400 °C in air.

Sample	a-axis (Å)	c-axis (Å)
Bare	2.871(5)	14.279(3)
Al coated	2.871(3)	14.273(5)

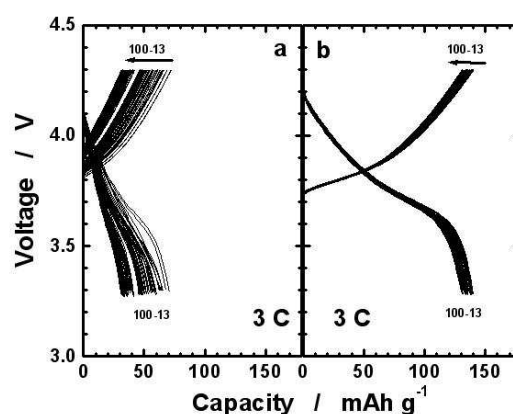


Figure 1. Continuous charge-discharge curves of (a) bare and (b) Al coated Li[Li<sub>0.05</sub>Ni<sub>0.4</sub>Co<sub>0.15</sub>Mn<sub>0.4</sub>]O<sub>2</sub> at 25 °C. Rate-capability tests for the initial 12 cycles were excluded. Then, the cycling test was done at 3 C rate (from the 13th cycle).