



## Effect of titanium addition as nickel oxide formation inhibitor in nickel-rich cathode material for lithium-ion batteries



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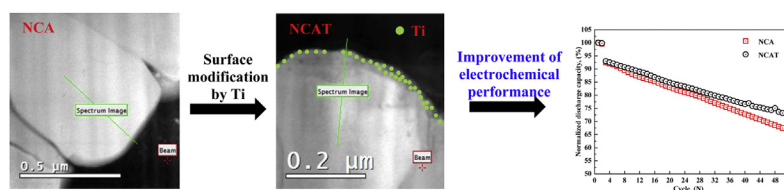
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### HIGHLIGHTS

- Nickel-rich NCA cathode for Li-ion batteries was modified with Ti.
- Ti doping enhanced electrochemical performance due to a reduction of NiO formation.
- Ti acts as a charge compensator hinders Ni<sup>2+</sup> formation and diffusion to Li sites.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Among high capacity cathodes, LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> has a high capacity and stable electrochemical performance, although it suffers from degradation upon cycling and aging as a result of the formation of inactive NiO on the surface edges. In this study, the role of Ti, which partially replaces Ni in the transition metal layer that is in particular intended to surface region not in bulk of LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>, is investigated on the electrochemical performance and interfacial phenomena using transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy, electron energy loss spectroscopy, and X-ray diffraction analyses before and after electrochemical cycling. As a result, formation of NiO inactive phase is inhibited for the Ti-doped LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>, so that the electrode could deliver higher capacity upon cycling test. Further electrochemical impedance analysis is performed to understand the interfacial behavior of Ti-doped LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.02</sub>Ti<sub>0.03</sub>O<sub>2</sub>).

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### 1. Introduction

Recent environmental issues and increasing demand for high capacity lasting portable devices are accelerating the technological

limits of current batteries. These concerns can be accomplished by improving existing battery components or through the innovation of new materials. So far, cathode materials have drawn the most attention because structural instability causing capacity fade upon cycling can be greatly improved through partial substitution [1–3] and surface modification [4–8].

Since the invention of lithium-ion batteries, the transition metal oxide cathodes have continuously evolved. Although LiCoO<sub>2</sub>, which was pioneered as the first cathode material, has good capacity and facile producibility, it is considered to be unsatisfactory due to its cost and toxicity [9]. LiNiO<sub>2</sub> was suggested as a replacement

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material for LiCoO<sub>2</sub>, but LiNiO<sub>2</sub> has its own shortcomings including difficulties in production and instability during cycling [10,11]. To balance the pros and cons of these two materials, Ni has been partially replaced by Co substitution in these systems to stabilize the two-dimensional layered structure [12,13]. For instance, LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> delivers a high capacity of 190 mAh g<sup>-1</sup> [14,15], though it cannot comply with battery safety which stems from thermal instability. Therefore, the cathode materials are necessarily modified by doping and coating with foreign materials (Al, Mn, Mg, Fe, Sr, etc.) to resolve the thermal stability issue [16,17]. According to our literature survey, one of the most favorable cathode materials would be LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) in terms of capacity and thermal stability among existing high capacity cathode materials. Although the addition of Al supports structural stability during electrochemical cycling, degradation, which is mainly caused by lowering Ni-oxidation state from Ni<sup>4+</sup> to Ni<sup>2+</sup> at charged state which is accompanied by oxygen loss and the formation of an inactive, and Li-deficient NiO phase on the particle surface are inevitable [18–20]. The formed inactive phase is thickened when it comes into contact with the electrolyte during cycling, which simultaneously affects the impedance and the charge transfer of Li<sup>+</sup> at the surface.

Elaboration has been made to reduce the inactive NiO phase formation by coating with an electrochemically inactive metal oxide such as TiO<sub>2</sub> [21]. Likewise, Ti substitution also demonstrates improvement of electrochemical properties derived from suppression of Ni<sup>2+</sup> migration into Li sites and a decrease in lattice changes during cycling [21–23]. It would be reasonable because Ti is electrochemically inactive and acts as a charge compensator, not allowing Ni<sup>2+</sup> to form. However, we should take into account that Ti is electrochemically inactive over a wide voltage range; doping the whole structure could also lead to an initial decrease in the capacity.

The above-mentioned indicates that hybridization of surface and structural stabilization would be highly effective in preventing the evolution of NiO phase. In this paper, therefore, a tiny amount of Ti is intentionally introduced onto both the surface and grain interfaces of NCA particles because deterioration process of active material is initiated from the surface region. NCA represents LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> and NCAT denotes LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.02</sub>Ti<sub>0.03</sub>O<sub>2</sub>, in which the Ni content was raised to 85% while decreasing Co and Al content together to incorporate Ti which satisfies the chemical composition of LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.02</sub>Ti<sub>0.03</sub>O<sub>2</sub>. Considering the available redox species are Ni<sup>3+/4+</sup> and Co<sup>3+/4+</sup>, both NCA and NCAT have the same amount of electrochemical active species, 95%. Effectiveness of Al doping or Al–Ti double doping can be found through electrochemical cycling performance and the resulting structural variation during cycling test. We also suggest degradation related to formation of the inactive NiO phase on the particle surfaces of NCA and NCAT (LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.02</sub>Ti<sub>0.03</sub>O<sub>2</sub>).

## 2. Experimental

The cathode active materials of NCA and NCAT, which were commercially available, were provided by Ecopro Co. Multi-metal hydroxide precursors for NCA and NCAT were prepared by coprecipitation, as reported previously [24]. An aqueous solutions of NiSO<sub>4</sub> · 6H<sub>2</sub>O, CoSO<sub>4</sub> · 7H<sub>2</sub>O, and Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O were pumped into a continuously stirred tank reactor (CSTR, capacity 90 L) in an N<sub>2</sub> atmosphere. Simultaneously, NaOH solution (25 wt%, aq.), an appropriate amount of NH<sub>4</sub>OH solution (28 wt%, aq.) and a chelating agent were fed separately into the reactor. The obtained NCA and NCAT precursors were filtered and washed with distilled water and then dried at 130 °C for 12 h. To synthesize NCA,

mixture of NCA precursor powder and LiOH · H<sub>2</sub>O (Li/Metal ratio = 1.02) were preheated to 550 °C for 6 h and then heated at 750 °C for 12 h in an O<sub>2</sub> atmosphere. To synthesize NCAT, NCAT precursor powder and TiO<sub>2</sub> nano-powder (Aldrich) were mixed with high speed mixer for 5 min and LiOH · H<sub>2</sub>O (Li/Metal ratio = 1.02) was added before additional mixing for 15 min. The mixture of NCAT precursor, TiO<sub>2</sub> and LiOH · H<sub>2</sub>O were preheated to 550 °C for 6 h and then heated at 750 °C for 12 h in an O<sub>2</sub> atmosphere.

Scanning electron microscopic (SEM, JEOL, JSM-7000F) studies were employed to characterize the synthesized powders. The crystalline phases of the above described products were characterized by powder X-ray diffraction (XRD, Rint-2000, Rigaku) analysis using Cu-Kα radiation. The XRD data were obtained at a 2θ range of 15–100°, with a step size of 0.03° and a count time of 5 s. The collected XRD intensity data were analyzed using the Rietveld refinement program Fullprof 2002 [25].

The cathode slurry was prepared by mixing 94% active material (NCA or NCAT) with 3% conducting agent Denka Black and 3% poly-vinylidene fluoride binder (PVDF) in *N*-methyl pyrrolidone (NMP) solution and mixing. Afterwards, the slurry was applied onto an Al foil using a doctor blade and dried in a conventional oven at 110 °C for 60 min. The foil with the electrode was roll-pressed and then punched into discs. These were dried again in the vacuum oven at 60 °C for 30 min to remove any traces of unwanted volatile substances. For all the electrochemical tests and spectroscopic analyses, 2016 coin-type cells were assembled in an argon filled glove box. The cells consisted of a positive electrode, Li metal as a negative electrode, a 1 M LiPF<sub>6</sub> electrolyte dissolved in a solvent of ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/diethyl carbonate (DMC) (1:1:1 volume ratio), and a microporous polypropylene Celgard 250 separator. The cycling tests were performed in the galvanostatic mode using a WonA tech WBCS 3000 battery cycler at a constant current of 1 C between 2.5 V and 4.5 V over 50 cycles at room temperature. The current rate was calculated from the actual current employed (C/5 in first 2 cycles and increased to 1 C rate to 50 cycles), the weight of the active material, and an assumed theoretical capacity (200 mAh g<sup>-1</sup>). The rate capability of the cathode materials was measured using the WonA tech WBCS 3000 battery cycler. The cells were first charged at a constant current rate of C/5 and discharged at different constant currents ranging from C/2 to 2 C between a voltage window of 2.5 V and 4.5 V at room temperature.

Transmission electron microscopy (TEM) combined with energy dispersive X-ray spectroscopy (EDX) elemental mapping and electron energy loss spectroscopy (EELS) analysis of the edge and central regions of the samples were carried out. The cells were disassembled in an Ar filled glove box and the positive material discs were washed with DMC to remove any LiPF<sub>6</sub> salt and traces of unwanted side products that were formed by reactions between the electrode and the electrolyte. Samples with a homogenous, thin thickness were prepared by focused ion beam (FIB), as provided by the Helios NanoLab DualBeam. TEM-EDX was carried out using a Bruker Quantax 400 EDX coupled to the TEM. EELS spectra were collected with a Gatan Enfina spectrometer operating at 200 keV attached to the TEM.

The electrochemical impedance spectroscopy (EIS) analysis was obtained using an Ivium nStat at room temperature. The EIS measurements were performed with 5 mV perturbation amplitude between 200 kHz and 0.005 Hz from high to low frequencies. The impedance spectra were recorded at the initial state (SOC 0%) and the fully charged state (SOC 100%) after an additional rest time of at least 5 h to achieve the same open circuit potential (OCP) in each step.

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