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Short communication

Improvement of long-term cycling performance of Li[$Ni_{0.8}Co_{0.15}Al_{0.05}$]$O_2$ by AlF_3 coating

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HIGHLIGHTS

- ► The surface of NCA (Li[$Ni_{0.8}Co_{0.15}Al_{0.05}$]$O_2$) was coated by AlF_3 through dry process.
- ► The AlF_3-coated NCA full cell showed excellent electrochemical performance.
- ► The AlF_3-coated NCA had better thermal stability than the pristine electrode.
- ► AlF_3 coating suppressed the increase in resistance and particle pulverization.

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ABSTRACT

The surface of a Li[$Ni_{0.8}Co_{0.15}Al_{0.05}$]$O_2$ cathode material was coated by a 50-nm thick AlF_3 layer using a simple dry coating process. Although the initial discharge capacity of pristine and AlF_3-coated Li[$Ni_{0.8}Co_{0.15}Al_{0.05}$]$O_2$ was nearly same, the AlF_3-coating significantly improved the electrochemical performances of Li[$Ni_{0.8}Co_{0.15}Al_{0.05}$]$O_2$ in a full cell configuration (graphite anode), especially at an elevated temperature (55 °C). Furthermore, the AlF_3-coated Li[$Ni_{0.8}Co_{0.15}Al_{0.05}$]$O_2$ had better thermal stability than the pristine electrode. 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.

1. Introduction

The demand for power sources in portable devices, hybrid electric vehicles (HEVs) and electric vehicles (EVs) increases every year. To become viable sources of electrical power, batteries need to possess a large capacity, an excellent rate capability, be safe, and must be inexpensive [1–3]. To date, the lithium-ion battery satisfies most of these requirements, but an improvement in the components of the cathode material is still needed. Nickel-rich Li[$Ni_{1-x}M_x$]O_2 (M = Co, Mn, Al, etc.) materials are considered to be the most promising cathode materials owing to their high specific capacity which is greater than 200 mA h g^{-1} [4,5]. Among these promising materials, the Li[$Ni_{0.8}Co_{0.15}Al_{0.05}$]$O_2$ cathode material shows improved electrochemical performance and thermal safety with cation substitution of Co and Al by increasing the structure stability [6,7]. 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 °C) 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 [8]. In addition, the accompanying oxygen evolution from the delithiated $Li_{1-\delta}$[$Ni_{0.8}Co_{0.15}Al_{0.05}$]$O_2$ causes poor safety of cathode.

One effective approach to solve these aforementioned problems is coating the Li[$Ni_{0.8}Co_{0.15}Al_{0.05}$]$O_2$ cathode material with a uniform layer of nanoscale metal oxides [9–11], metal hydroxide [12], metal fluoride [13,14], and metal phosphates [15,16]. The coated cathode material showed a much improved capacity retention, rate capability, and even thermal stability. These coating layers may serve as i) a HF scavenger that reduces the acidity of non-aqueous electrolyte and suppresses metal dissolution from the cathode materials; and

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ii) as a physical protection layer of the cathode surface from HF attack and electrolyte decomposition that impedes a side reaction [17]. To date most of the coated cathode materials are based on the wet process that uses aqueous or nonaqueous solvents (mostly alcohol) which are both costly and flammable. Moreover, these wet-coating techniques require additional and complicated coating processes of mixing, drying, and heating as well as a special facility which translate into a higher production cost for the cathode material. The high production cost in this process is not widely acceptable in practical applications. Hence, a simple dry-coating process has been recently reported and is garnering attention [18,19].

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 high-speed mechanofusion without any solvent. The electrochemical performance of an AlF_3-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ cell was characterized and compared with a pristine $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ cell in a full cell configuration using MCMB as an anode to accurately evaluate the coating effect. To elucidate the improved electrochemical performance of the C/AlF_3-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ cell, X-ray diffraction (XRD), electrochemical impedance spectroscopy (EIS) and transmission electron microscopy (TEM) were used to characterize the electrode in detail.

2. 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 NH_4F 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 °C and the solvent was evaporated. The obtained $(NH_4)_3AlF_6$ powders were heated at 400 °C for 5 h in continuously flowing nitrogen and AlF_3 powders were obtained.

The $[Ni_{0.8}Co_{0.15}Al_{0.05}](OH)_2$ precursor was prepared by a co-precipitation method [20]. An aqueous solution of $NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$ and $Al_2(SO_4)_3 \cdot 16H_2O$ was pumped into a continuously stirred tank reactor (CSTR, capacity of 4 L) with a N_2 atmosphere. At the same time, a NaOH solution and a desired amount of NH_4OH solution were fed separately into the reactor. To synthesize the $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$, a mixture of $[Ni_{0.8}Co_{0.15}Al_{0.05}](OH)_2$ with $LiOH \cdot H_2O$ was calcined at 780 °C for 15 h under a steady flow of oxygen. 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.

Powder X-ray diffraction (XRD, Rigaku, Rint-2000) employing Cu-Kα radiation was used to identify the crystalline phase of the prepared powder at each stage. The XRD data were obtained at $2\theta = 10°–80°$, with a step size of 0.03° and a count time of 5 s. From XRD data, the lattice parameters were calculated by a least-squares method. The morphology of the powders was determined with scanning electron microscopy (SEM, S-4800, Hitachi). The surface of the AlF_3-coated powder was also observed using transmission electron microscopy (TEM, JEOL 2010).

The electrochemical performance of the synthesized cathodes was assessed in a 2032 coin-type cell. The cell consisted of a cathode and a lithium metal anode separated by a porous polypropylene film. The cathode was fabricated with a mixture of prepared powder, carbon black, polyvinylidene fluoride in *N*-methyl-2-pyrrolidone. The slurry was spread onto aluminum foil and dried in a vacuum oven at 110 °C. The electrolyte used was 1 M $LiPF_6$ in a 1:1 volume mixture of ethylene carbonate and diethyl carbonate (PANAX ETEC Co., Ltd, Korea). The cells were charged and discharged by applying a constant current density of 100 mA g^{-1} (0.5 C rate) at 55 °C in the 2.7–4.3 V range.

Cells were charged to 4.3 V and opened in an Ar-filled dry box for differential scanning calorimetry (DSC) experiments. Samples of 3–5 mg were collected in a stainless steel sealed pan with a capacity of 30 μL and a gold-plated copper seal capable of withstanding a pressure of 150 atm. Thermal stability was determined in a differential scanning calorimeter (DSC, 200PC, Netzsch, Germany) using a temperature scan of 1 °C min^{-1}. The weight was constant in all cases, indicating that no leaks occurred during the experiments.

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 °C and 55 °C. AC-impedance measurements were performed using an impedance analyzer (IM6, Zahner Elektrik) over a frequency range from 1 MHz to 1 mHz with an amplitude of 10 mV_{rms}. Transmission electron microscopy (TEM) was used to observe the morphology of cycled electrodes.

To measure the extent of dissolution of elemental Ni, Co, and Al, a full cell was charged to 4.2 V and then carefully disassembled to obtain the active materials, which were subsequently stored in the electrolyte at 55 °C for four weeks. The amount of dissolved Ni, Co, and Al was measured by inductively coupled plasma (ICP-AES, PerkinElmer, Optima-4300 DV).

3. Results and discussion

Scanning electron microscopy (SEM) images of the $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ powders are shown in Fig. 1. 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. 1f. This confirmed the competency of the simple dry-coating process using the Nobilta in fully coating the surface of the $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ with an AlF_3 layer. As anticipated, this coating layer should improve electrochemical performances of $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ by protecting its surface from HF attack.

Fig. 2 illustrates the initial charge/discharge curves of Li/pristine and AlF_3-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ cells at a current density of 20 mA g^{-1} (0.1 C-rate) between 2.7 V and 4.3 V at 55 °C. Both cells demonstrate almost a similar discharge capacity of 200 mA h g^{-1}. The cycling performance of Li/pristine and AlF_3-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ cells over 100 aggressive cycles (voltage between 2.7 and 4.3 V, current density of 100 mA g^{-1} (0.5 C-rate) and temperature of 55 °C) are shown in Fig. 3. As expected, the AlF_3-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ showed improved cycling performance exhibiting capacity retention of 84.7% compared to that of pristine $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ (79.1%). The capacity retention was similar to the that of a previous AlF_3-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ material prepared by a wet-coating process [13,14].

The long-term cycling performance was evaluated using a laminated-type full cell (25 mA h capacity) with mesocarbon microbeads (MCMB, graphite) as an anode. The full cells were charged and discharged for 1000 cycles at current density of 190 mA g^{-1} (1 C-rate) and 25 °C between 3.0 and 4.2 V as shown in Fig. 4. The cycling performance of the AlF_3-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ significantly improved, showing a capacity retention of 86.2% after 1000 cycles, while the pristine electrode illustrated a slow decrease in capacity, leading to a capacity retention of only 66.5% during the same cycling period.

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 °C and the results are shown in Fig. 5. The C/pristine Li