Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Surface Coating of a $LiNi_xCo_yAl_{1-x-y}O_2$ (x > 0.85) Cathode with Li_3PO_4 for Applying a Water-Based Hybrid Polymer Binder during Li-ion Battery Preparation

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Experimental

(1) SEM-EDX

The observation of pristine and coated NCA particles was performed with field emission type scanning electron microscope (FE-SEM, SU-8010, Hitachi) equipped with Energy Dispersive X-ray microanalyzer (EMAX ENERGY EX-250, HORIBA).

(2) STEM-EDX

A 200 kV transmission electron microscope (TEM and/or STEM, JEM-2100F, JEOL) equipped with two aberration correctors (CEOS GmbH) for the image- and probe-forming lens systems and an X-ray energy-dispersive spectrometer (EDX, JED-2300T, JEOL) were used for compositional analysis of the particle surfaces. Both aberration correctors were optimized to realize the point-to-point resolutions of TEM and scanning transmission electron microscopy (STEM) as 1.3 and 1.1 Å, respectively.

(3) Thermogravimetric differential thermal analysis

The coated layer was characterized by the difference in weight of the coated NCA samples before and after the heat-treatment with a differential thermoanalyzer (ThermoPlus EVO TG 8120, Rigaku).

(4) *p*XRD

The powder X-ray diffractometry (*p*XRD) experiments were performed using CuKα radiation (RINT- Ultima III; λ = 0.1548 nm, Rigaku) at increments of 0.02 degrees from 20 to 80 degrees. An obliquely finished Si crystal (non-reflection Si plate) was used as a sample holder to minimize the background diffraction.

(5) XPS

X-ray photoelectron spectroscopy (XPS) measurements (JP-9010 MC, JEOL) were performed to examine the chemical states of the samples. MgKα was used as the X-ray source with an anodic voltage of 10 kV and a current of 10 mA. All of the XPS spectra for the samples were obtained with a take-off angle of 45° relative to the specimens, and pass energies of 100 and 200 eV for the narrow and survey scans, respectively, were used.

(6) Cathode preparation

Li_3PO_4-coated NCA cathode was prepared as follows: 910 mg of accurately weighed Li_3PO_4-coated NCA particles and 50 mg of acetylene black (AB, Denka Black, Denki Kagaku Gogyo, Japan) were mixed on a mortar with a pestle, and 10 mg of carboxymethyl cellulose (CMC, Polyscience Inc, cat.#6139) and 30 mg of water-based hybrid polymer binder (TRD202A, JSR, Japan) were mixed in Milli-Pore water (1.1 g, > 18 MΩ). Then, the mixture of Li_3PO_4-coated NCA particles and AB was added to the CMC/TRD202A-mixed aqueous solution. The resulting mixed solution containing Li_3PO_4-coated NCA particles, TRD202A, AB and CMC was further mixed with a planetary mixing equipment (Mazerustar, KK-250S, KURABO, Japan) until it became a homogenous slurry. The weight % of Li_3PO_4-coated NCA powder:TRD202A:AB:CMC in the slurry was 91:3:5:1. The homogenous slurry was casted on Al current collector (thickness: 20 μm) with a doctor-blade having the gap of 100 μm. The slurry layer on the Al current collector was dried by evaporating water at 130 °C for 5 h in a vacuum drying oven. For comparison, polyvinylidene difluoride (PVdF, KF9130, Kureha, Japan) was

also used as a binder. The weight % of the cathode films was kept as pristine NCA:PVdF:AB = 91:4:5. In every case, the loading amount of the cathode material on the Al current collector was 3.0-3.4 mg cm^{-2}.

(7) Cell preparation and electrochemical tests

Charging/discharging cycle and rate performance tests of the cathode materials prepared were performed using a CR2032 coin-type cell. In the test cell, each cathode was paired with a lithium metal anode and both electrodes were separated by a porous polypropylene film (Celgard 3401). The electrolyte solution containing 1 M $LiPF_6$ in the mixture of ethylene carbonate (EC) / dimethyl carbonate (DMC) (1/2 volume ratio) (Ube Chemicals, Japan) was impregnated into the separator. The charge/discharge cycle and rate performance tests were carried out using a multi-channel battery tester (HJ1001SD8, Hokuto Denko Corporation, Japan) in thermostatic oven at room temperature (25±1 °C). A constant-current/constant-voltage (CC-CV) mode was used for the charging/discharging cycle processes. The upper and lower voltage limits for the charging/discharging cycle processes were 4.25 and 2.5 V (*vs.* Li/Li^+), respectively. The charge/discharge capacities ($mAhg^{-1}$) were calculated using the weight of NCA particles loaded on the Al current collector in which the weight of the Li_3PO_4 coating was neglected. The charging/discharging cycle tests were done with 0.1 C-rate. The C rate was calculated using the specific capacity of 200 $mAhg^{-1}$ which was obtained with the cathode prepared from pristine (*i.e.*, uncoated) NCA, PVdF binder and AB at a low C-rate of 0.1 C. In the case of high C-rate performance tests, discharge capacity retentions were evaluated assuming that the discharge capacity obtained at 0.1 C corresponds to 100% of discharge capacity retention.

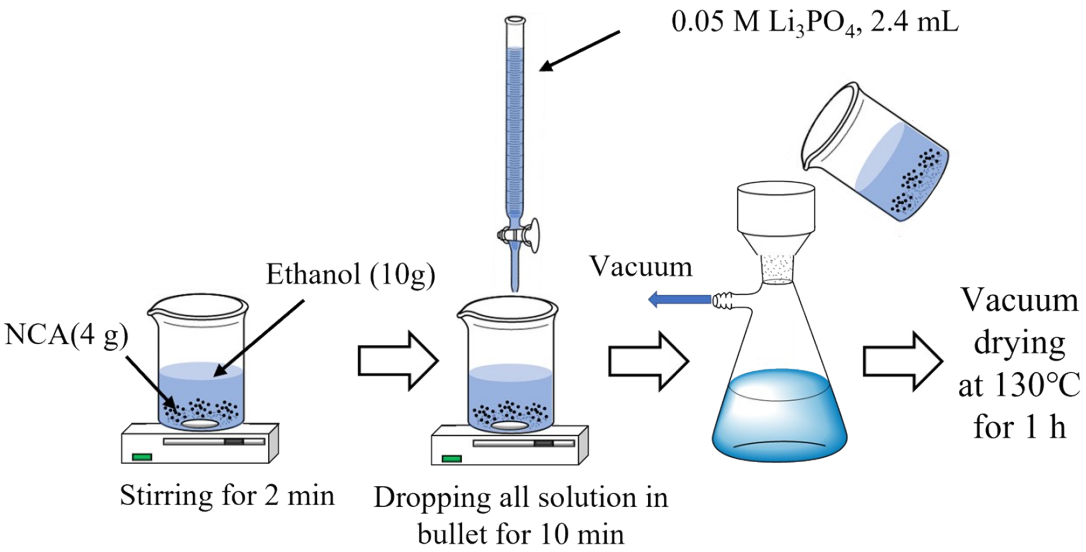

Fig. S1 Schematic description of the Li_3PO_4 coating process on NCA.

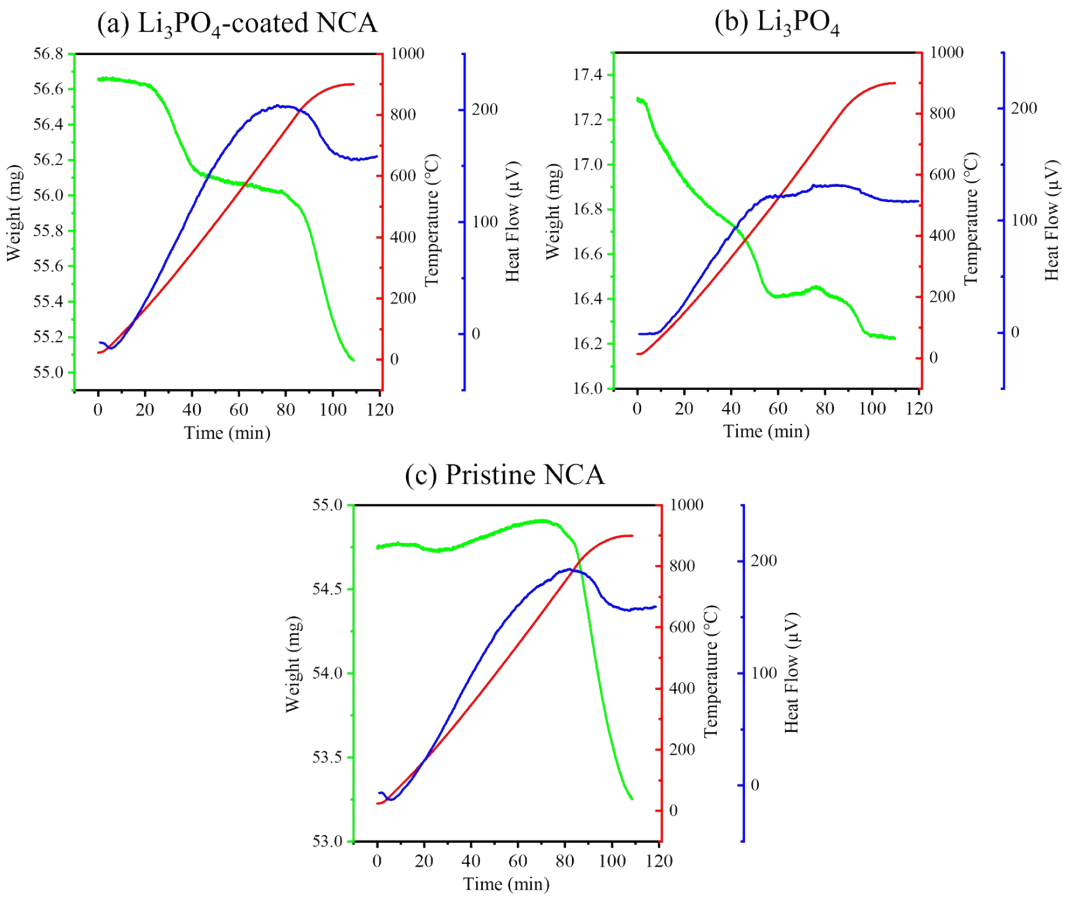

Fig. S2 TG–DTA charts of (a) coated NCA, (b) Li_3PO_4 and (c) pristine NCA in an air atmosphere.

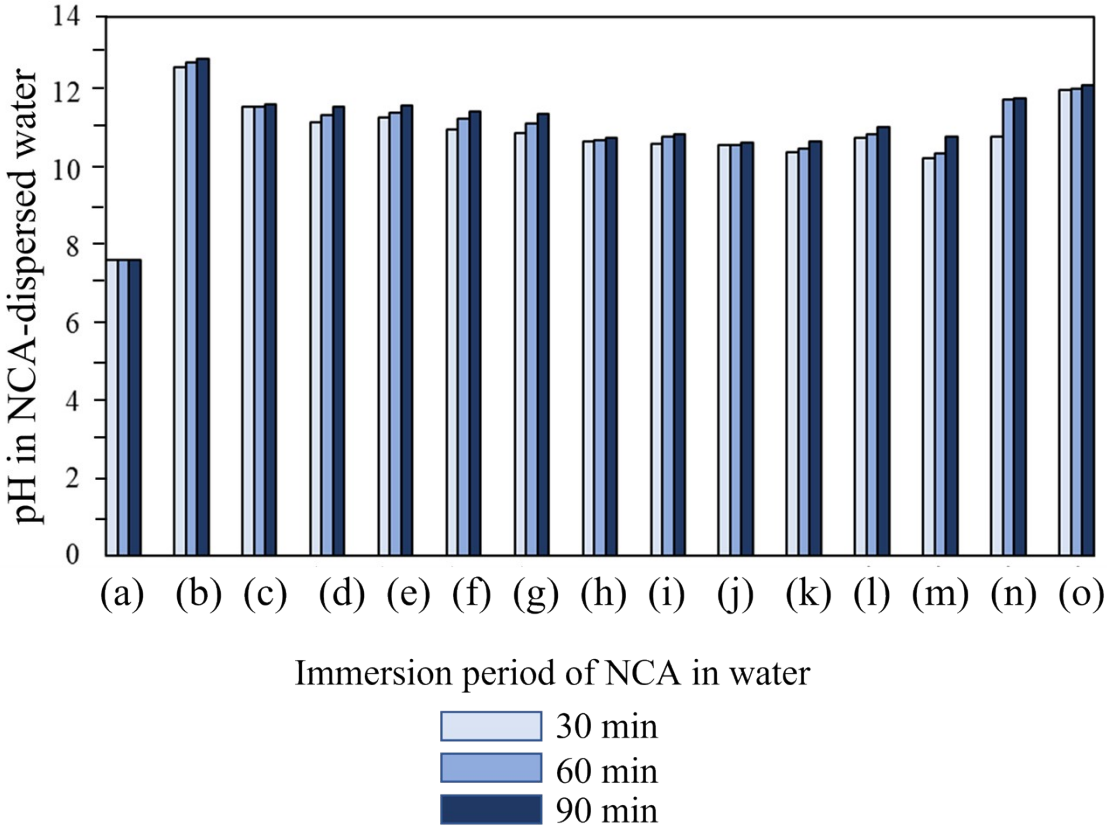

Fig. S3 pH of NCA-dispersed water after immersion periods of 30, 60 and 90 min. (a) Water in which carboxymethyl cellulose (CMC), acetylene black (AB) and TRD202A binder was dispersed for cathode preparation slurry, (b) pristine NCA, (c) coated NCA without heat treatment, (d, f, h, j, l, n) coated NCA with heat treatment at 200(d), 250(f), 300(h), 350(j), 400(l) and 450(n) °C in Ar, (e, g, i, k, m, o) coated NCA with heat treatment at 200(e), 250(g), 300(i), 350(k), 400(m) and 450(o) °C in air. CMC, AB and TRD202A binders were dispersed in the water in which the samples (c-o) were dispersed.