Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Surface Double Coating of $LiNi_aCo_bAl_{1-a-b}O_2$ (a > 0.85) Cathode with TiO_x and Li_2CO_3 to Apply a Water-Based Hybrid Polymer Binder to Li-Ion Batteries' Preparation

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Experimental

Equipments and measurement conditions of TEM, STEM, STEM-EELS and 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. The distribution of Li, O, C, Ni and Ti atoms on the coated- NCA samples was evaluated by Cs-corrected STEM analysis with an electron energy-loss spectroscopy (EELS, Gatan, GIF Quantum). In order to find out their distributions, Li-K edge was simultaneously obtained, and O-K, C-K, Ni-L, and Ti-L edges were also obtained at the same area. We mapped the Li distribution by Li K-edge. Linear background subtraction was made in order to purely get the Li K-edge in distinction from Ni K-edge. Power law back ground subtraction was made in order to get the Ni and Ti L-edges.

Thermogravimetry (TG) experiment

Moisture contents of the cathode electrodes were measured with differential thermoanalyzer (ThermoPlus EVO TG 8120, Rigaku). Tested samples of 44-47 mg were obtained from pristine and TiO_x/Li_2CO_3-coated NCA cathodes by scratching the cathode surfaces. The scratched powders were heated at the temperature elevation rate of 10 $^{\circ}C min^{-1}$ under argon atmosphere. The weight % of water in the cathode was calculated from the difference in weight in the temperature region from 100 to 200$^{\circ}C$.

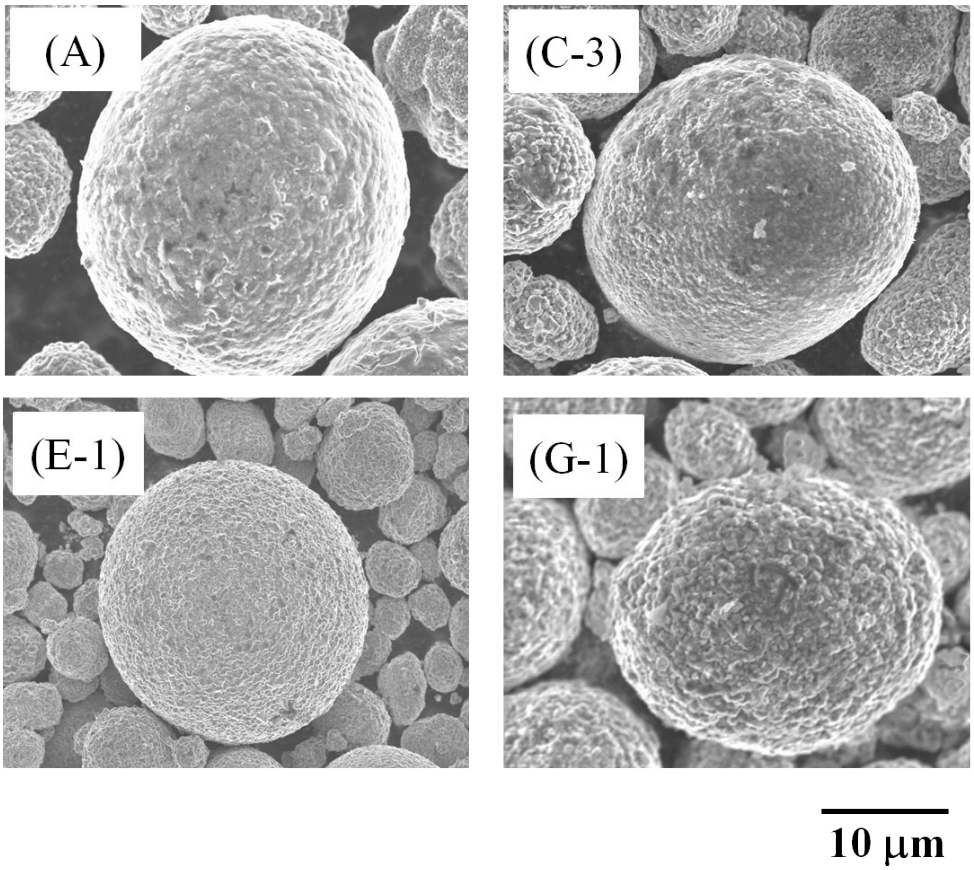
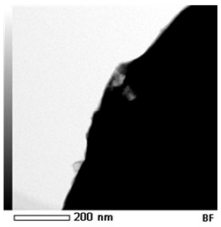
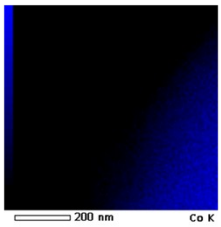
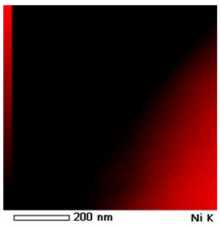


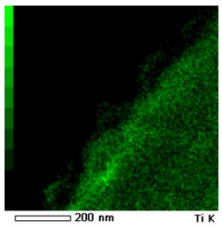
Fig. S1 SEM images of NCA particles prior to water treatment. (A) pristine (un-coated) NCA, (C-3) TiO_x-coated NCA, (E-1) Li_2CO_3-coated NCA and (G-1) TiO_x/Li_2CO_3-coated NCA.

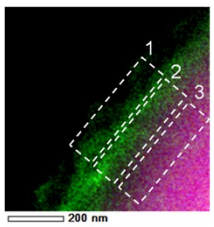
Sample C-1







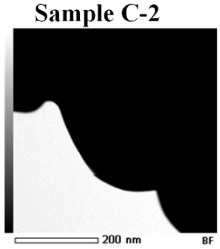


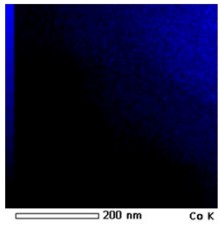


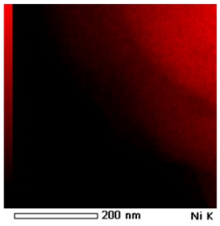
Atomic ratios

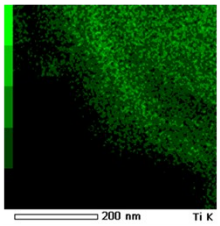
Area	Ti	Ni	Co
1	15.03	75.93	9.03
2	6.43	84.02	9.56
3	1.46	88.64	9.90

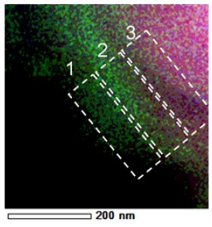
Sample C-2







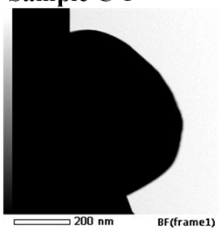


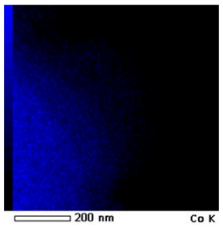


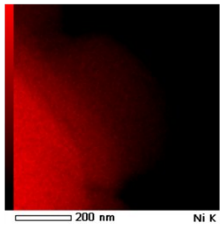
Atomic ratios

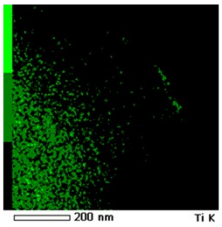
Area	Ti	Ni	Co
1	6.22	81.69	12.09
2	5.08	83.48	11.43
3	1.69	88.22	10.09

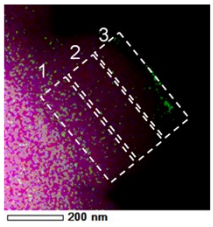
Sample C-3







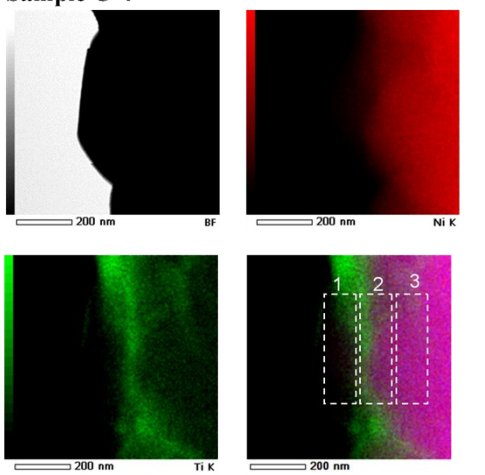




Atomic ratios

Area	Ti	Ni	Co
1	10.17	79.74	10.08
2	1.21	87.85	10.95
3	-	88.49	11.51

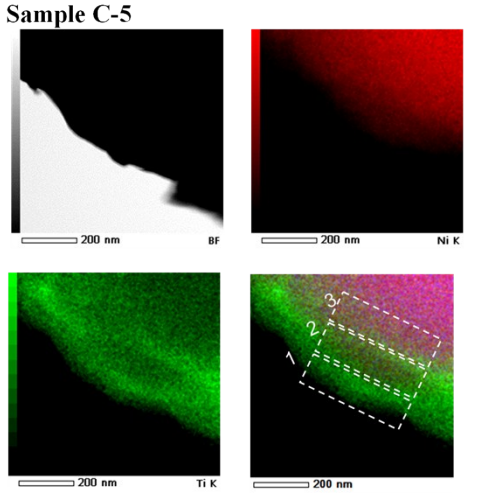
Sample C-4



Atomic ratios

Area	Ti	Ni	Co
1	35.16	57.63	7.21
2	12.40	78.34	9.27
3	3.45	86.58	9.97

Sample C-5



Atomic ratios

Area	Ti	Ni	Co
1	50.28	43.71	6.01
2	21.04	69.56	9.41
3	7.90	81.45	10.64

Fig. S2 TEM-EDX mapping of TiO_x-coated NCA samples C-1~C-5.

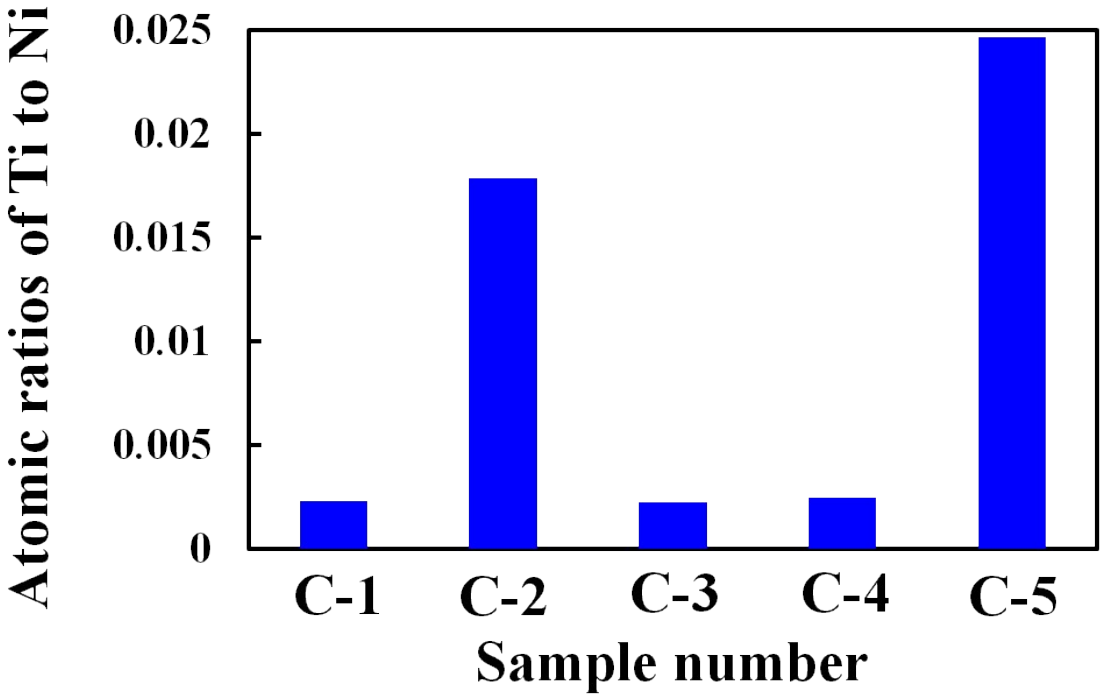


Fig. S3 Atomic ratios of Ti to Ni in TiO_x-coated NCA samples C-1~C-5 estimated from the XRF experiments.

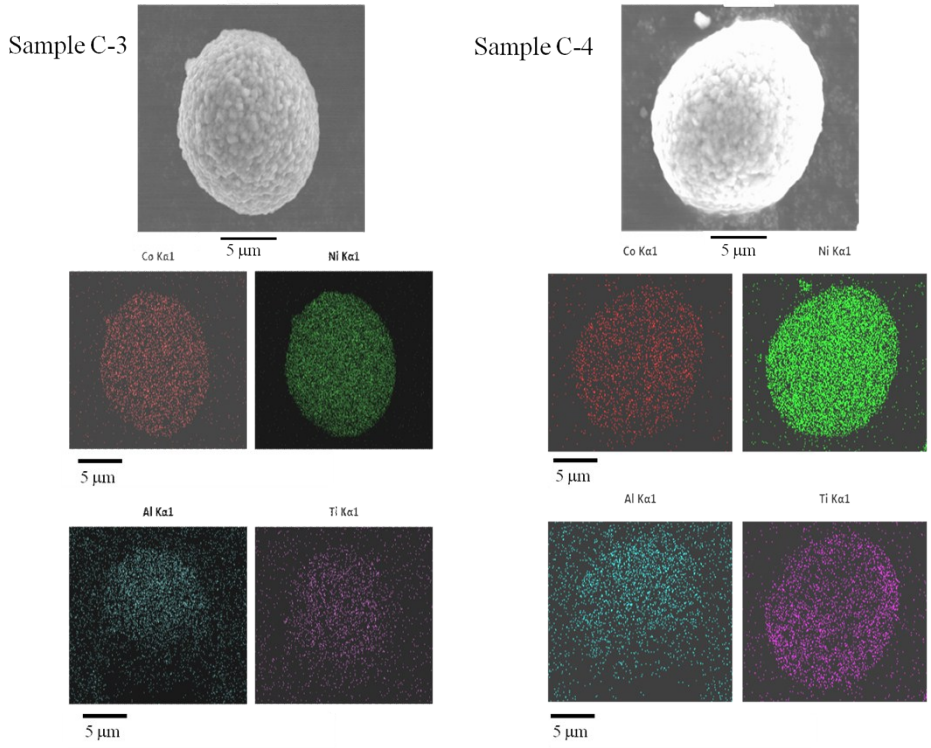


Fig. S4 SEM-EDX images of TiO_x-coated NCA samples C-3 and C-4.

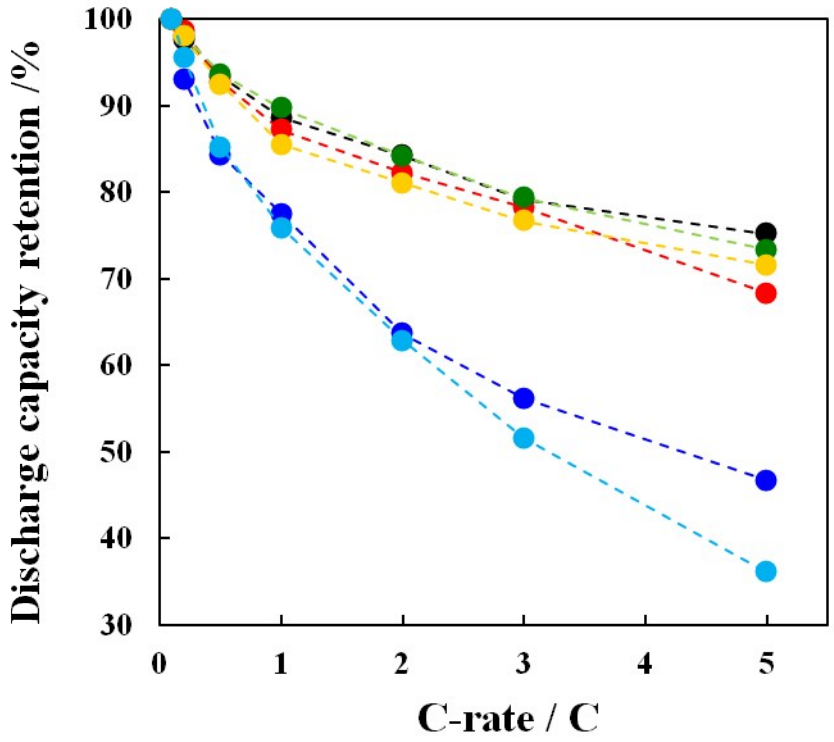


Fig. S5 Plots of discharge capacity retention *vs.* C-rate obtained with the cathodes prepared from (●) the slurry consisting of pristine NCA, PVdF and AB, (●, ●, ●, ●, ●) the water-based slurries consisting of TiO_x-coated NCA (samples C-1~C-5), TRD202A, CMC and AB at 25℃. In the calculation of the discharge capacity retention, the discharge capacity obtained at 0.1 C with each cathode was considered as 100% of capacity retention. Samples C-1: ●, C-2: ●, C-3: ●, C-4: ●, and C-5: ●.

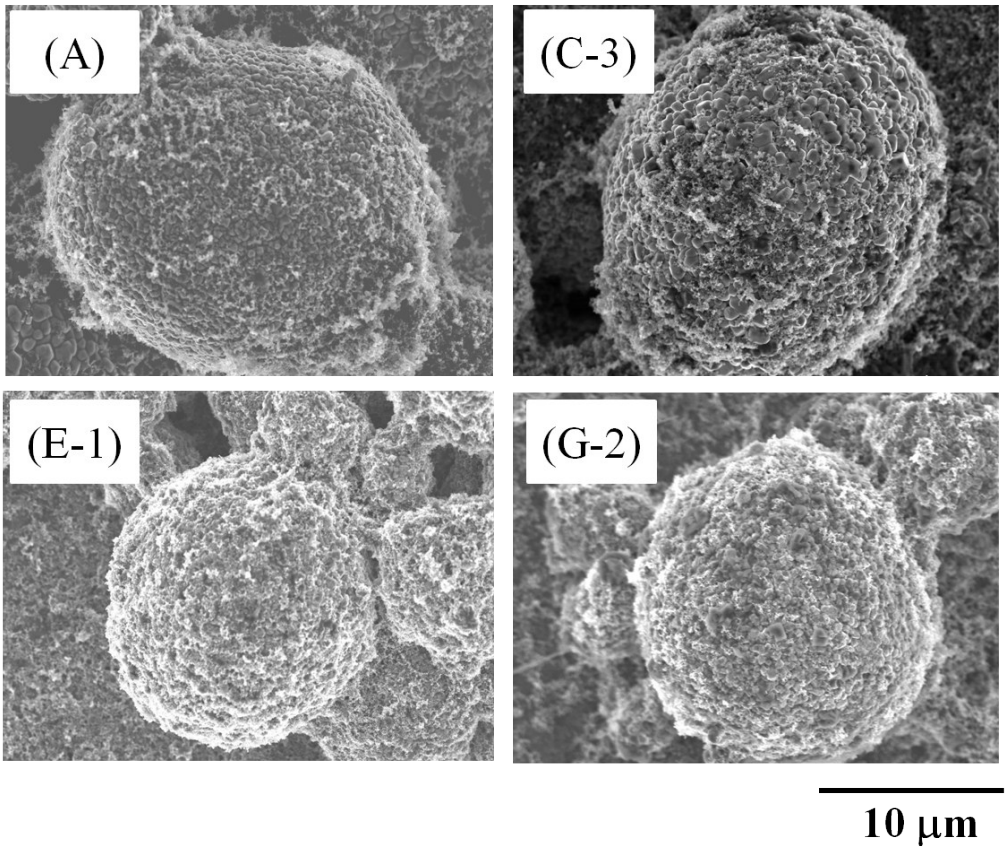


Fig. S6 SEM images of NCA particles on cathodes after 30 charging/discharging cycles at the charging/discharging rate of 0.1 C at 25 °C. The cathodes were prepared with (A) the NMP slurry consisting of pristine NCA (A), PVdF and AB, (C-3) the water-based slurry consisting of TiO_x-coated NCA, TRD202A, CMC and AB, (E-1) the water-based slurry consisting of Li_2CO_3-coated NCA (the slurry was kept for 1 h under CO_2 atmosphere), TRD202A, CMC and AB, and (G-2) the water-based slurry consisting of TiO_x/Li_2CO_3-coated NCA (the slurry was kept for 7 days under CO_2 atmosphere), TRD202A, CMC and AB.

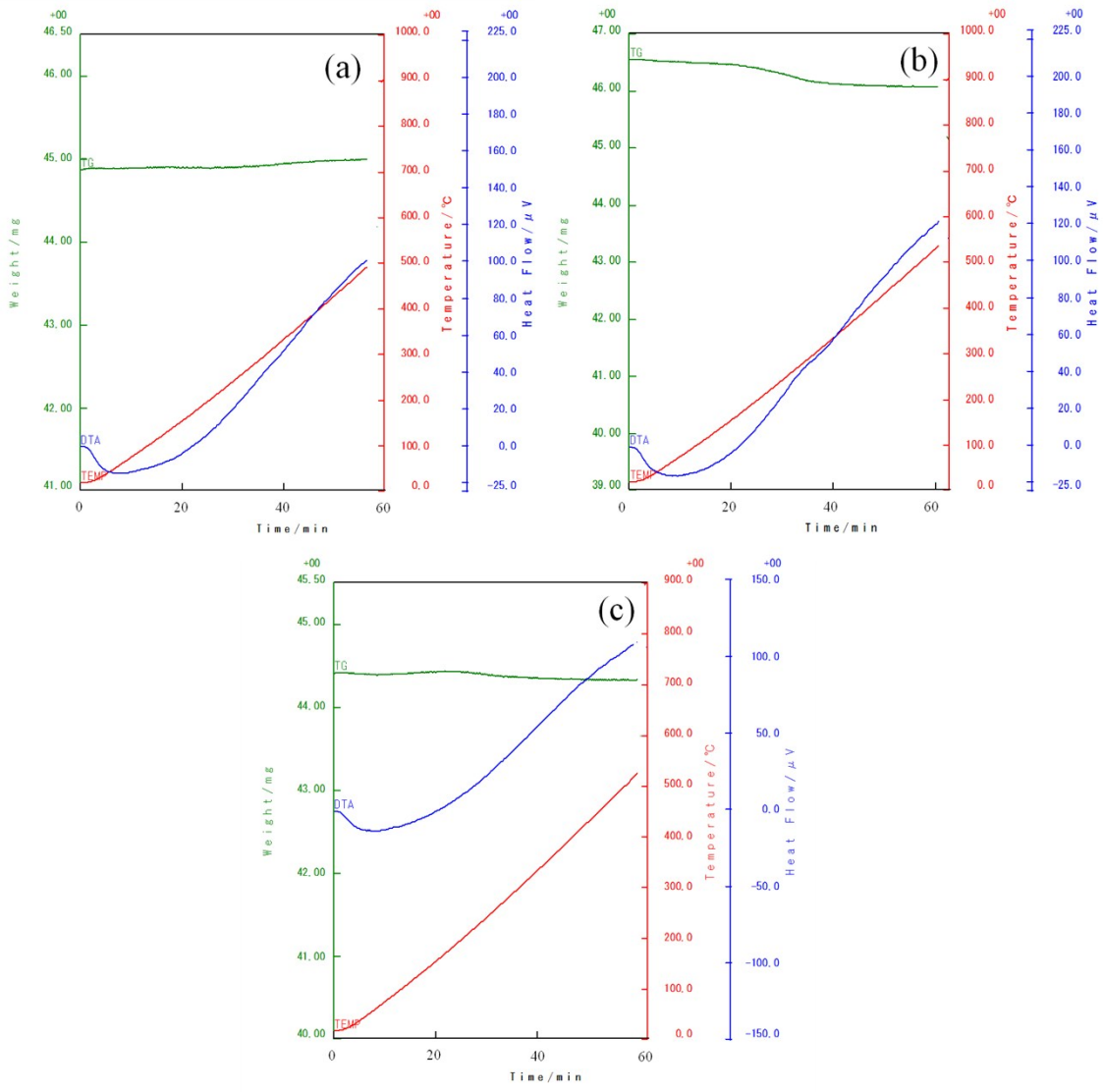


Fig. S7 The results of TG measurements of the sample powders obtained from the cathodes composed of (a) pristine NCA (A), PVdF and AB and (c) TiO_x/Li_2CO_3-coated NCA (G-2), TRD202A, CMC and AB, and (b) TiO_x/Li_2CO_3-coated NCA (G-2) particles prepared.

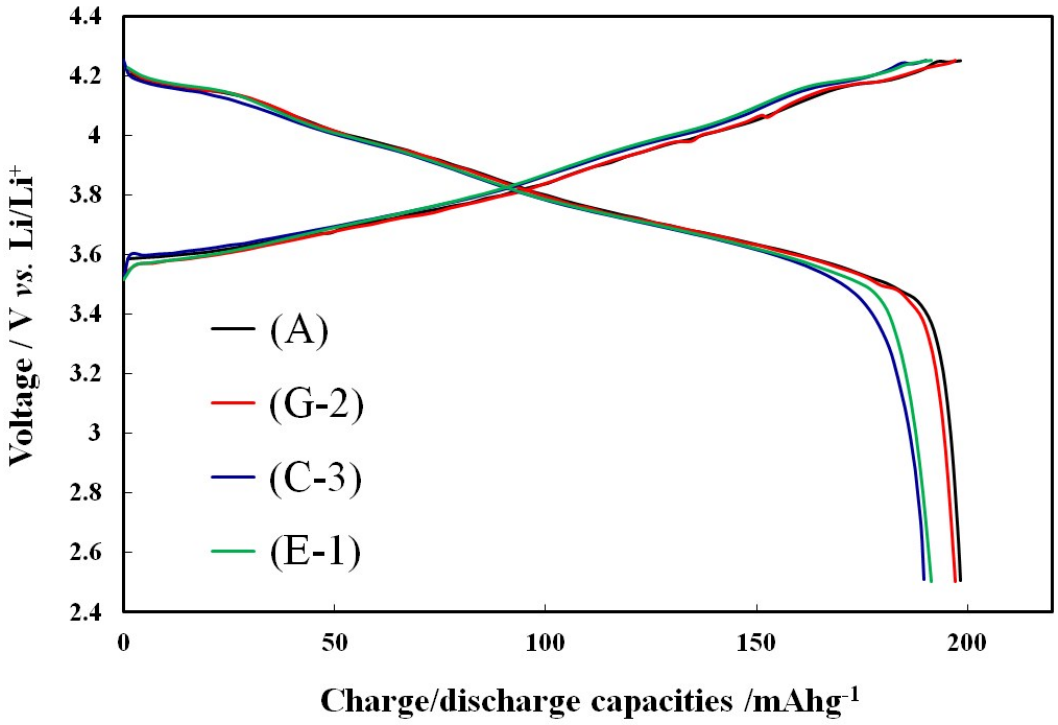


Fig. S8 Charge/discharge voltage-capacity curves observed at the 10th cycle and 0.1 C with the cathodes prepared with pristine (A), TiO_x/Li_2CO_3 (G-2)-, TiO_x(C-3)- and Li_2CO_3 (E-1)-coated NCA particles.

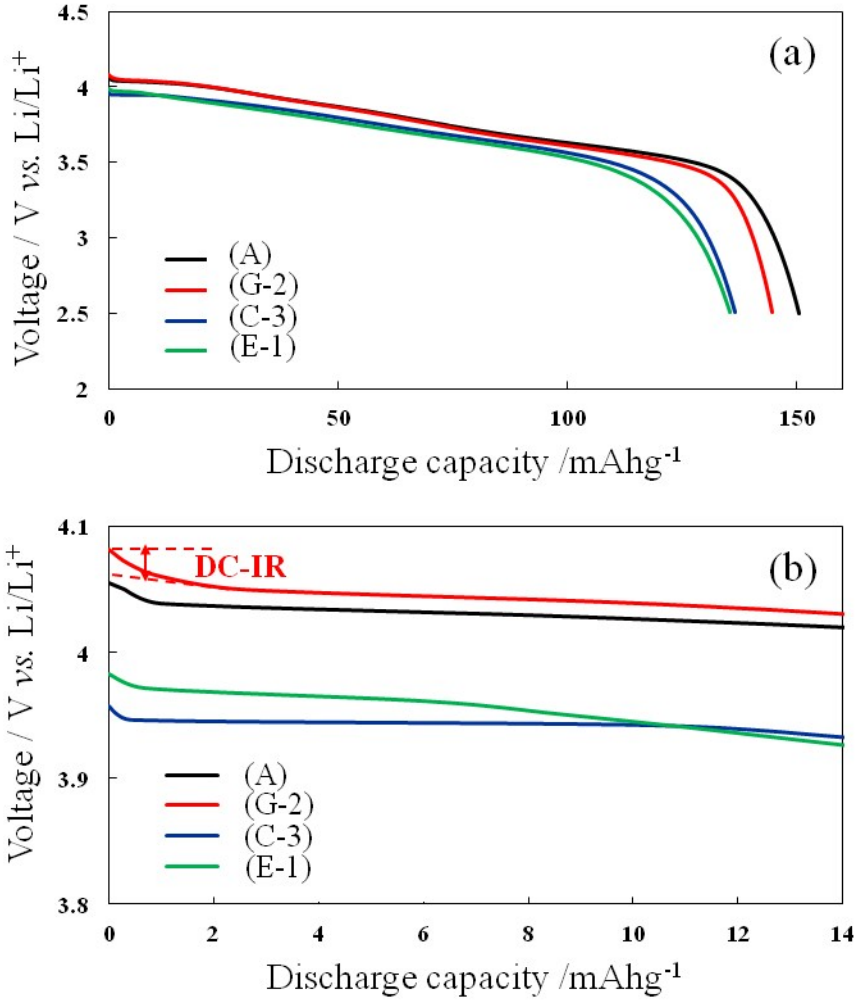


Fig. S9 (a) Discharge voltage-discharge capacity curves observed at 5 C in the rate performance test of **Fig. 13** with the cathodes prepared with pristine (A), TiO_x/Li_2CO_3 (G-2)-, TiO_x(C-3)- and Li_2CO_3 (E-1)-coated NCA cathodes. (b) Enlarged discharge voltage-discharge capacity curves to show the DC-IR drop.