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Electronic Supplementary Information

Room temperature, liquid-phase Al_2O_3 surface coating approach for Ni-rich layered oxide cathode material

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Synthesis: All syntheses were performed in an Ar-filled glovebox ([O_2], [H_2O] < 1 ppm; MBraun) using pre-dried equipment. TMA solution (650 µL, 2 M in toluene; Sigma-Aldrich) was diluted with anhydrous toluene (35 mL; Sigma-Aldrich) and the resulting solution was passed through a PTFE syringe filter (0.2 µm pore size; Corning Inc.). NCM811 (25 g; BASF SE) was slowly added to the TMA solution (25 mL) and the suspension was stirred at room temperature for 4 h. The solid product was filtered off, washed with anhydrous toluene (4 × 15 mL) and finally dried at room temperature in vacuum.

Preparation of Electrodes: *Positive electrode*: PVDF binder (Solef 5130) was dissolved in NMP (Merck) to produce a 7.5 wt.% solution. For electrode preparation, binder solution (3 wt.%), graphite (SFG6L, 2 wt.%), and carbon black (Super C65, 1 wt.%) were suspended in NMP. After mixing using a planetary centrifugal mixer (ARE-250; Thinky Corp.), the bare or Al_2O_3-coated NCM811 (94 wt.%) was added and the suspension was mixed again to achieve a slurry. The solid content was adjusted to 65%. The slurry was coated onto Al foil using a KTF-S roll-to-roll coater (Mathis AG). Prior to use, the electrodes were calendared to a density of 3.2 g cm^{-3}. The areal loading was 9.7 and 9.5 mg_{NCM811} cm^{-2} for the bare and Al_2O_3-coated NCM811, respectively.

Negative electrode: Graphite anodes of areal loading 6.8 $mg_{graphite}$ cm^{-2} were received from BASF SE.

Cell Assembly and Testing: Pouch cells were assembled in a dry room (T_{dp} < −50 °C) by stacking 50 × 50 mm^2 cathode, 60 × 60 mm^2 Celgard 2500 polypropylene separator and 52 × 52 mm^2 graphite anode using 1000 µL of LP472 electrolyte (1 M $LiPF_6$ in 3:7 by weight ethylene carbonate/diethyl carbonate + 2 wt.% vinylene carbonate; BASF SE). Electrochemical testing was performed at 25 and 45 °C using a multichannel battery cycler (Series 4000; MACCOR Inc.). After 12 h of equilibration, formation was done by a C/10 constant current charge step to 4.2 V at 25 °C, followed by pouch cell degassing. Long-term cycling was carried out at 45 °C in the voltage range between 2.8 and 4.2 V, with a constant voltage (CV) step at the charge cut-off, followed by a 5 min resting period before discharge. The CV step was limited either by time (1 h) or by residual current (0.02C). In the electrochemical testing at 45 °C, the cells were cycled at 1C rate, with a rate capability test after 10 and 310 cycles, and then, after every 200 cycles. The rate capability test comprised two full cycles at C/2, 1C, 2C and 3C, after which long-term cycling was continued at 1C rate (with 1C = 150 mA g_{NCM811}^{-1}).

Coin cells (CR2032; Hohsen Corp.) comprising cathode (Ø14 mm), glass fiber separator (Whatman GF/A; GE Healthcare Life Sciences) soaked with electrolyte solution (100 µL LP472) and graphite anode (Ø15 mm) were assembled in an Ar-filled glovebox and sealed using an MSK-160D crimper (MTI Corp.). After equilibration for 6 h, the coin cells were cycled at 25 °C and at a rate of C/10 in the same voltage range of 2.8-4.2 V.

Instrumentation: The H_2O content was determined by Karl-Fischer titration using an 860 KF Thermoprep attached to a Metrohm 851 Titrando. All samples were prepared in an Ar-filled glovebox, transferred to the oven directly before the measurement and heated to 250 °C.

Specimens for transmission electron microscopy (TEM) were embedded in Epofix (Struers GmbH) and cut via ultramicrotomy to a thickness of about 350 nm. Samples were imaged using a Tecnai Osiris microscope (FEI Company) operated at 200 keV under bright-field and high-angle annular dark-field scanning TEM conditions. Chemical composition maps were acquired by energy-dispersive X-ray spectroscopy (EDX). Images and elemental maps were evaluated using both the iTEM (version 5.2.3554; Olympus) and Esprit (version 1.9; Bruker) software packages. Note that microtomy is not able to cut the NCM811 primary particles. The particles break along the grain boundaries of secondary particles. Holes in the cross-sections are artefacts from preparation, which was validated by test preparations using focused ion-beam milling.

Electrochemical impedance spectroscopy (EIS) measurements were conducted on three-electrode Swagelok cells. Two glass microfiber separators of 12 mm diameter (Whatman GF/A) were soaked with 100 ml of LP47 electrolyte, and then, they were placed between the working (WE) and counter electrode (CE). Additionally, two more separators of 10 mm diameter with 70 ml of LP47 electrolyte were placed between the WE/CE and reference electrode (RE). Li metal disks of 12 and 5 mm diameter (Albemarle Germany GmbH) were used as the CE and RE, respectively. In order to remove the native oxide present on the Li surface, the metal was gently scratched until it became shiny. Disks of 12 mm diameter were punched from the graphite and Al_2O_3-coated NCM811 electrodes and served as the WE. After cycling, the pouch cells were opened in an Ar-filled glovebox and the electrodes were rinsed with dimethyl carbonate, followed by drying overnight before assembling Swagelok T-cells. The experiments were performed at 25 °C and C/10 rate using a VMP-3 potentiostat (Bio-Logic).

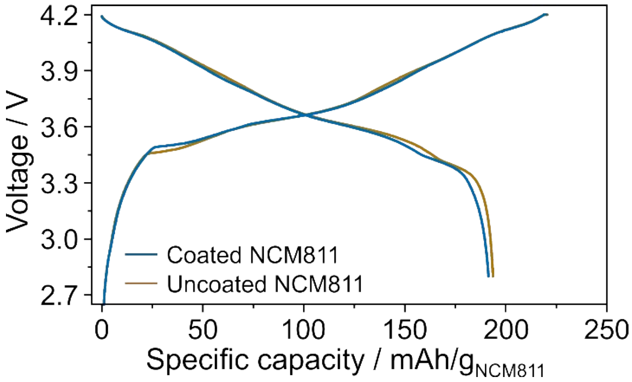

Fig. S1 First cycle charge/discharge curves at 25 °C and C/10 rate of coin cells with a graphite anode using the Al_2O_3-coated and bare NCM811 CAM.

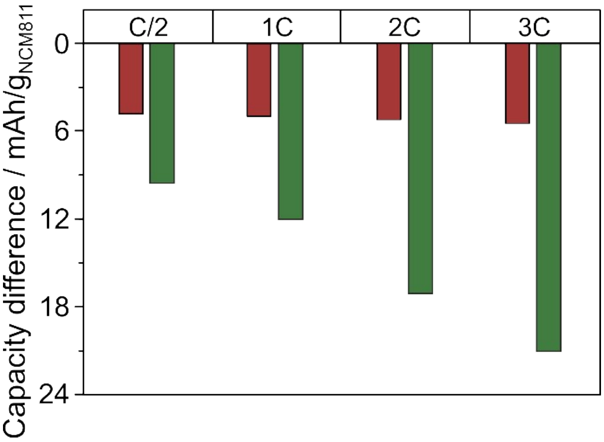

Fig. S2 C-rate-dependent differences in specific discharge capacity between single-layer pouch cells with a graphite anode using the Al_2O_3-coated and bare NCM811 CAM. Red and green bars denote the rate capability test after 10 and 310 cycles, respectively.

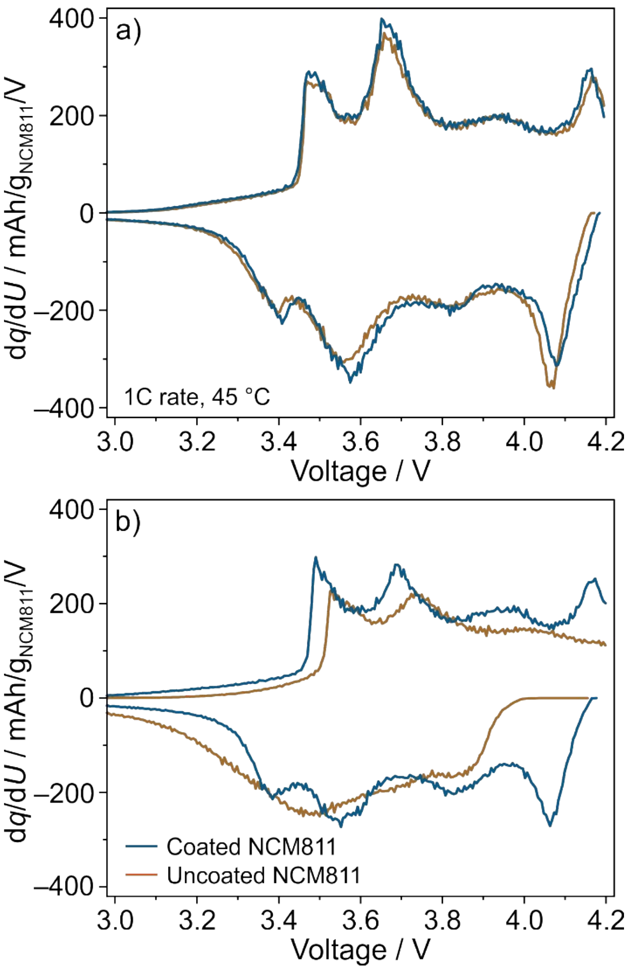

Fig. S3 Differential capacity curves for the 2nd cycle after cell formation (a) and the 500th cycle (b) of single-layer pouch cells with a graphite anode using the Al_2O_3-coated and bare NCM811 CAM.

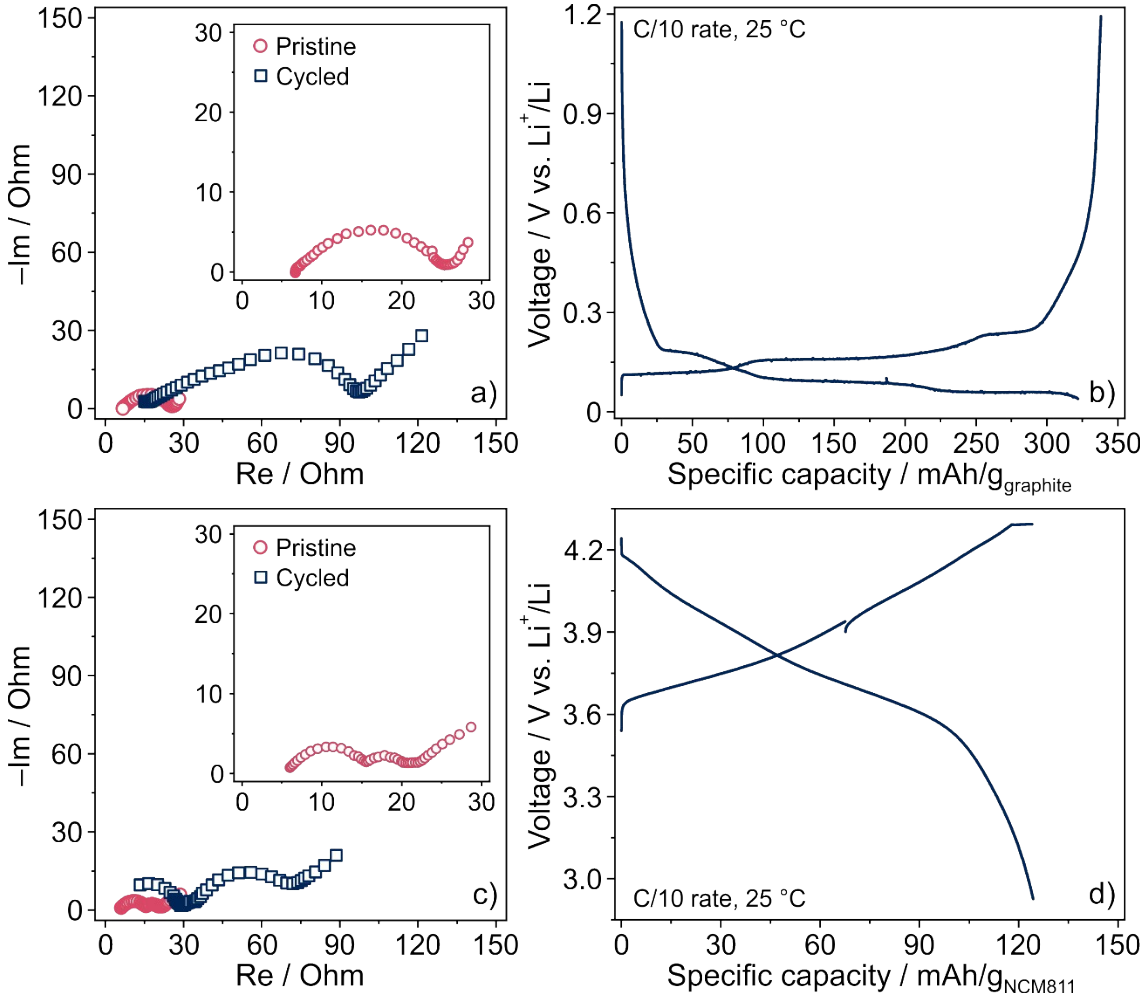

Fig. S4 Nyquist plots of graphite anode (a) and Al_2O_3-coated NCM811 cathode (c) before and after cycling in full-cell configuration for 1100 cycles. EIS data were collected under an open-circuit voltage in the frequency range between 200 KHz and 10 mHz after 50% state-of-charge was reached. Charge/discharge curves—after 1100 cycles—at 25 °C and C/10 rate obtained on half-cells using the graphite and Al_2O_3-coated NCM811 CAM are shown in (b) and (d), respectively.