

**Electronic Supporting Information
to**

**Coating of NCM 851005 Cathode Material with Al⁰@Al₂O₃ and subsequent
Treatment with Anhydrous HF**

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Determination of the Coating Conditions

A large Schlenk tube was loaded with NCM811 on one side and with $(\text{H}_2\text{AlO}^t\text{Bu})_2$ on the other side (Figure S-1). Under a constant Ar flow the $(\text{H}_2\text{AlO}^t\text{Bu})_2$ was heated until it started to melt ($\sim 80^\circ\text{C}$). Then the NCM811 was heated to the same temperature and the temperature was raised step-wise until a white layer formed on top of the CAM. The Schlenk tube was immediately opened and the temperature of the NCM811 was measured. By this method the optimized coating temperature was determined to be 160°C .

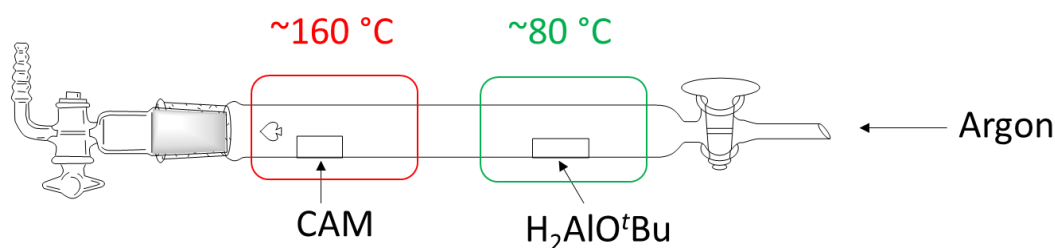


Figure S-1: Apparatus to determine the decomposition temperature of $(\text{H}_2\text{AlO}^t\text{Bu})_2$ at the CAM's surface.

Powder XRD spectra of coated and pristine NCM811

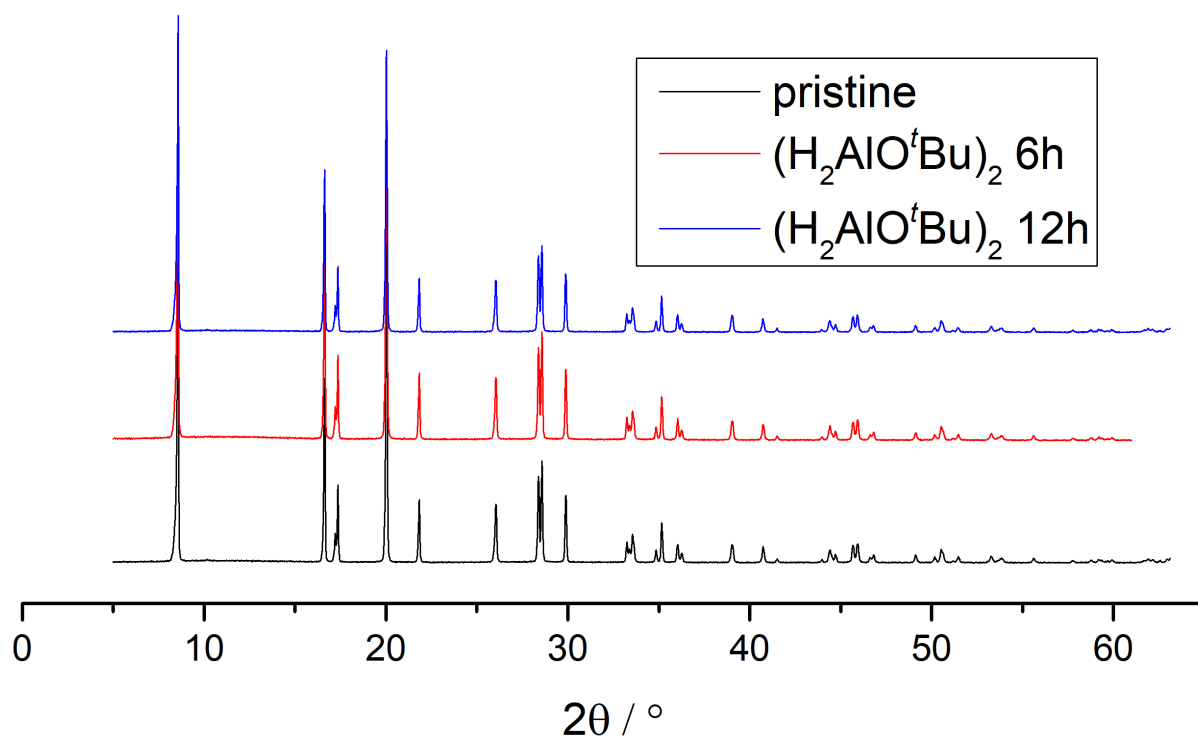


Figure S- 2: pXRD spectra of pristine (black) NCM811 and after coating with 5 wt-% $(\text{H}_2\text{AlO}^t\text{Bu})_2$ for 6 h at 180°C (red) and an additional 6 h at 250°C (blue).

Powder XRD spectra of coated and pristine NCM851005

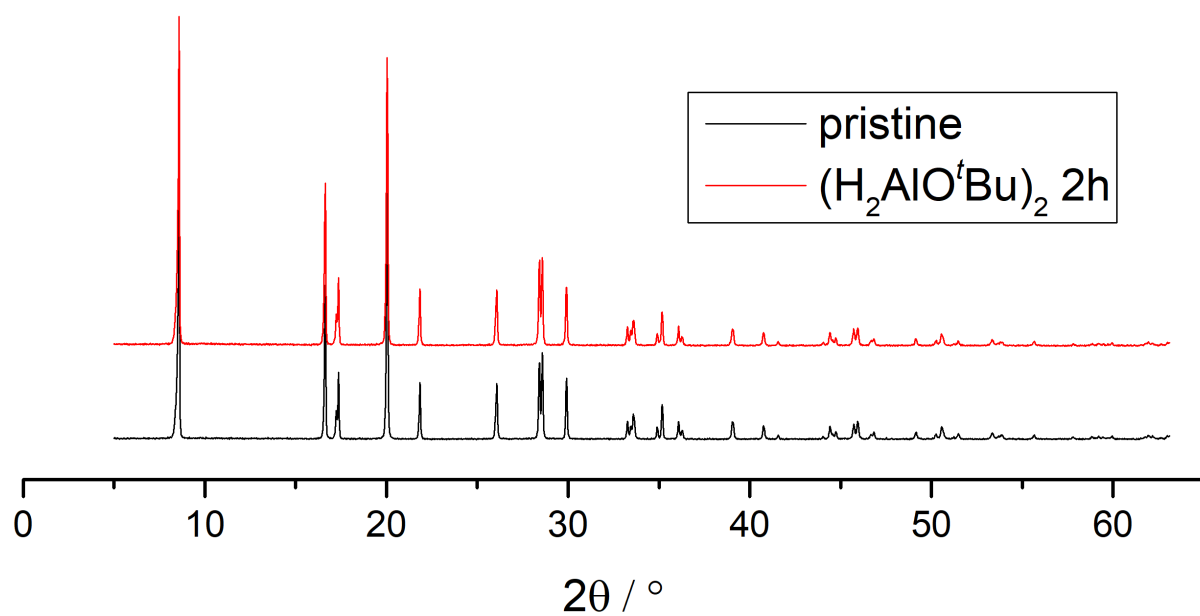


Figure S- 3: pXRD spectra of pristine (black) NCM851005 and after coating with 5 wt-% $(\text{H}_2\text{AlO}^t\text{Bu})_2$ for 2 h at 180 °C (red).

MAS NMR Spectra of the $(\text{H}_2\text{AlO}^t\text{Bu})_2$ coated NCM

^{27}Al NMR spectra

^{27}Al NMR spectra were recorded at 30 and 33 kHz, respectively, in order to allow for a reliable assignment of the signals (Figure S- 4). After two months, the sample showed an increased signal for Al_2O_3 and a decreased signal of HAIO due to diffusion of O_2 into the sample (Figure S- 5).

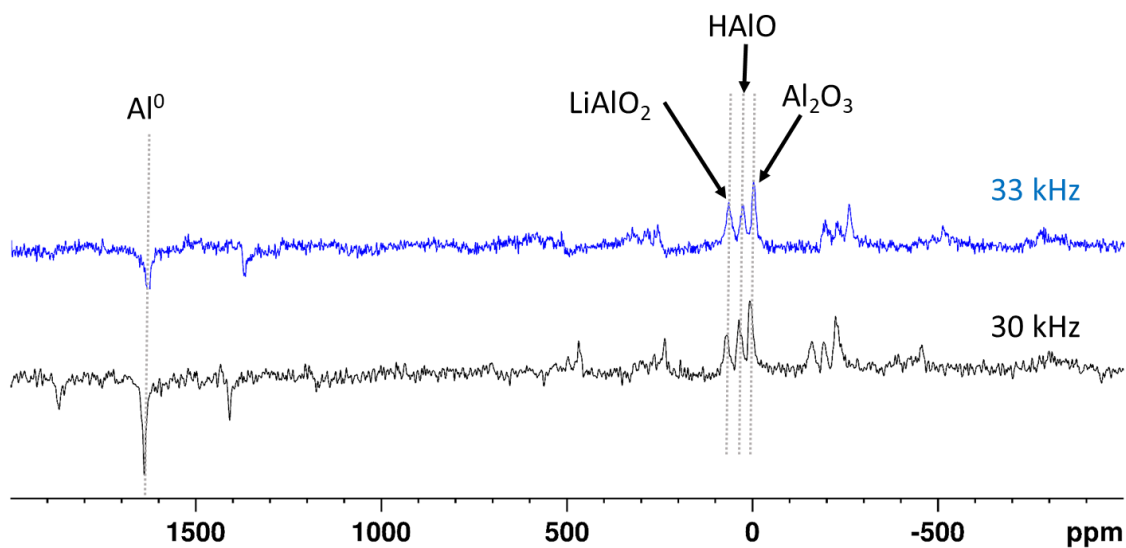


Figure S- 4: ^{27}Al MAS NMR spectra of $(\text{H}_2\text{AlO}^t\text{Bu})_2$ (5 wt-%) coated NCM851005 at 30 (black) and 33 kHz (blue).

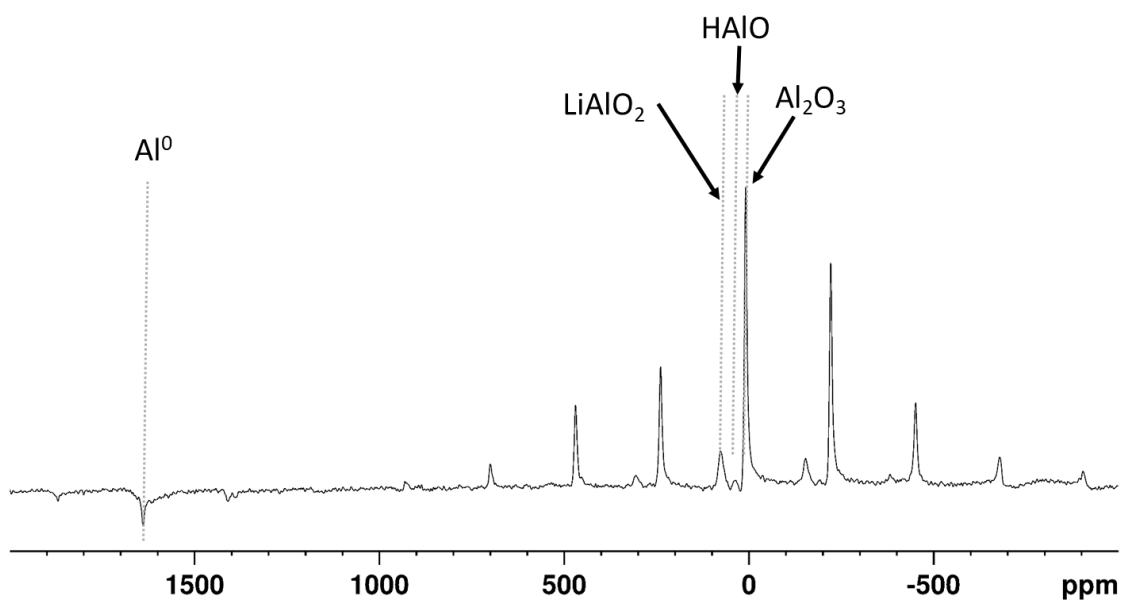


Figure S- 5: ^{27}Al MAS NMR spectra of $(\text{H}_2\text{AlO}^t\text{Bu})_2$ (5 wt-%) coated NCM851005 at 30 kHz after two months.

MAS NMR Spectra of the $(\text{H}_2\text{AlO}^t\text{Bu})_2 + 2 \text{ HF}$ coated NCM

^{19}F NMR spectra

^{19}F NMR spectra were recorded at 25 and 30 kHz, respectively, in order to allow for a reliable assignment of the signals (Figure S- 6 and Figure S- 7).

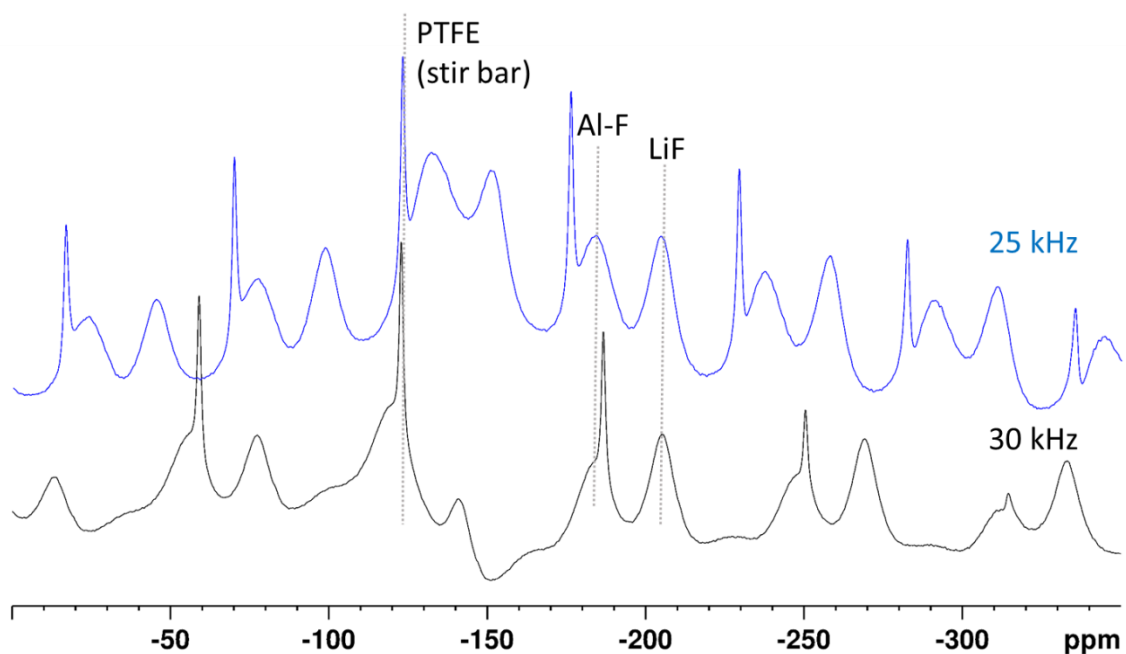


Figure S- 6: ^{19}F MAS NMR spectra of $(\text{H}_2\text{AlO}^t\text{Bu})_2$ (5 wt-%) coated NCM851005 after treatment with HF at 30 (black) and 25 kHz (blue).

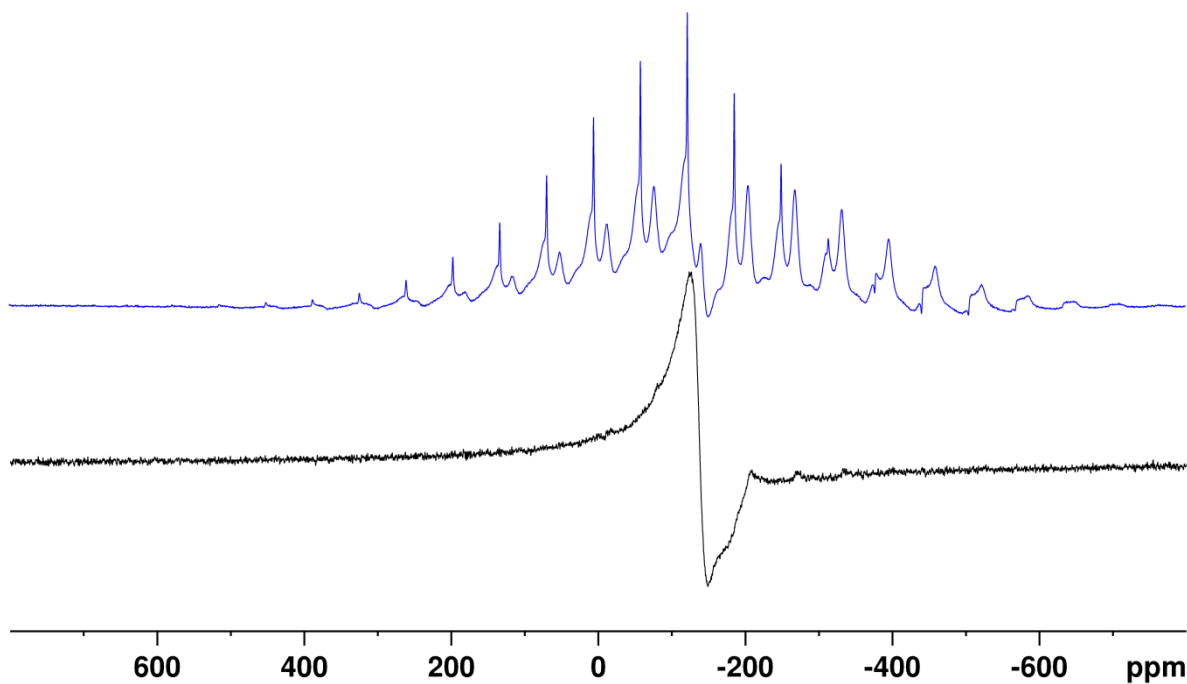


Figure S- 7: Full ^{19}F MAS NMR spectra of $(\text{H}_2\text{AlO}^t\text{Bu})_2$ (5 wt-%) coated NCM851005 before (black) and after (blue) treatment with HF.

²⁷Al NMR spectra

²⁷Al NMR spectra were recorded at 30 and 33 kHz, respectively, in order to allow for a reliable assignment of the signals (Figure S- 8).

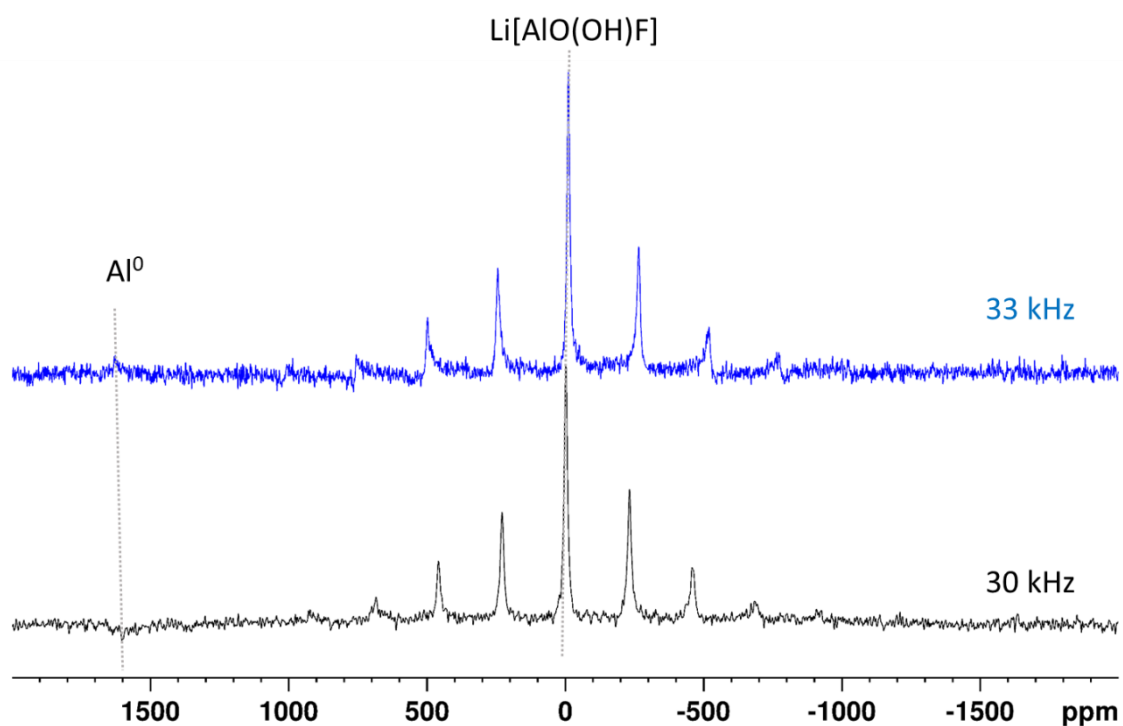


Figure S- 8: ²⁷Al MAS NMR spectra of $(\text{H}_2\text{AlO}^i\text{Bu})_2$ (5 wt-%) coated NCM851005 after treatment with HF at 30 (black) and 33 kHz (blue).

^7Li MAS NMR Spectra of the $(\text{H}_2\text{AlO}^t\text{Bu})_2$ coated NCM before and after HF Treatment

^7Li NMR spectra of the $(\text{H}_2\text{AlO}^t\text{Bu})_2$ coated NCM before and after HF treatment were recorded at 30 kHz (Figure S- 9). Both spectra were scaled to give similar intensities for the bulk Li, thus the difference in the amount of surface Li between the samples is visible.

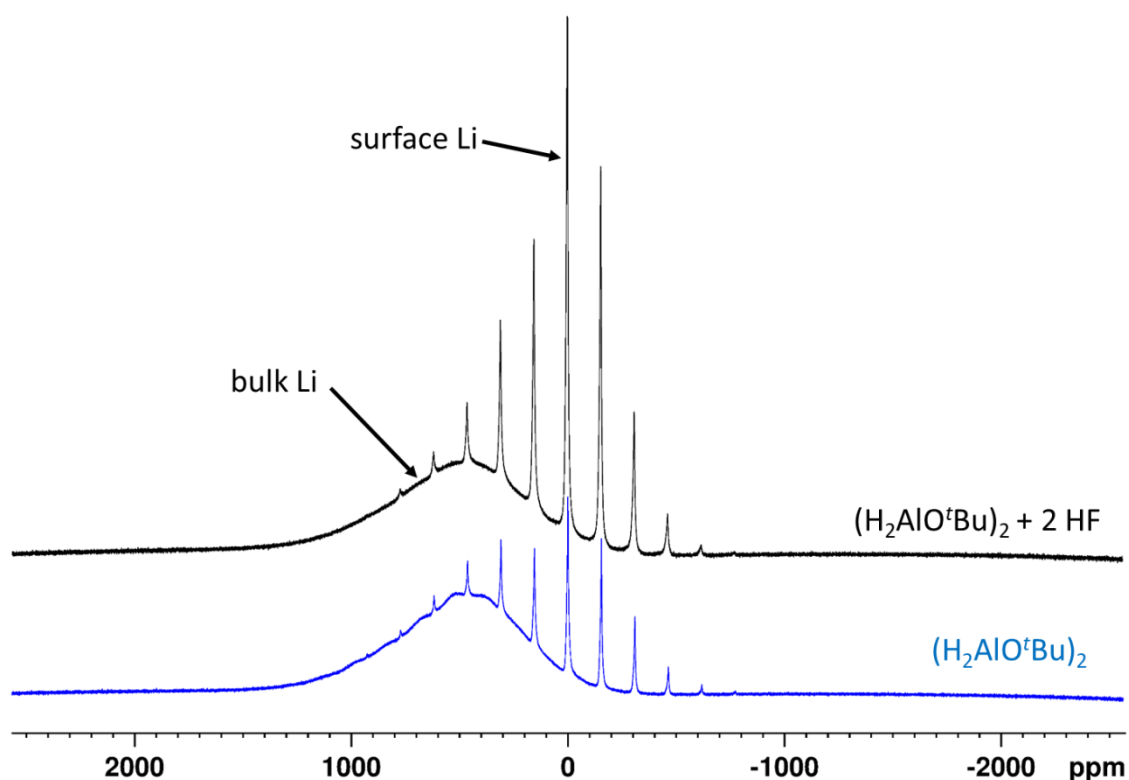


Figure S- 9: ^7Li MAS NMR spectra of $(\text{H}_2\text{AlO}^t\text{Bu})_2$ (5 wt-%) coated NCM851005 before (blue) and after (black) treatment with HF at 30 kHz (blue). Spectra were scaled to obtain similar intensities of the bulk Li.

EDX Elemental Analysis of the $(\text{H}_2\text{AlO}^t\text{Bu})_2$ coated NCM before and after HF Treatment

EDX element analysis spectra of the $(\text{H}_2\text{AlO}^t\text{Bu})_2$ coated (0.3 wt-%) NCM851005 before and after treatment with HF are shown in Figure S- 10. Before HF treatment the Al-content of the CAM was determined to be 0.17 atom-%, after the HF treatment it was 0.16 atom-%.

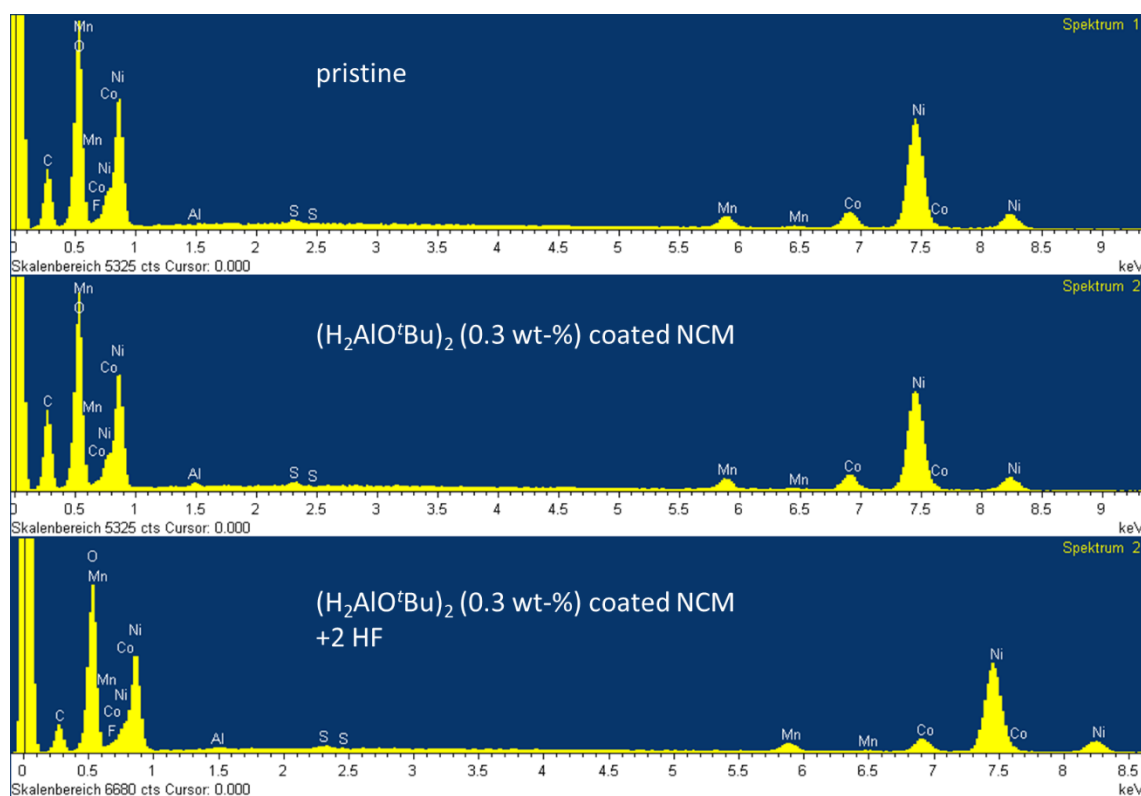


Figure S- 10: EDX elemental analysis spectra of NCM851005 without coating (top) and with 0.3 wt-% $(\text{H}_2\text{AlO}^t\text{Bu})_2$ coating (center) after HF treatment (bottom).

Additional SEM images of the $(\text{H}_2\text{AlO}^t\text{Bu})_2$ coated NCM before and after HF Treatment

$(\text{H}_2\text{AlO}^t\text{Bu})_2$ coated NCM before HF treatment

From the SEM images in Figure S- 11 no impurity phases are visible next to the coated NCM.

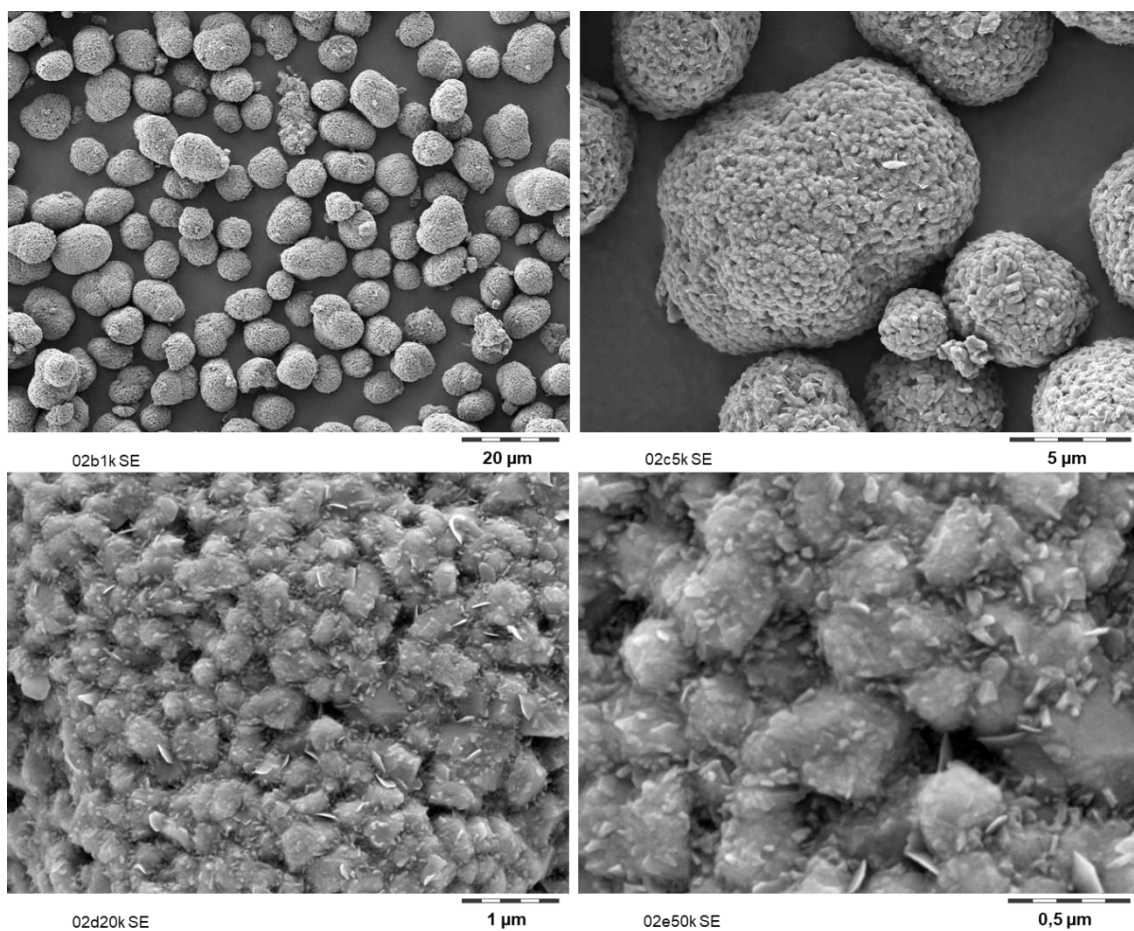


Figure S- 11: SEM images of $(\text{H}_2\text{AlO}^t\text{Bu})_2$ (0.3 wt-%) coated NCM851005.

$(\text{H}_2\text{AlO}^t\text{Bu})_2$ coated NCM after HF treatment

From the SEM images in Figure S- 12 no impurity phases are visible next to the coated NCM.

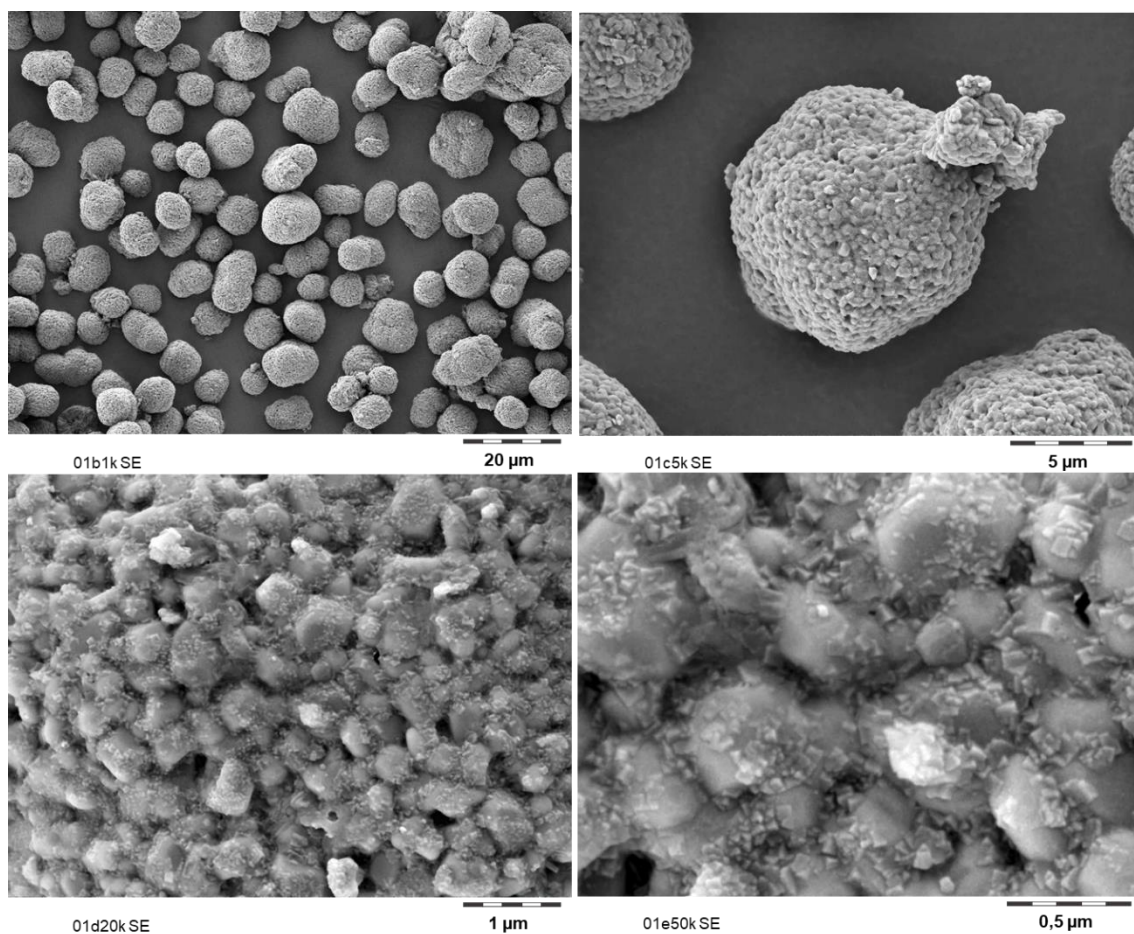


Figure S- 12: SEM images of $(\text{H}_2\text{AlO}^t\text{Bu})_2$ (0.3 wt-%) coated NCM851005 after treatment with HF.

Average Voltages During Charge/Discharge in the Half Cell

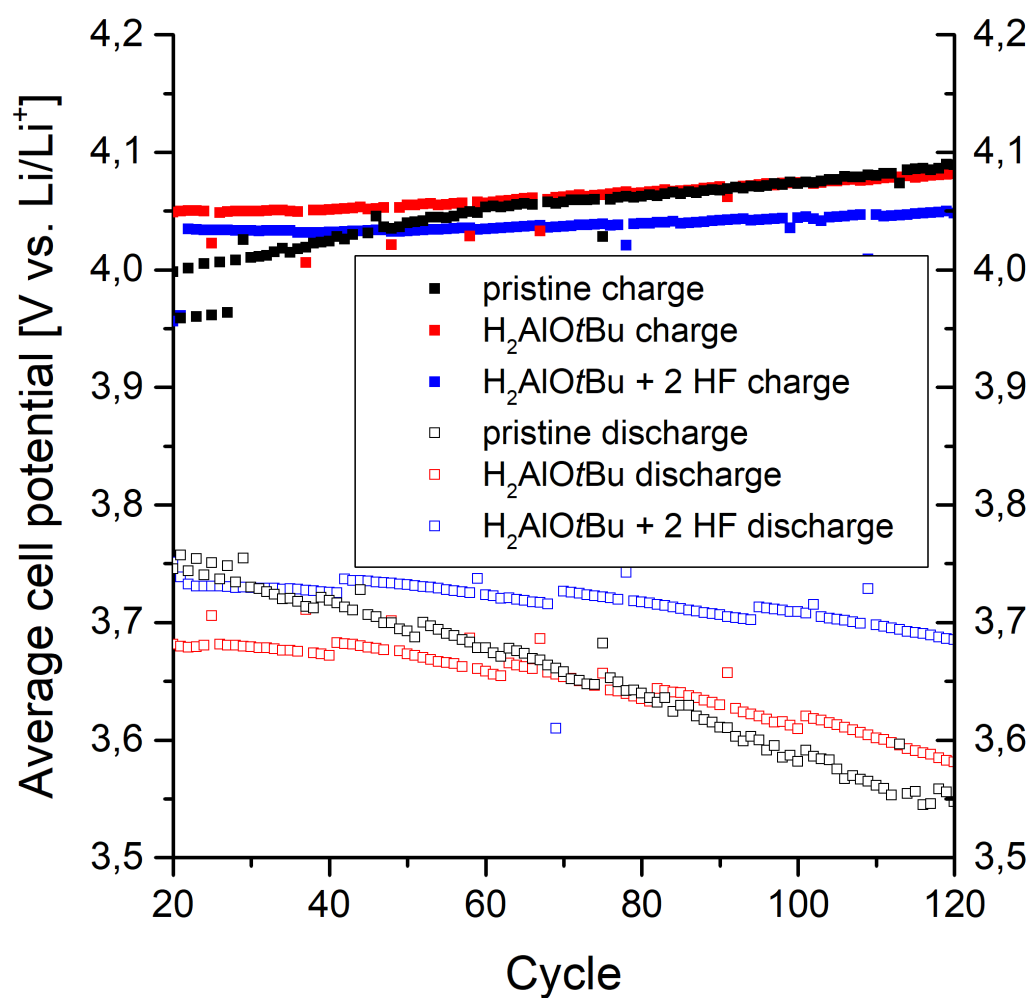


Figure S- 13: Average Voltages during charge/discharge in the half-cell of pristine (black) and (H₂AlOtBu)₂ (0.3 wt-%) coated NCM851005 prior (red) and after treatment with HF (blue) at 25 °C.

Full Cell Cycling Data at 45 °C

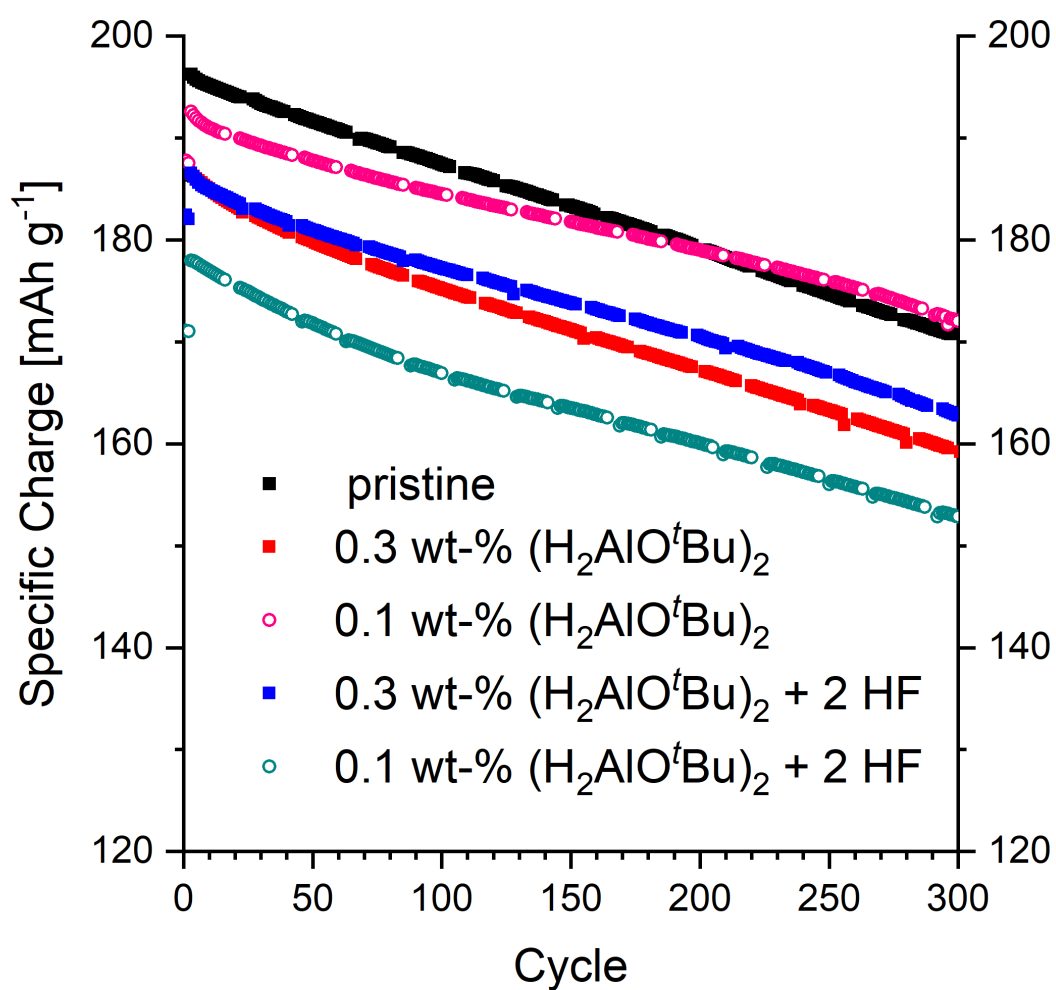


Figure S- 14: Discharge capacity during full-cell cycling of the pristine (black) and coated NCM851005 prior (red) and after treatment with HF (blue) using LP572 electrolyte. Cycling was performed at 1 C rate at 45 °C with resistance measurements every 25 cycles at 25 °C. The coating was performed using 0.3 wt-% and 0.1 wt-%(H₂AlO^tBu)₂, respectively. The data from the resistance measurements performed at 25 °C have been removed (see experimental section).

Full Cell Cycling Data at 25 °C

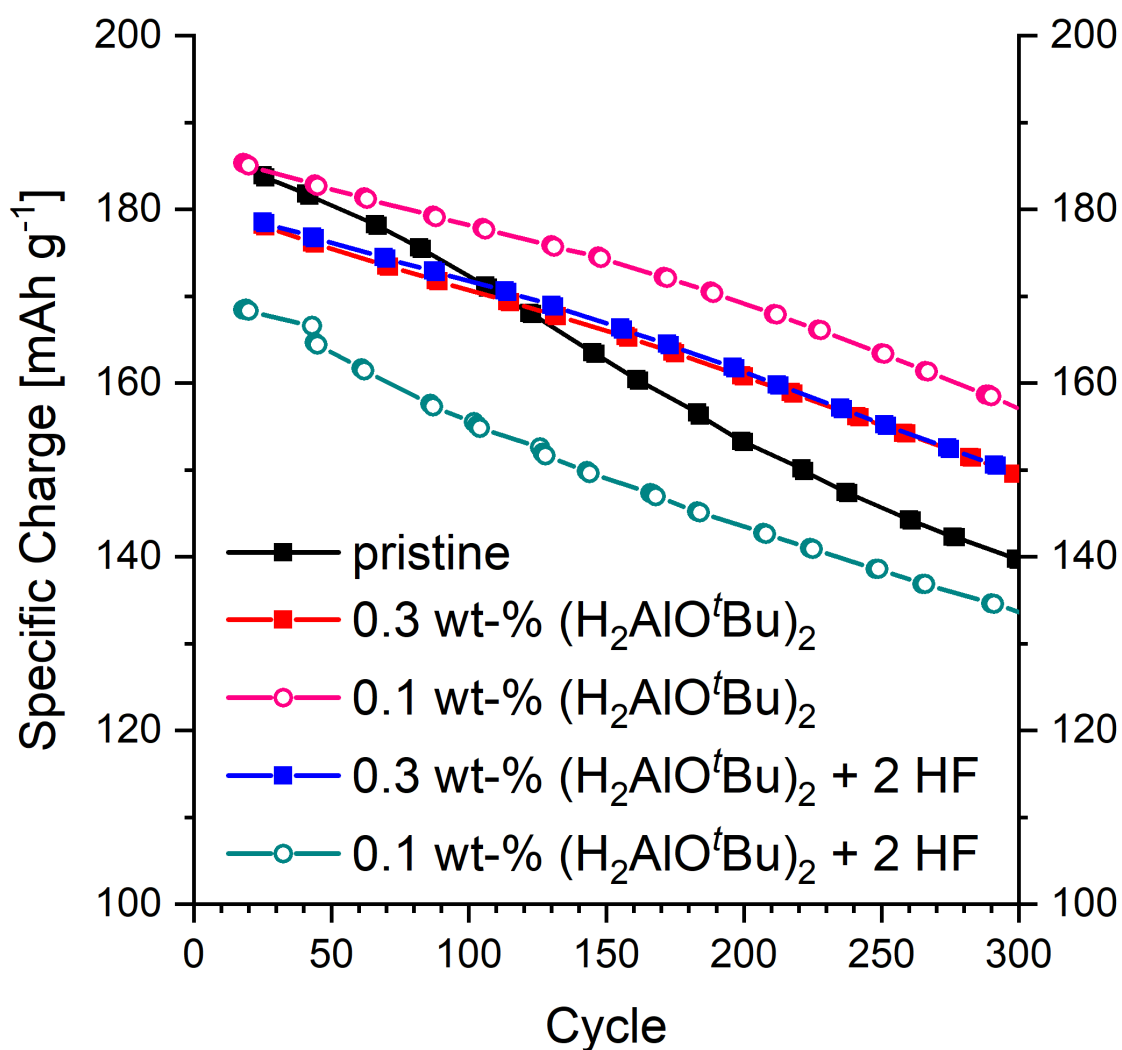


Figure S- 15: Discharge capacity during full-cell cycling of the pristine (black) and coated NCM851005 prior (red) and after treatment with HF (blue) using LP572 electrolyte. Cycling was performed at 1 C rate at 45 °C with resistance measurements every 25 cycles at 25 °C. The coating was performed using 0.3 wt-% and 0.1 wt-%(H₂AlO^tBu)₂, respectively. The data from the cycling performed at 45 °C have been removed (see experimental section).