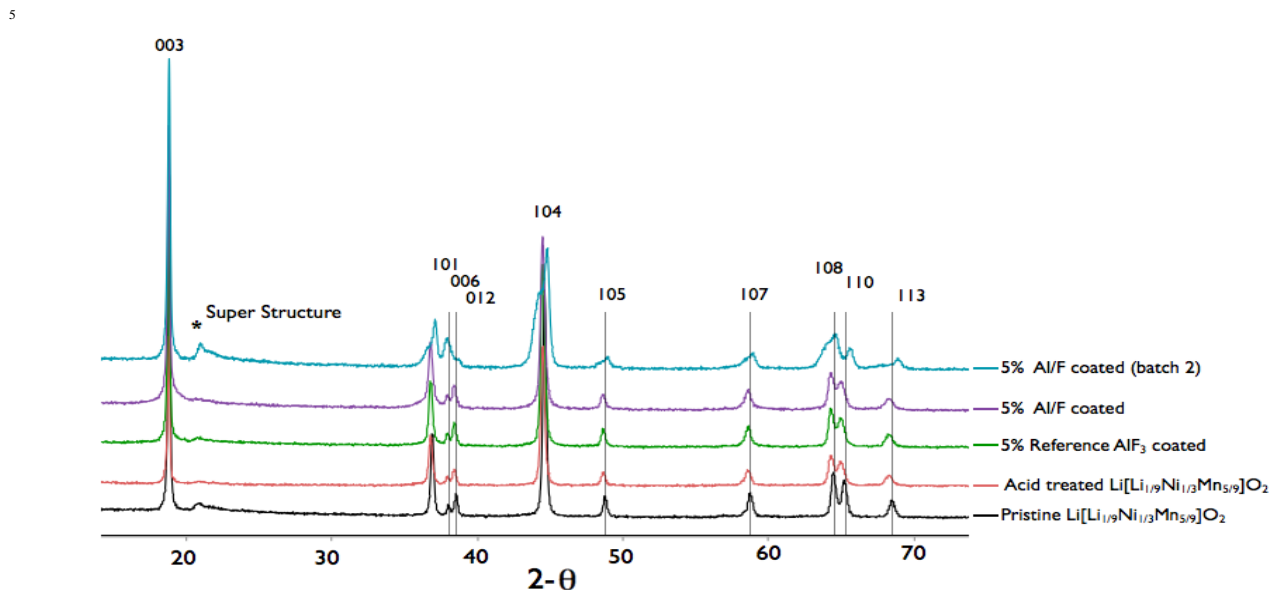


## Supplemental Information:

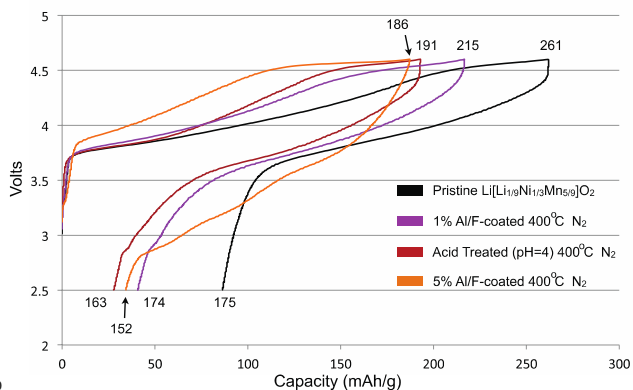
### 1. X-ray Diffraction



**Figure S1:** Powder XRD patterns of pristine, acid treated (pH=4), 5% reference AlF<sub>3</sub>-coated, and 5% Al/F-coated Li[Li<sub>1/9</sub>Ni<sub>1/3</sub>Mn<sub>5/9</sub>]O<sub>2</sub> after sintering at 400°C in N<sub>2</sub>. These patterns were acquired on a Panalytical Empyrean diffractometer with Copper K $\alpha$  radiation, using a scan of between 5 and 80° 2 $\theta$ , for 100 minutes.

No indication of AlF<sub>3</sub> is seen in any of the coated samples, but some samples did show peak broadenings and splittings that indicate the formation of a second phase (or large domain) on heating to 400 °C. This was most pronounced for the 5% Al/F sample prepared from a second batch of Li[Li<sub>1/9</sub>Ni<sub>1/3</sub>Mn<sub>5/9</sub>]O<sub>2</sub>. The structural rearrangement is most likely associated with the proton exchange/Li loss that occurs during the initial coating process but may also be associated with Al migration. Attempts to investigate the structure in more detail are ongoing.

### 2. Electrochemistry



**Figure S2:** First cycle charge / discharge curves (4.6-2.5V at rate C<sub>th</sub>/20) of pristine, Al/F treated, and acid treated Li[Li<sub>1/9</sub>Ni<sub>1/3</sub>Mn<sub>5/9</sub>]O<sub>2</sub>. The charge and discharge capacities decrease with increasing amount of Al/F and with acid pretreatment.

### 3. Energy Dispersive X-ray Spectroscopy (EDS)

Average Aluminum Content Normalized to Mn:				
	Surface	Bulk	Ratio	
	Al:Mn - Surface	Al:Mn - Bulk	Surface:Bulk	Sample Size
10% AlF <sub>3</sub> 400°C	0.2 (0.09)	0.1 (0.06)	2.00	(30 images)
10% AlF <sub>3</sub> 120°C	0.4 (0.3)	0.09 (0.02)	4.44	(23 images)
5% AlF <sub>3</sub> 400°C	0.2 (0.06)	0.05 (0.03)	4.00	(17 images)
5% AlF <sub>3</sub> 120°C	0.2 (0.1)	0.07 (0.02)	2.86	(32 images)
Average	0.3 (0.1)	0.08 (0.03)	<b>3.33</b>	-

**Table S1:** Aluminum content (and standard deviation) of the amorphous surface and crystalline bulk regions obtained via EDS and normalized to Mn content, which is uniform throughout the particle and is unaffected by the coating procedure and sintering at 400°C. The large standard deviations reflect both the difficulty in imaging the coating only (without a contribution from the bulk) and some variation in Al coating thickness.

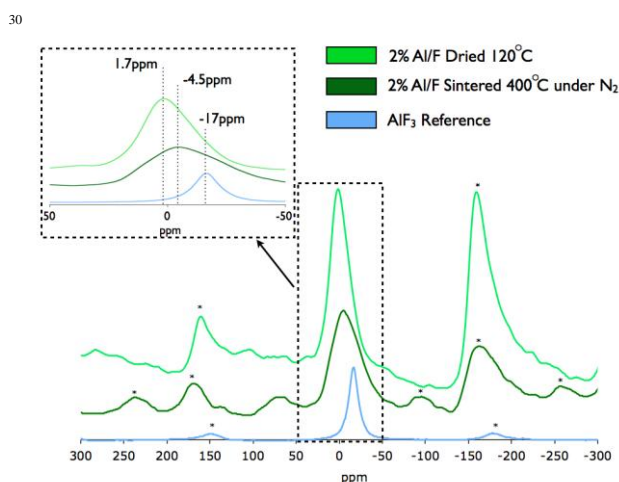
### 4. <sup>27</sup>Al NMR Spectroscopy

<sup>27</sup>Al MAS NMR spectra were acquired at two different field strengths. The experimental details for the high field data (16.4 T; 700 MHz for <sup>1</sup>H) were given in the main text. Spectra were

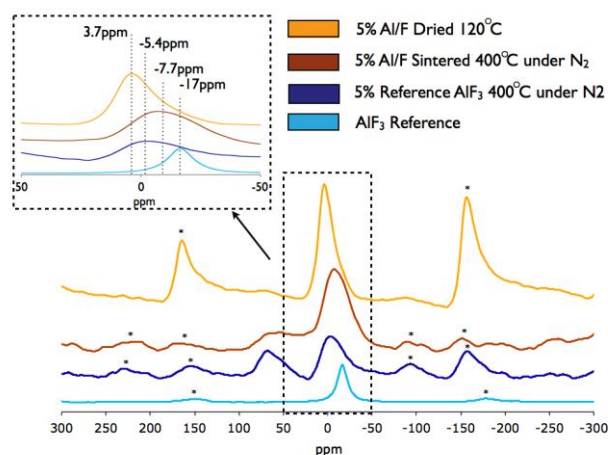
also acquired on a Chemagnetics-360 (CMX) spectrometer with a magnetic field of 8.46 T and an operating frequency of 93.81 MHz with a 3.2mm probe with spinning rate  $\nu_r = 15$  kHz and a rotor-synchronized echo pulse sequence ( $90^\circ\text{-}\tau\text{-}180^\circ\text{-}\tau\text{-acq}$ ) where  $\tau=1/\nu_r$ . A  $\pi/2$  pulse width of  $5.0 \mu\text{s}$  was used with pulse delays of 0.6s. All spectra were referenced to aqueous  $\text{Al}_2(\text{SO}_4)_3$  at 0 ppm.

Octahedral aluminum environments are present in the  $^{27}\text{Al}$  spectra of the 2% and 5% Al/F samples following heat treatment at  $120^\circ\text{C}$  and  $400^\circ\text{C}$  (Figures S3 and 4), while the signal from tetrahedral aluminum only appears after sintering at  $400^\circ\text{C}$  in both the Al/F coated samples and the sample coated with the commercial  $\text{AlF}_3$  sample. No evidence is observed for  $\text{AlF}_3$ . The  $^{27}\text{Al}$  signals from the octahedral environments shift to lower frequency and broaden on heating at higher temperatures. We ascribe this to an increase in the distortion of the local environment and a larger second order quadrupolar induced shift rather than an increased fluorination level (which would also cause a similar shift to lower frequency), because this shift to lower frequencies was not observed in the spectra presented in the main text (Figure 3) or Figure S5.

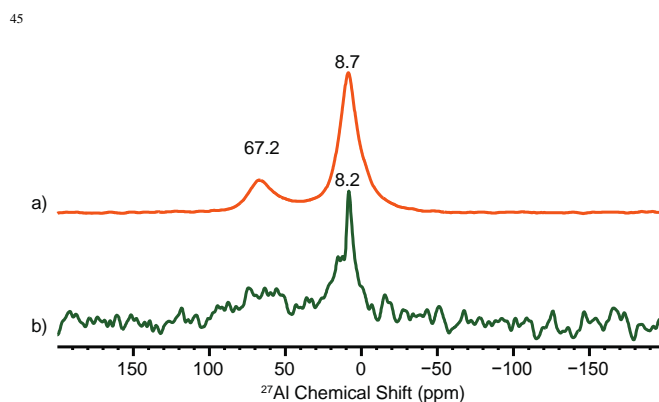
The spectra of the 5% Al/F coated sample (Figure S5) shows that, although the signal-to-noise is much lower for the spectrum of the sample sintered in air, both tetrahedral and octahedral environments are formed following sintering in air and nitrogen. No  $\text{AlF}_3$  is observed.



**Figure S3:** Comparison between the  $^{27}\text{Al}$  MAS NMR spectra of 2% Al/F-coated  $\text{Li}[\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9}]\text{O}_2$  after heating at  $120^\circ\text{C}$  (in air) and  $400^\circ\text{C}$  (in  $\text{N}_2$ ), and the  $\text{AlF}_3$  reference. The spectra were acquired at low fields (8.46 T); asterisks mark spinning sidebands in these and subsequent spectra.



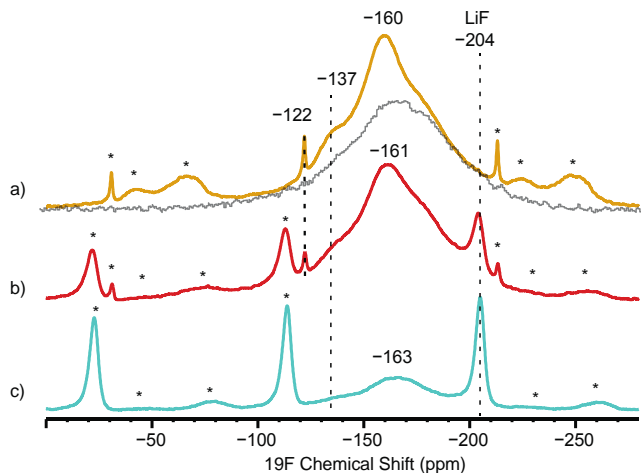
**Figure S4:**  $^{27}\text{Al}$  NMR of 5% Al/F-coated  $\text{Li}[\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9}]\text{O}_2$  after heating at  $120^\circ\text{C}$  (in air) and  $400^\circ\text{C}$  (in  $\text{N}_2$ ), 5% reference  $\text{AlF}_3$ -coated  $\text{Li}[\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9}]\text{O}_2$ , and the  $\text{AlF}_3$  reference. All spectra were acquired at 8.46T with an operating frequency of 93.81MHz.



**Figure S5:**  $^{27}\text{Al}$  MAS NMR spectra of 5% Al/F-coated  $\text{Li}[\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9}]\text{O}_2$  after sintering at  $400^\circ\text{C}$  (a) in  $\text{N}_2$  and (b) in air acquired at 16.4 T and an operating frequency of 182.4 MHz. A spinning rate 60 kHz and a rotor-synchronized echo pulse sequence ( $90^\circ\text{-}\tau\text{-}180^\circ\text{-}\tau\text{-acq}$ ) where  $\tau=1/\nu_r$  was used with a pulse delay of 0.5s.

## 5. $^{19}\text{F}$ NMR Spectroscopy

$^{19}\text{F}$  NMR was performed at high field (16.4 T) on a Bruker Avance III 700 MHz spectrometer at an operating frequency of 658.7 MHz. All experiments were performed using a 1.3 mm probe with spinning rate 60kHz and a rotor-synchronized double adiabatic echo pulse sequence [4]. A  $\pi/2$  pulse width of  $0.93 \mu\text{s}$  was used with pulse delays of 0.05s. All spectra were referenced to LiF at -204 ppm.



**Figure S6:**  $^{19}\text{F}$  NMR spectra of (a) 1% Al/F-coated  $\text{Li}[\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9}]\text{O}_2$  after heating at  $120^\circ\text{C}$  in air (b) and  $400^\circ\text{C}$  in  $\text{N}_2$ . (c) Model compound prepared with 5% commercial  $\text{AlF}_3$  slurry after heating at  $400^\circ\text{C}$  in  $\text{N}_2$ . The grey spectrum in (a) represents the  $^{19}\text{F}$  background of the probe, i.e., the spectrum acquired under identical conditions with an empty rotor.

Three areas of interest are observed in the  $^{19}\text{F}$  spectra (Figure S6). The first is a large broad component centered around  $-161$  ppm for all samples. Although there is a broad background fluorine signal in the probe, shown in (a), the extra intensity around  $-160$  ppm and presence of spinning sidebands show this feature is not only due to the background but also indicates the presence of  $\text{AlF}_{6-x}\text{O}_x^{3+x-}$  fluoride ions, which are expected to resonate in this frequency range.[1][2] Note that  $\text{AlF}_6^{3-}$  units in the various  $\text{AlF}_3$  polymorphs resonate at lower frequencies ( $-172$  to  $-175$  ppm).[3] A second broad resonance is seen at approximately  $-137$  ppm due to  $\text{AlF}_{6-x}\text{O}_x^{3+x-}$  resonances with higher values of  $x$ . Comparing the 1% Al/F-coated samples (a, b) to the 5% model compound (c) we notice that the 1% samples have an additional sharp resonance at  $-122$  ppm. This resonance is assigned to terminal fluoride ions, the sharp nature of the resonance suggests that the environment is either due to highly mobile species (such as an  $\text{SiF}_6^{2-}$  impurity) or is due to isolated fluoride ions in a low fluorine content alumina. Comparing the  $120^\circ\text{C}$  (a) and  $400^\circ\text{C}$  (b, c) samples, we can see that LiF resonance ( $-204$  ppm) only appears after sintering at high temperature. Definitive assignments of the aluminum fluoride species are not currently possible without performing  $^{27}\text{Al}$ - $^{19}\text{F}$  correlations experiments. These are ongoing but are extremely challenging due to the low concentration of aluminum and fluorine species and the paramagnetic nature of the samples, which broadens the signals noticeably. Note that it was not possible to obtain high quality  $^{19}\text{F}$  NMR spectra of these samples without use of newer pulse sequences, [4] which allow the very broad signals to be excited.

[1] W. Zhang, M. Sun, R. Prins, J. Phys. Chem. B., 2002, **106**, 11805.

[2] R. König, G. Scholz, A. Pawlik, C. Jäger, B. van Rossum, E. Kemnitz, J. Phys. Chem. C, 2009, **113**, 15576

[3] R. König, G. Scholz, K. Scheurell, D. Heidemann, I. Buchem, W.E.S. Unger, E. Kemnitz, J. Fluorine Chemistry, 2010, **131**, 91.

[4] G. Kervern, G. Pintacuda, L. Emsley, Chem. Phys. Lett., 2007, **435**, 157.