

Supporting information

A general route of fluoride coating on the cyclability regularity of high-voltage NCM cathodes

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Experimental

Preparation of precursor and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$

The target $[\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}](\text{OH})_2$ precursor was synthesized by hydro-thermal reaction. Nickel acetate, manganous acetate, cobaltous acetate and urea were dissolved in 26 mL alcohol and 39 mL H_2O to form uniform solution. After stirring, the solution was transferred into 100 mL Teflon-lined autoclave and kept at 180 °C in the oven for 24 hours. The precursor was obtained after filtering, washing and drying. With the stoichiometric amount of 1:1.05, the precursor $[\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}](\text{OH})_2$ was fully mixed with Li_2CO_3 , and the mixture was calcined at 850 °C for 12 h in a muffle furnace to form large layered oxide particles.

Fluoride coatings of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$

0.5, 1 and 2 mol% AlF_3 were used to modify $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ materials (NCM523) by simple wet chemical method. Aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was dissolved in 30 mL H_2O and then 0.3 g NCM523 powders were immersed into the aluminum nitrate solution. Ammonium fluoride (NH_4F) was dissolved in 10 mL H_2O and the solution was added into the mixture drop by drop. The mixture was evaporated at 120 °C for about 8 hours. The obtained powders were calcined at 350 °C in tube furnace for 6 hours following the nitrogen. It was worth noting that 0.5, 1, 2 mol% AlF_3 coatings are named as 0.5 AlF_3 , AlF_3 and 2 AlF_3 coated NCM523 samples, respectively. Other fluoride coatings including BaF_2 , ZnF_2 , NiF_2 , CeF_3 , ZrF_4 , YF_3 , BiF_3 , PrF_3 and SmF_3 were performed using the same as the above procedure.

Materials characterization

X-ray diffraction (XRD, Rigaku MiniFlex600) with Cu $K\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$) was used to identify structure. Raman spectra were recorded on HROIBA Jobin Yvon (LabRAM HR Evolution) using the 532 nm line argon-ion laser. The morphology of the materials was observed by scanning electron microscopy (SEM, Hitach-SU8220, Japan). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images were taken on FEI-Talos F200S, Czechs). X-ray Photoelectron Spectroscopy (Thermo fisher Scientific-K-Alpha⁺) was used to determine ion valence states.

Electrochemical measurement

The positive electrode was prepared by 80 wt% synthesized material, 10 wt% super P, 10 wt% PVDF using the N-methyl-pyrrolidone as the solvent following. The slurry was coated on Al foil and dried at 120 °C in vacuum oven for 12 hours. The coin cell

was assembled in argon-filled glove box where the amount of water and oxygen is below 0.1 ppm. Lithium foil was used as the counter and reference electrode and the electrolyte was a solution of 1 mol L⁻¹ LiPF₆ dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume). The coin cells were charged and discharged on test instrument (LAND Electronic Co.) at room temperature.

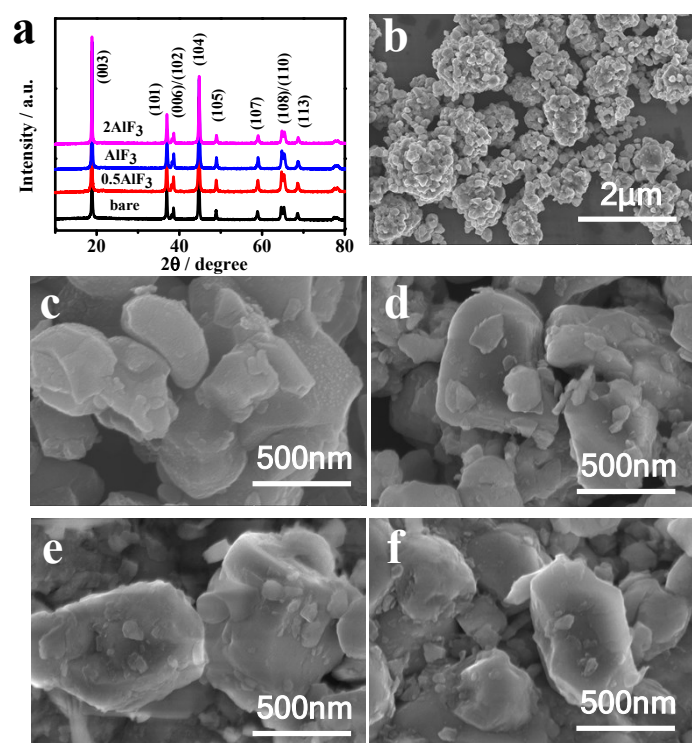


Figure S1. (a) XRD patterns of bare and different amount of AlF₃ coated NCM523 samples. SEM images of (b, c) bare, (d) 0.5AlF₃, (e) AlF₃ and (f) 2AlF₃ coated NCM523 samples.

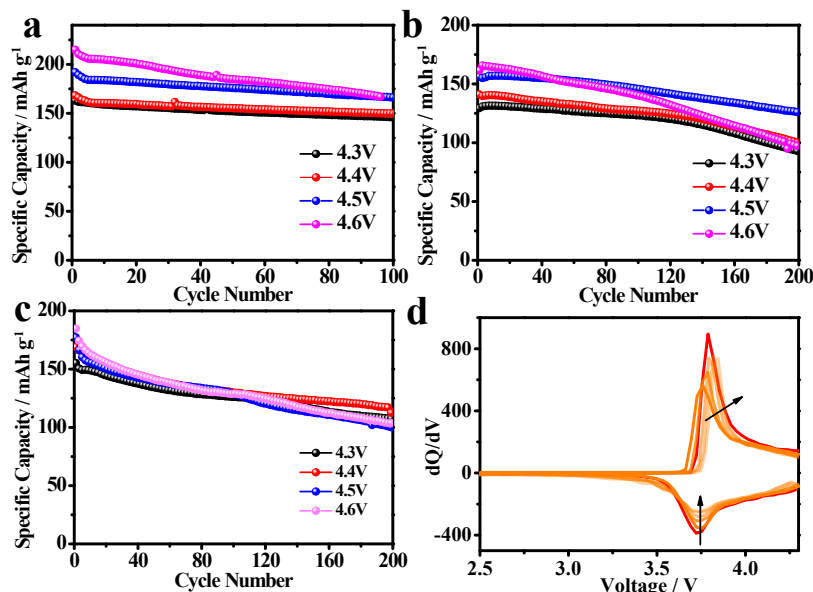


Figure S2. Cycling performance of (a) 0.5AlF_3 , (b) 2AlF_3 coated and (c) bare NCM523 samples at a current density of 100 mA g^{-1} with different cutoff voltages. (d) The differential capacity versus voltage curve (dQ/dV) performed in 1st, 10th, 20th, 30th, 40th and 50th cycles.

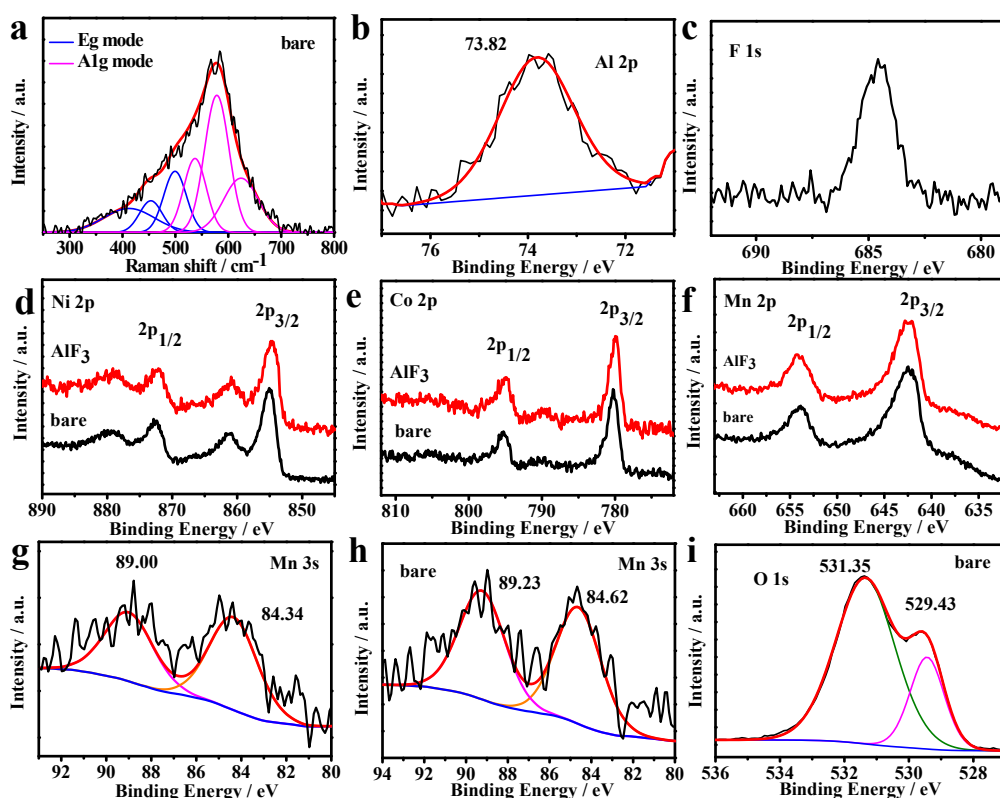


Figure S3. (a) Raman spectra of bare NCM523 sample. (b) Al 2p and (c) F 1s spectrum of AlF_3 coated NCM523 sample. (d) Ni 2p, (e) Co 2p, (f) Mn 2p and (g, h) Mn 3s spectrum of bare and AlF_3 coated NCM523 samples. (i) O 1s spectra of bare NCM523 sample.

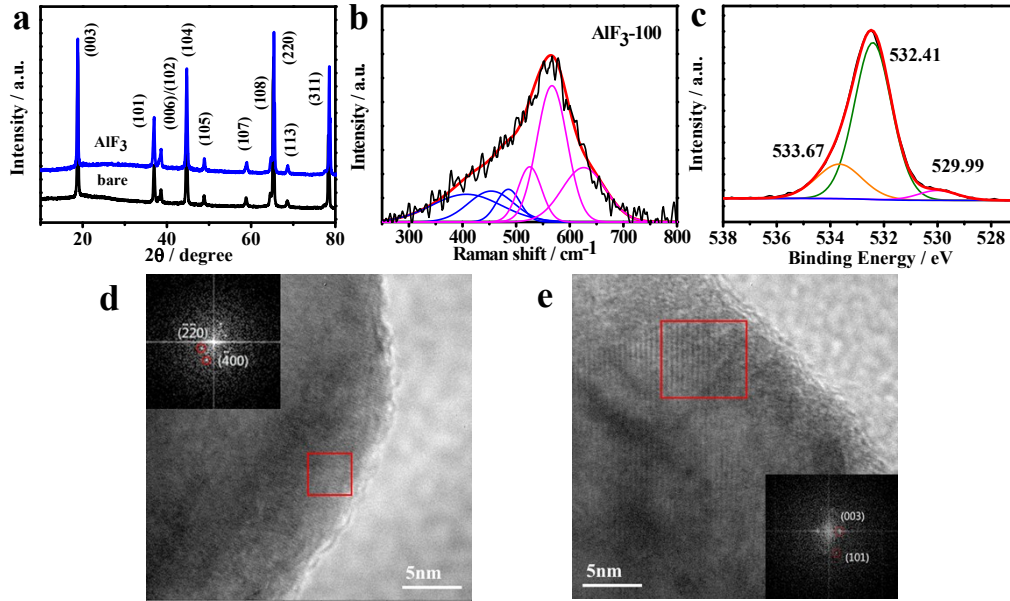


Figure S4. (a) XRD patterns of bare and AlF₃ coated NCM523 samples after 100 cycles. (b) Raman and (c) O 1s spectrum of AlF₃ coated NCM523 samples after 100 cycles. (d, e) HRTEM images and corresponding FFT patterns of bare and AlF₃ coated NCM523 samples after 100 cycles.

HRTEM with local FFT images were performed to confirm phase transformation. For bare NCM532 sample after 100 cycles, the *d*-spacings signed by red circle in **Figure S4 (d, e)** are separately ~ 2.93 and ~ 2.08 Å, corresponding to $(\bar{2}\bar{2}0)$ and $(\bar{4}00)$ planes of *Fd-3m* spinel structure. This means serious phase transformation has occurred during cycling. In cycled AlF₃ coated sample, the *d*-spacings of 4.89 and 2.41 Å suggest the two signed diffraction spots are assigned to (003) and (101) facets of *R-3m* layer structure. The structure stability benefits from the protection of AlF₃ coating.

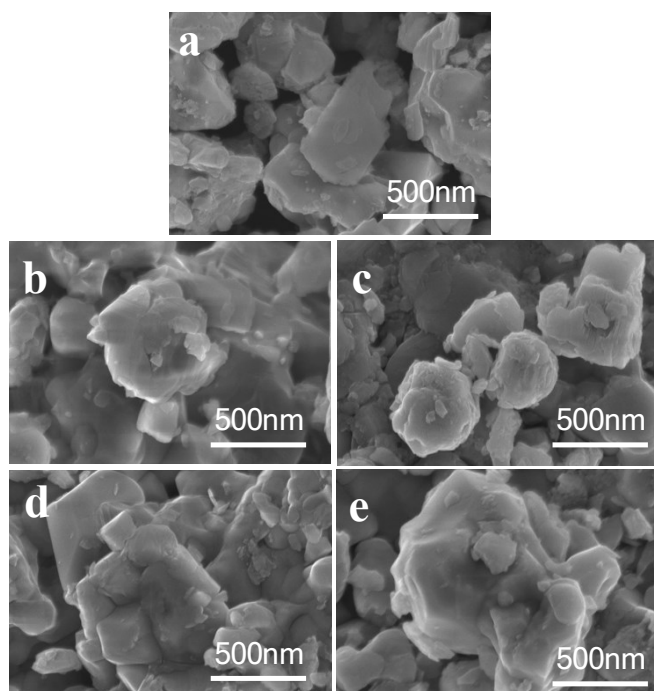


Figure S5. SEM images of (a) ZrF_4 , (b) YF_3 , (c) PrF_3 , (d) BaF_2 and (e) SmF_3 coated NCM523 samples.

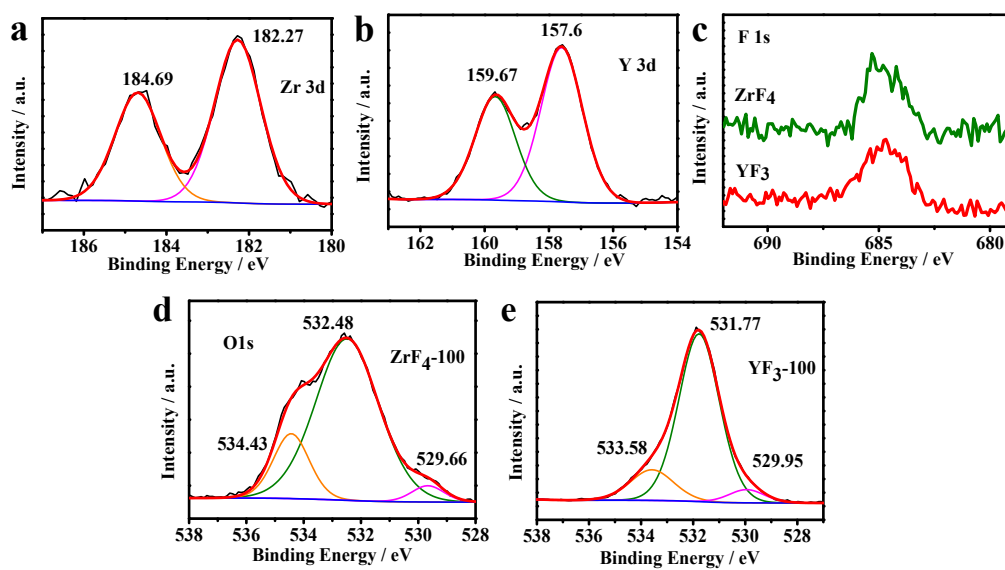


Figure S6. (a) Zr 3d and (b) Y 3d spectrum, (c) F 1s and (d, e) O 1s spectrum of ZrF_4 and YF_3 coated NCM523 samples.

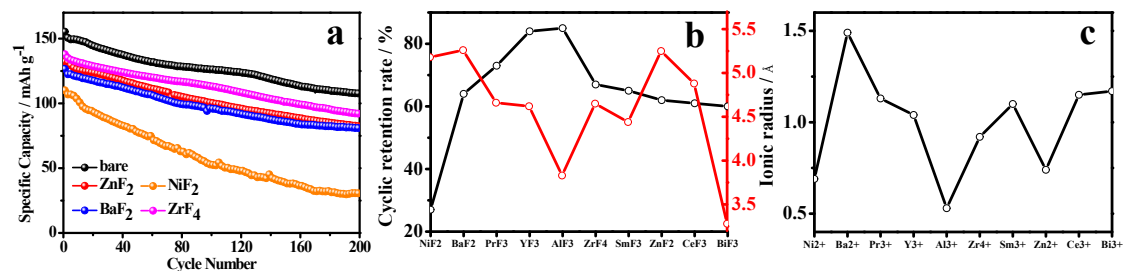


Figure S7. (a) Cycle performance of bare, ZnF₂, BaF₂, NiF₂ and ZrF₄ coated NCM523 samples at a current density of 100 mA g⁻¹. Fluoride coatings of (b) pH and cyclic retention rate (c) ionic radius curves.