Supporting Information

Improving surface structural stability of Li-rich layered cathodes by cation-anion doping

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Experimental Section

The modification material with 1mol% ZnF_2 may be obtained with the following steps. The precursor $Mn_{0.75}Ni_{0.25}CO_3$ was dispersed in 50mL deionized water and been stirring for 30 minutes. $ZnSO_4 \cdot 7H_2O$ (0.0289g) and NH_4F (0.00772g) were added, after which stirring was processed for another 30 minutes. The suspension was heated and stirred until the material was dry thoroughly. The left solid was uniformly mixed with Li_2CO_3 (5%mol excess), KCl (3.5964g) and NaCl (1.8795g), then the mixture was sintered in a muffle furnace at 850 °C (ramp rate of 2 °C min^{-1}) for 12 hours. Rinsing was processed after sintering to remove extra Na^+, K^+, Li^+ and Cl^-. Another sintering process at 400 °C for 4 hours was executed after drying the material in a blast oven at 180 °C.

The control materials without modification could be obtained by executing the process above without adding $ZnSO_4 \cdot 7H_2O$ and NH_4F.

The crystalline structure was identified by Rigaku MiniFlex600 X-ray diffractometer with Cu Kα radiation (k=1.54059 Å, 40 kV, 50.0 mA). X-ray Photoelectron Spectroscopy test verifying ion valence states was carried out with Thermo Scientific K-Alpha. Scanning Electron Microscopy was used to analyse the morphology of the materials with ZEISS Sigma 300. Transmission electron microscopy, high-resolution TEM images were taken on JEOL JEM 2100F.

All the electrochemical examinations were carried out in CR2016 coin cells, with lithium metal as the anode, $LiPF_6$ as the electrolyte and a chip of Al foil with the materials as the cathode.

As preparing the cathode, the coating on the Al foil was made of 80 wt% synthesized material, 10 wt% super P, 10 wt% PVDF using the N-methyl-pyrrolidone as the solvent following. The coated slurry was dried at 120 °C for 12h in a vacuum oven. The electrolyte was a solution of 1 mol L^{-1} $LiPF_6$ dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) with a ratio of 1:1 in volume. The coin cells were assembled in an Ar-filled glove box with <0.1 ppm of water and oxygen.

The coin cells were charged and discharged on test instrument from Neware Technology Ltd. under a galvanostatic mode between 2.0 and 4.8 V (1C = 200 mAg^{-1}) at room temperature.

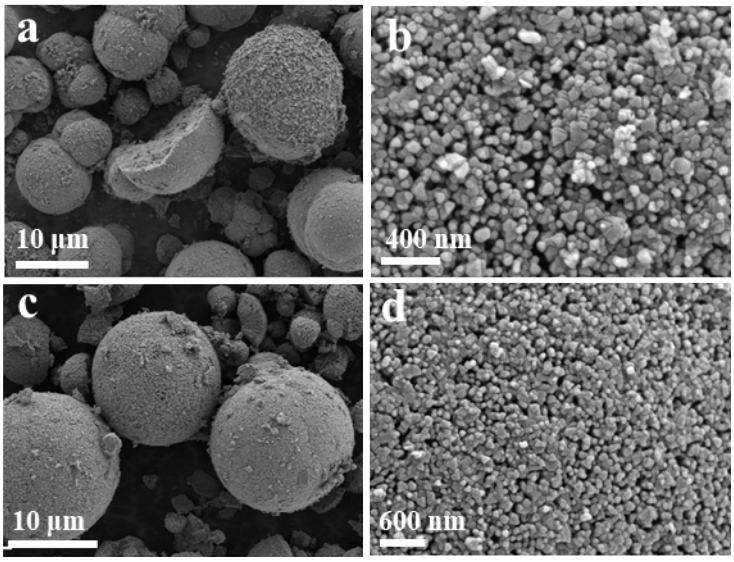

Figure S1. SEM images of (a,b) the PRI sample and (c,d) the ZF sample.

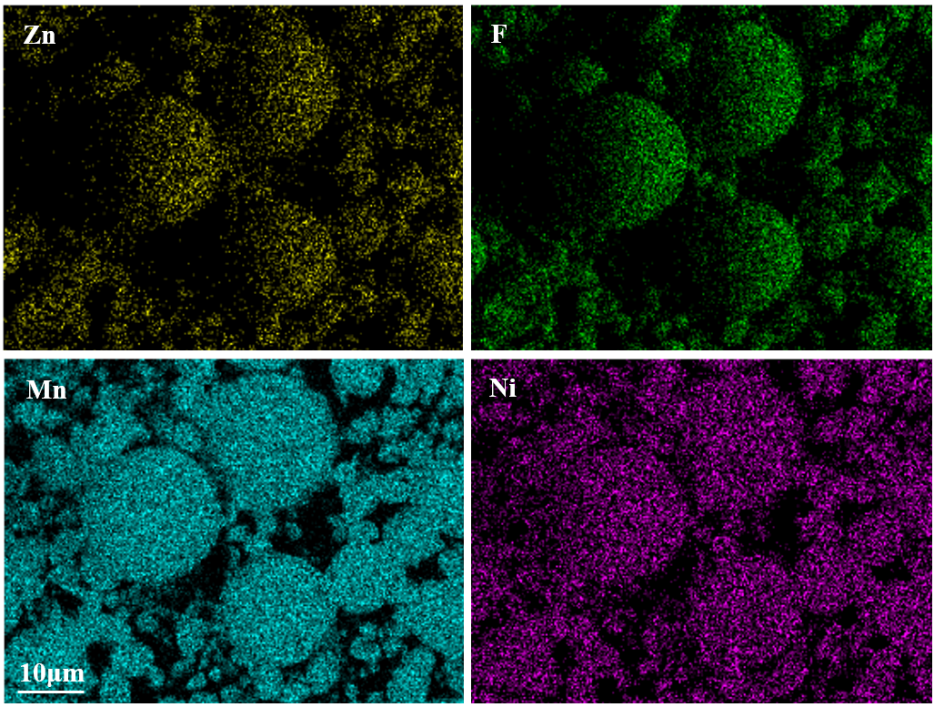

Figure S2. EDS elemental mapping patterns of the ZF.

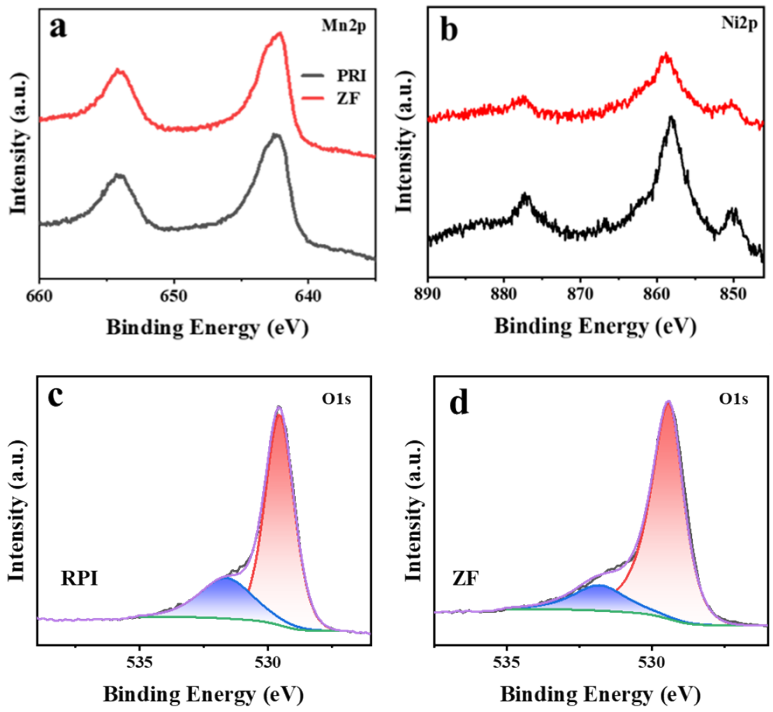

Figure S3. XPS spectra of (a) Mn2p, (b) Ni2p and (c,d) O 1s for the PRI and ZF samples.

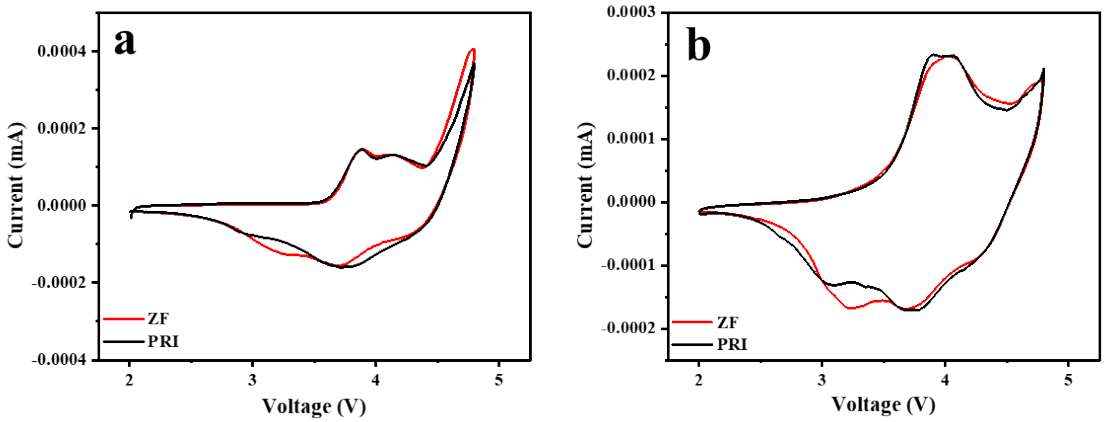

Figure S4. The cyclic voltammetry curves of two samples during the (a) first and (b) second cycle.

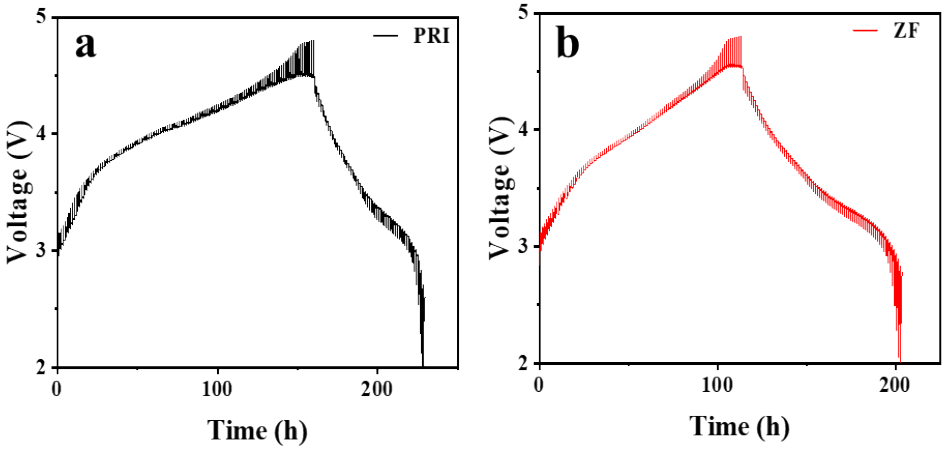

Figure S5. GITT curves of the initial charging-discharging process for (a) the PRI sample and (b) the ZF sample.

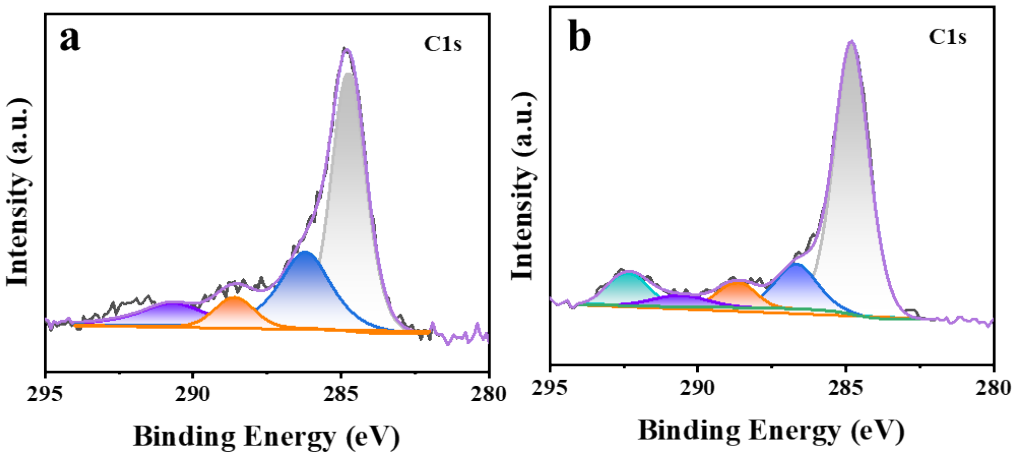

Figure S6. XPS spectra of C1s for (a) the PRI sample and (b) the ZF sample.

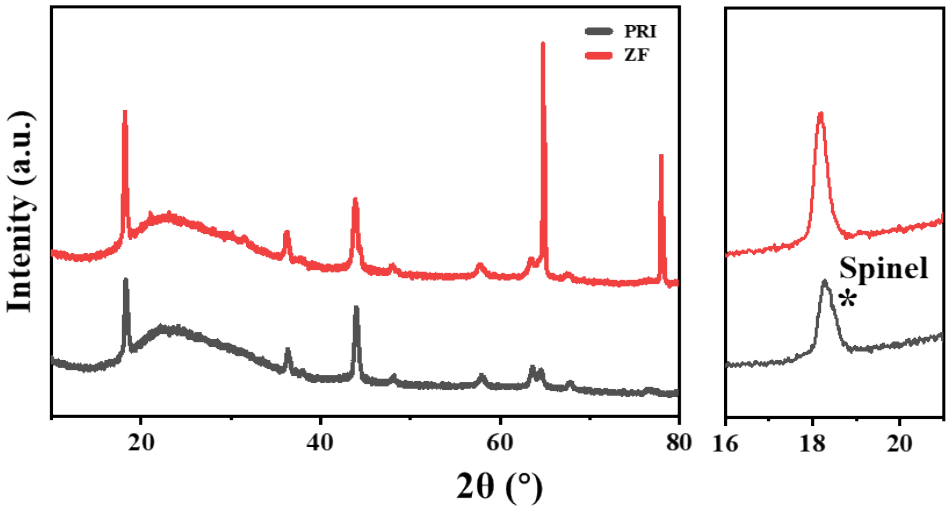

Figure S7. XRD patterns of the PRI and ZF samples after 100 cycles.