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SUPPLEMENTARY INFORMATION

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Tailoring grain boundary structures and chemistry of Ni-rich layered cathodes for enhanced cycle stability of lithium-ion batteries

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Supplementary Information for

Tailoring Grain Boundary Structures and Chemistry of Ni-rich Layered Cathode for Enhanced Cycle Stability of Lithium-Ion Batteries

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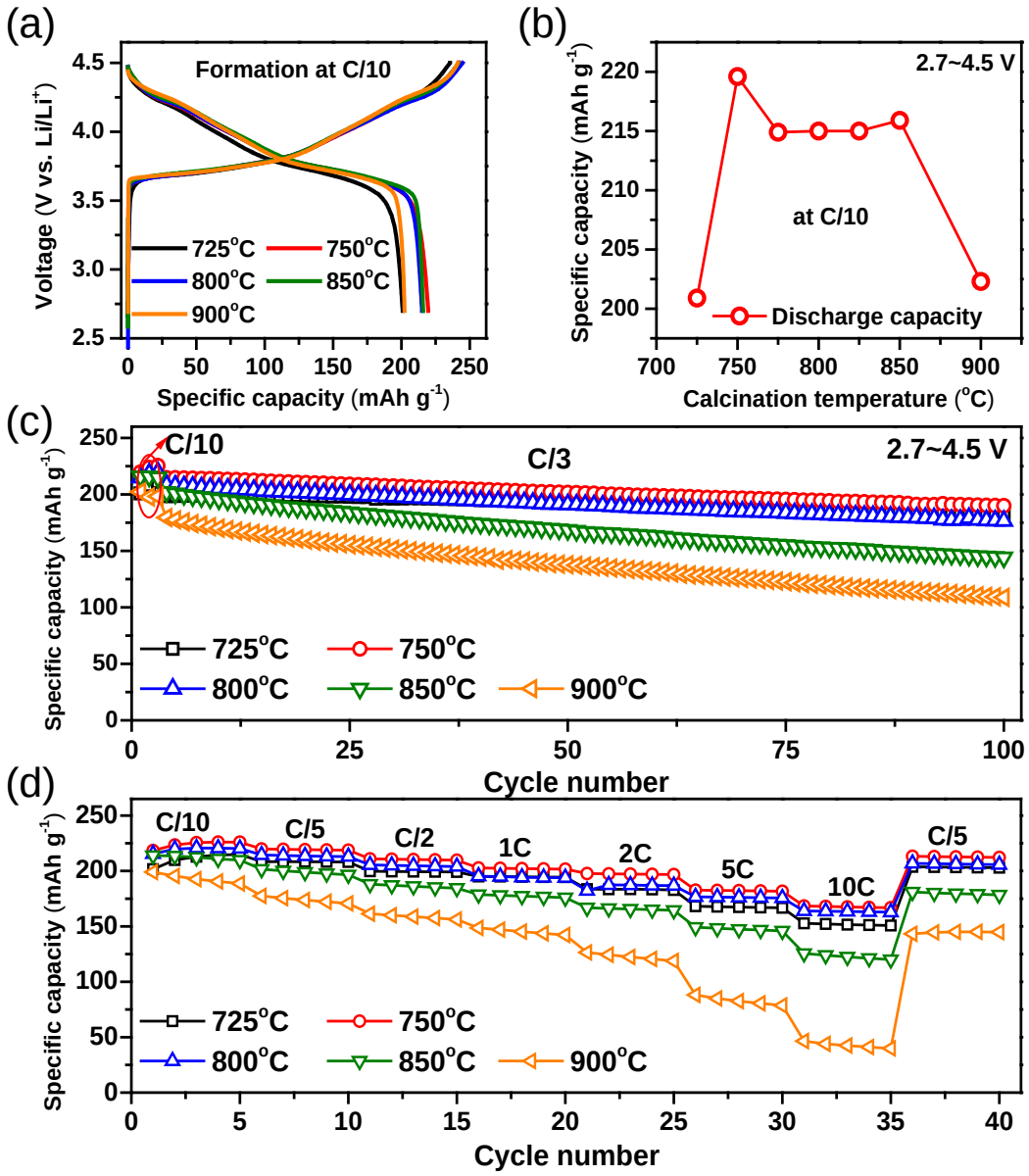
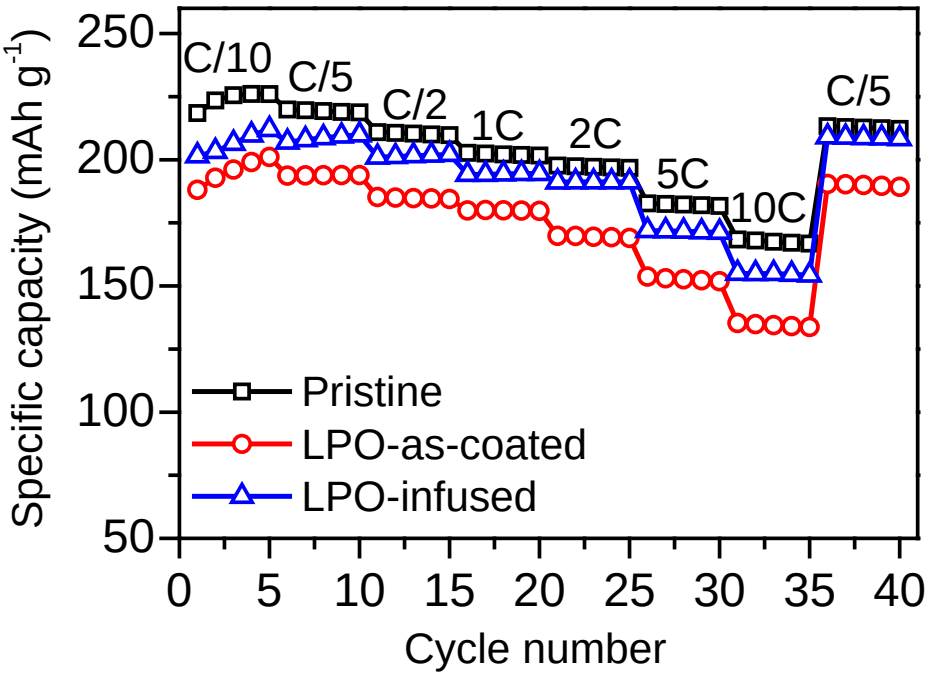
Supplementary Figures

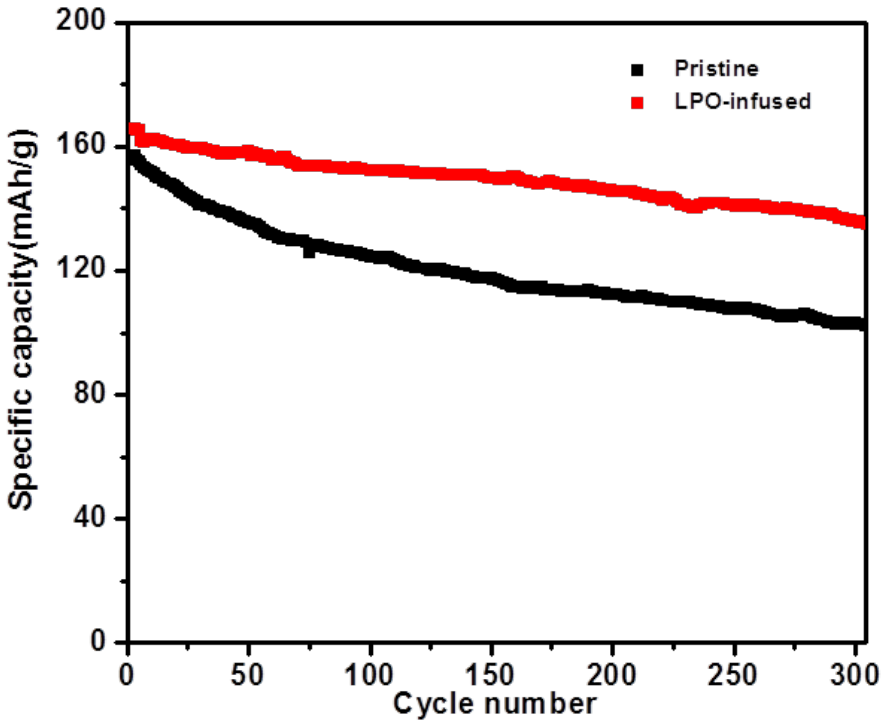


Supplementary Figure 1 | Effect of calcination temperature on the electrochemical performances of Ni-rich $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$ cathode. **a**, Initial charge/discharge voltage profiles; **b**, summary of discharge capacity of materials prepared at different temperatures; **c**, cycling performance and **d**, rate performance of $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$ cathodes prepared at different temperatures in the voltage range of 2.7 – 4.5 V at room temperature (1C = 200 mA g^{-1}). The optimal calcination temperature for Ni-rich $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$ cathode is identified to be 750 °C. Lithium phosphate coating and

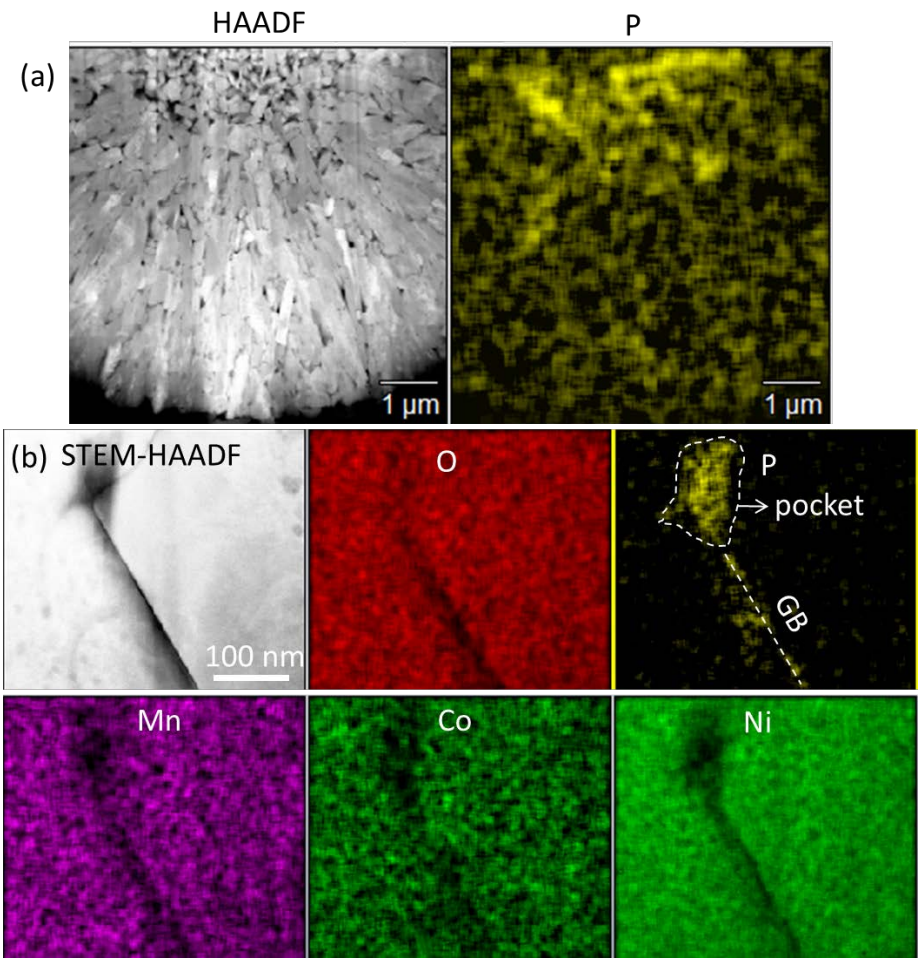
infusion treatment is performed on the $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$ cathode prepared at optimal condition of 750 ^oC to further enhance the long-term cycle life.



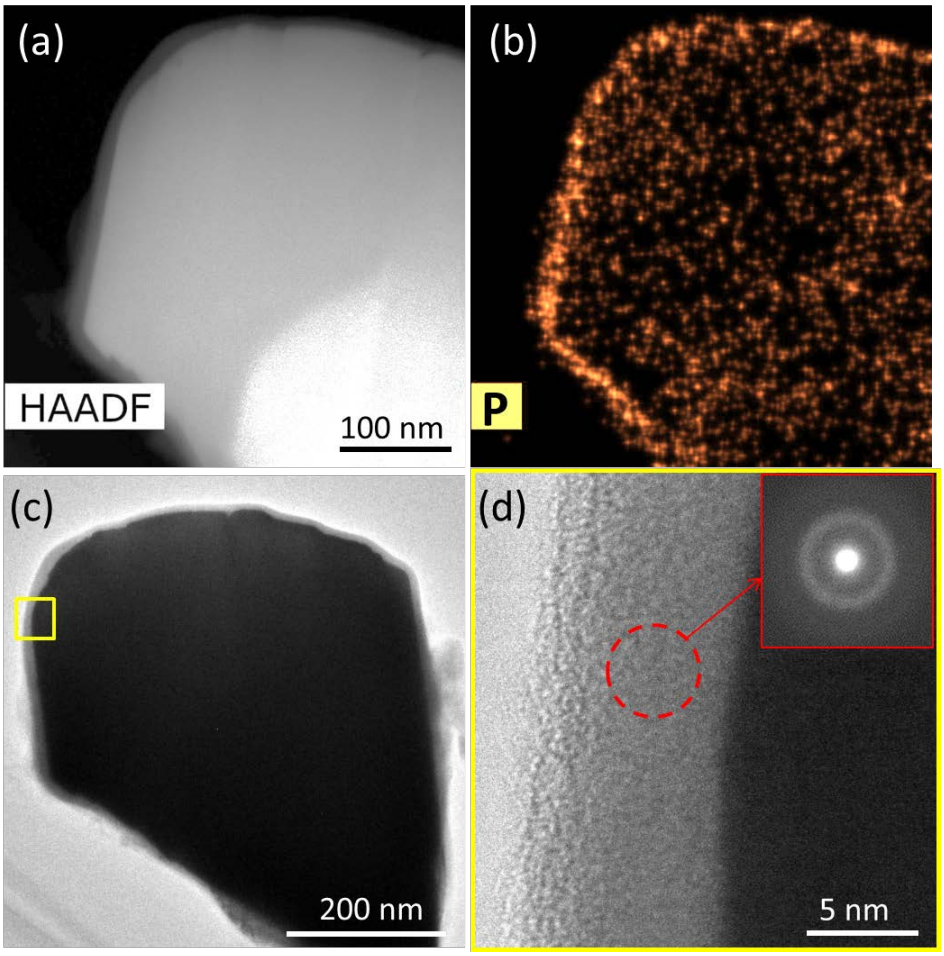
Supplementary Figure 2 | Rate performance of $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$ cathodes before and after LPO treatment in the voltage range of 2.7 – 4.5 V at room temperature (1C = 200 mA g^{-1}).



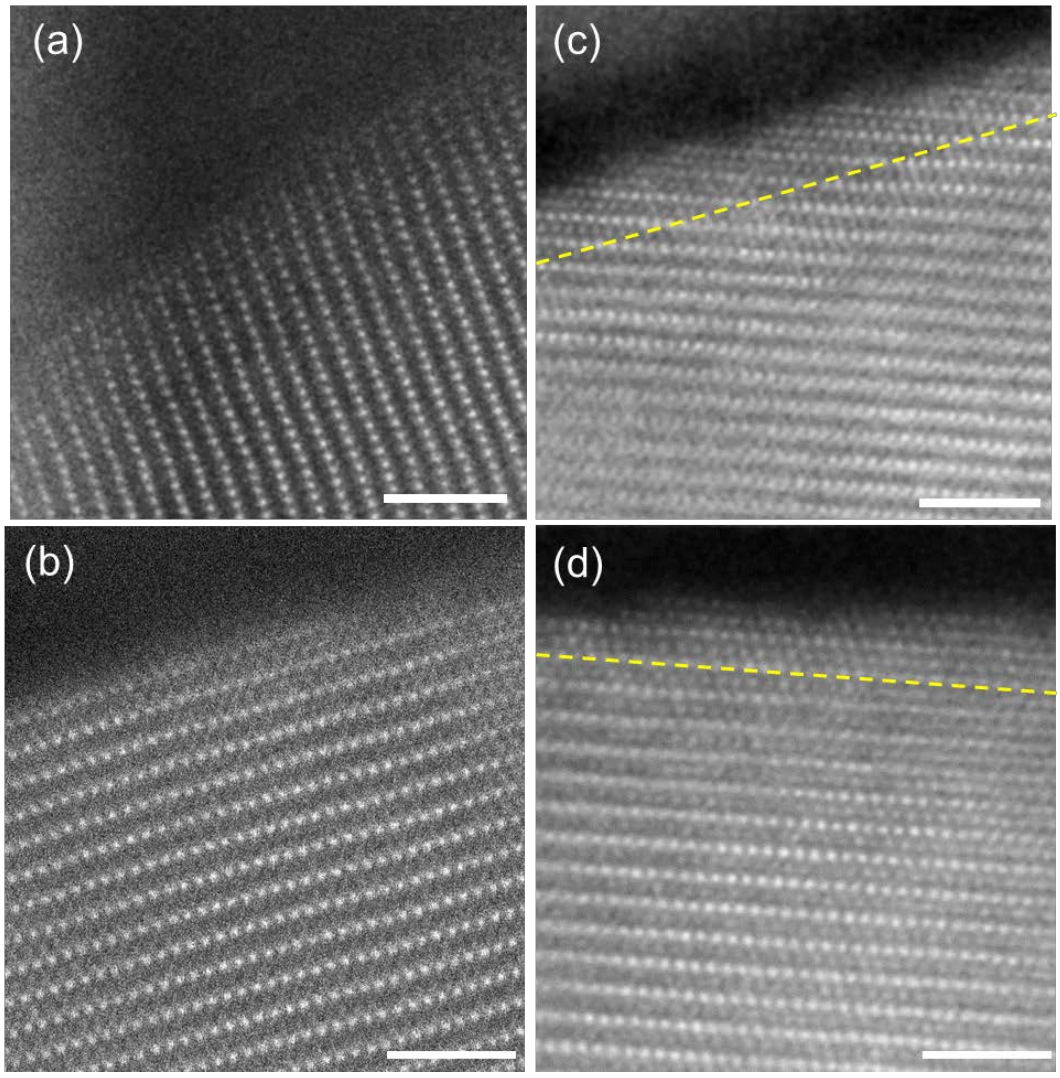
Supplementary Figure 3 | Full cell electrochemical test with graphite as anode. The LPO-infused material shows better long-term cycling stability as compared with pristine material in full cell with graphite anode. The full cell test was at 1C rate after 2 formation cycles at 0.1C.



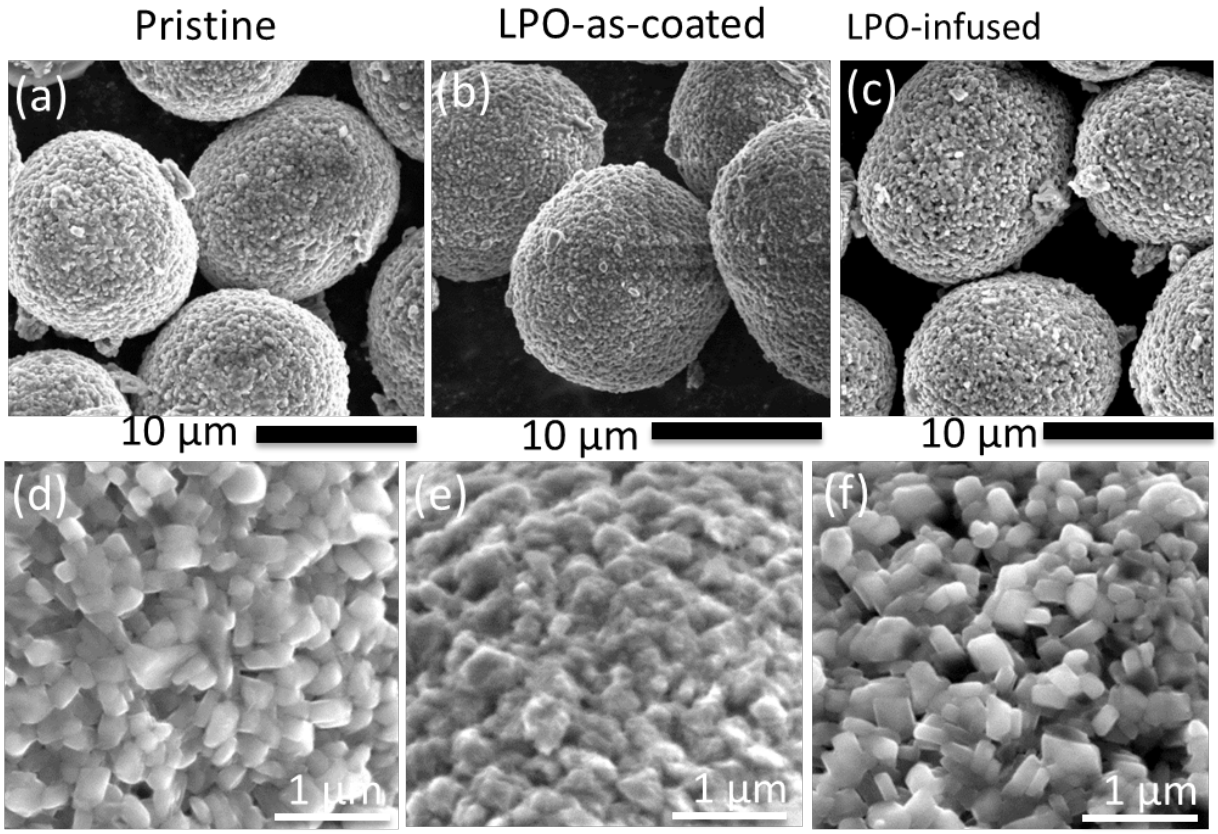
Supplementary Figure 4 | STEM-EDS mapping on the LPO-infused cathode particles. (a) P aggregates at the core region of a secondary particle after annealing. (b) grain boundary and pocket region are enriched of P.



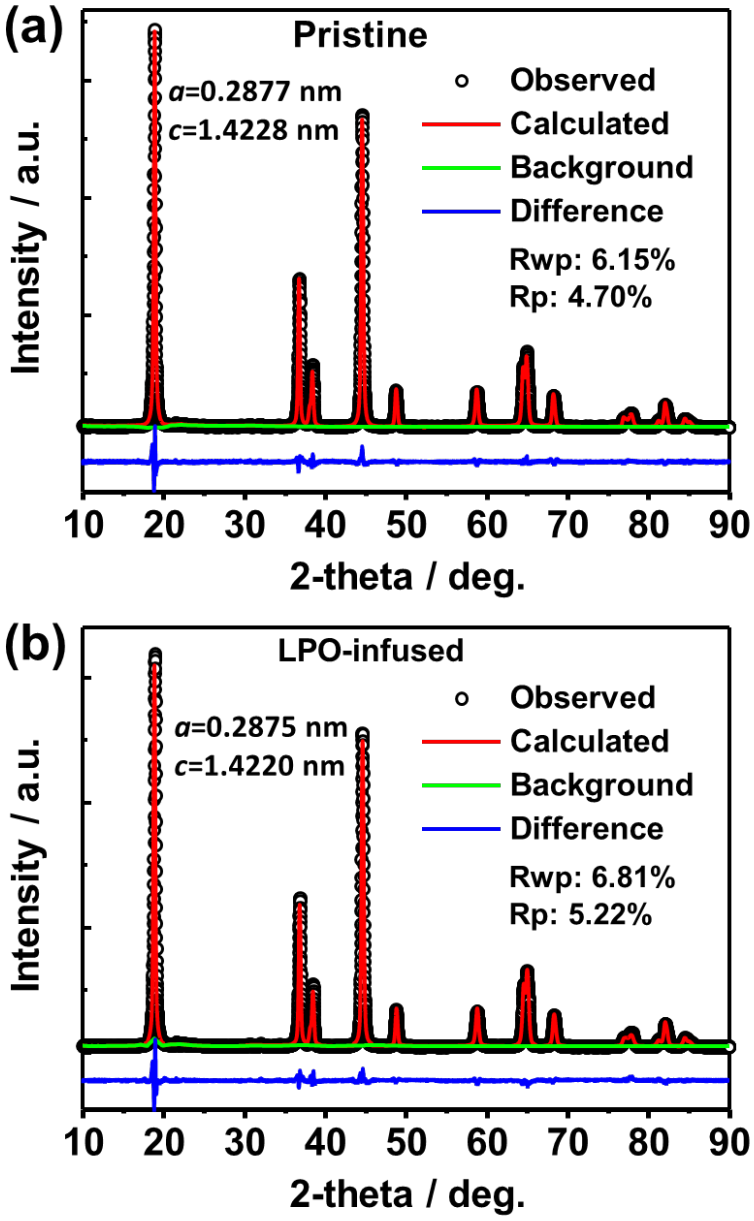
Supplementary Figure 5 | (a, b) STEM-EDS mapping on a LPO-as-coated cathode particle, showing a conformal P-enriched coating layer. (c) low magnification TEM bright field image of the same particle in (a). (d) HRTEM image showing surface coating layer is in amorphous state, inset figure shows nano beam diffraction (NBD) pattern with amorphous feature .



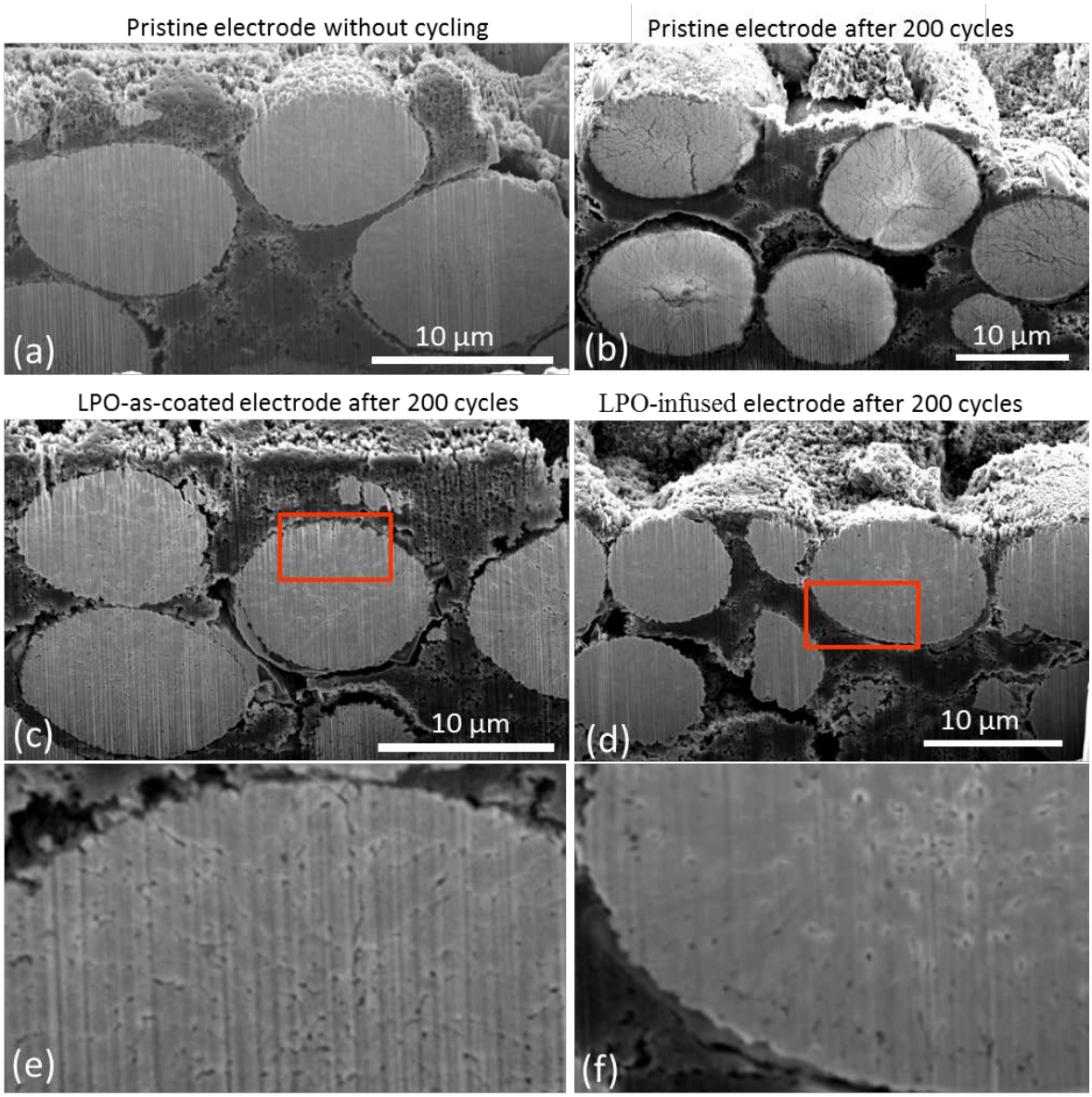
Supplementary Figure 6 | STEM-HAADF images of the outmost surface layer from **a**,**b**, the pristine electrode and **c**,**d**, the LPO-infused electrode. Interlayer Li/TM mixing slightly increases in the LPO-infused electrode, as denoted by the dashed yellow lines. The scale bars are 2 nm.



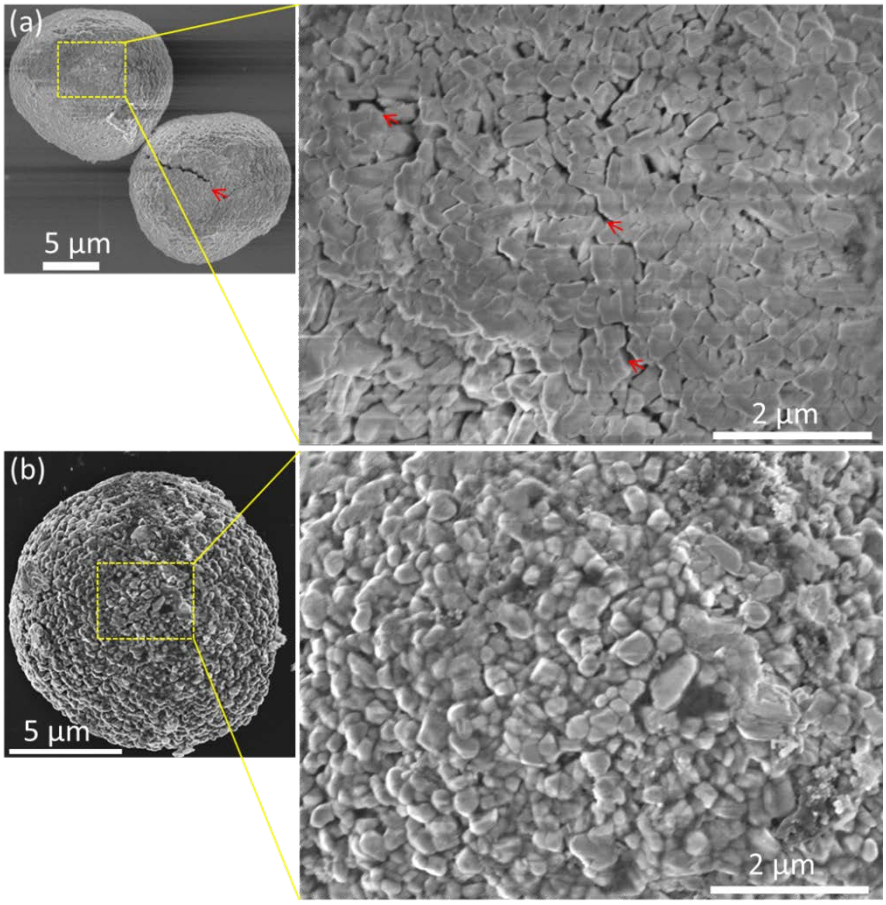
Supplementary Figure 7 | **a-c**, Low magnification SEM images showing all three samples with similar feature. **a**, pristine sample; **b**, LPO-as-coated sample; **c**, LPO-infused sample. **d-f**, high magnification SEM images showing surface morphology change from **d**, pristine sample to **e**, LPO-as-coated sample and then **f**, the LPO-infused sample.



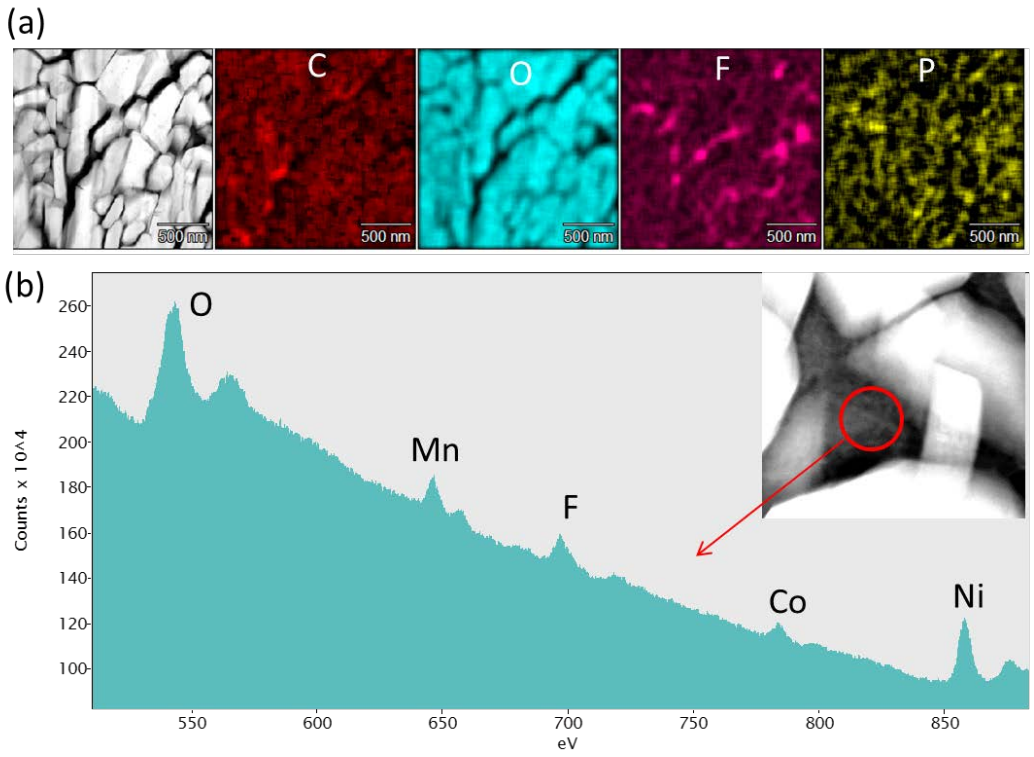
Supplementary Figure 8 | XRD measurements on (a) pristine powders and (b) LPO-infused powders. Our analysis indicates negligible difference between these two samples.



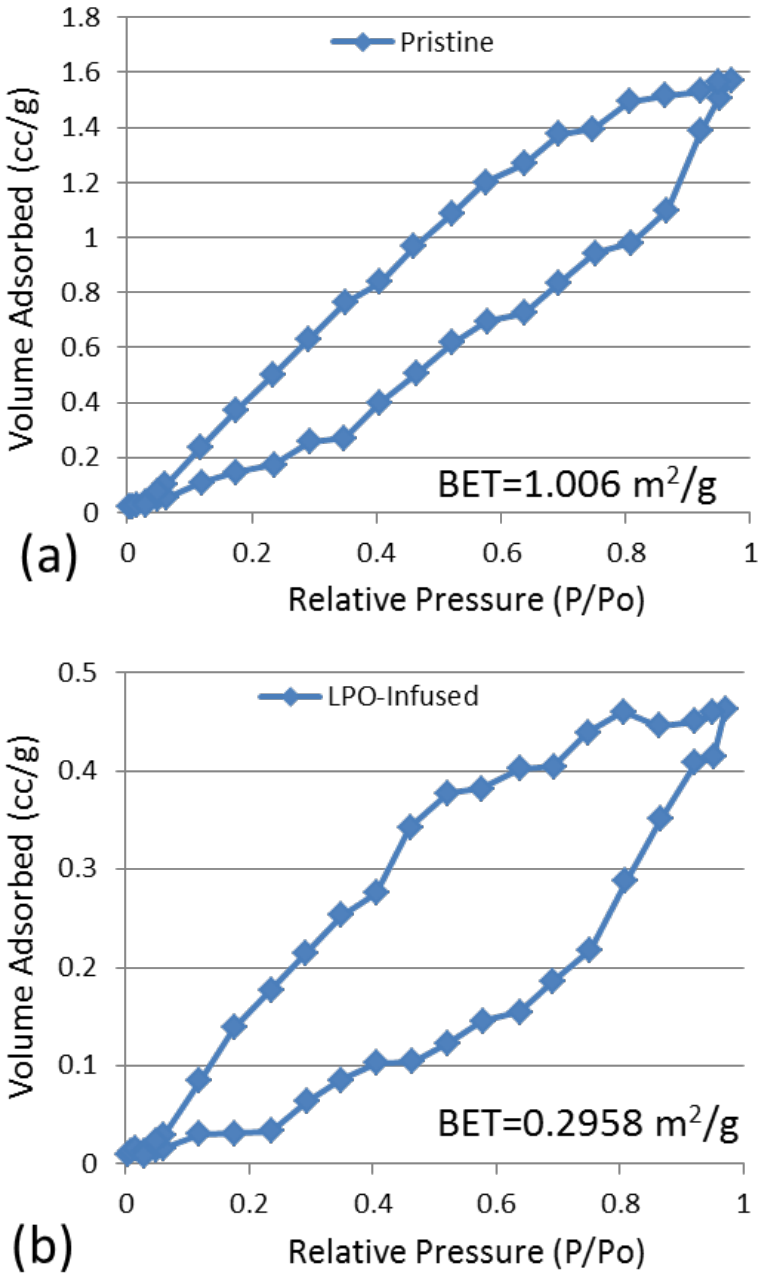
Supplementary Figure 9 | Cross sectional SEM images of **a**, pristine electrode without cycling, **b**, pristine electrode after 200 cycles, **c**, LPO-as-coated electrode after 200 cycles, and **d**, LPO-infused electrode after 200 cycles. (e, f) enlarged areas in (c) and (d) showing microcracks.



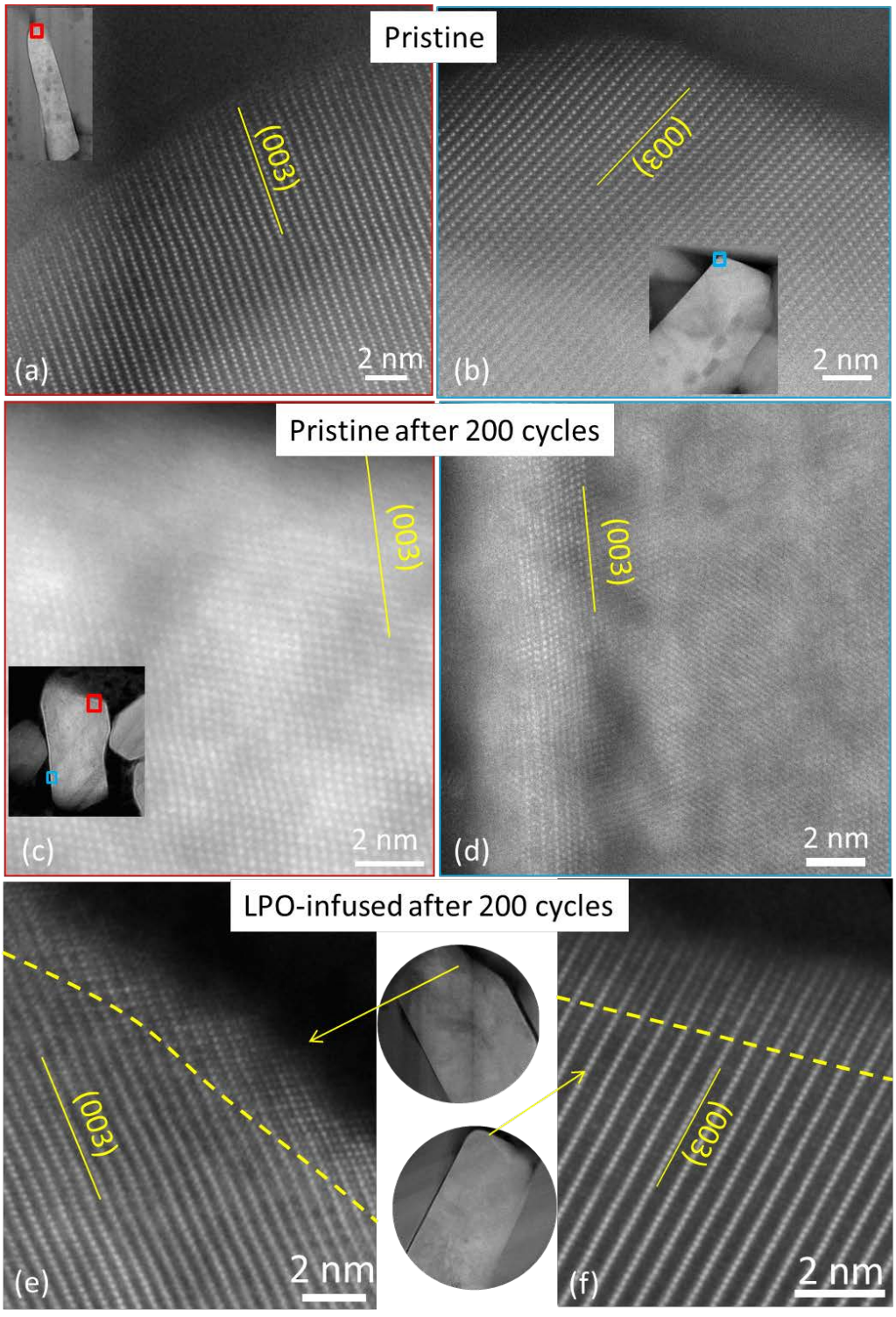
Supplementary Figure 10 | Surface morphology observations by SEM. (a) Pristine electrode after 200 cycles shows big cracks and tiny cracks as illustrated by red arrows. (b) LPO-infused electrode after 200 cycles shows good integrity and well preserved surface morphology.



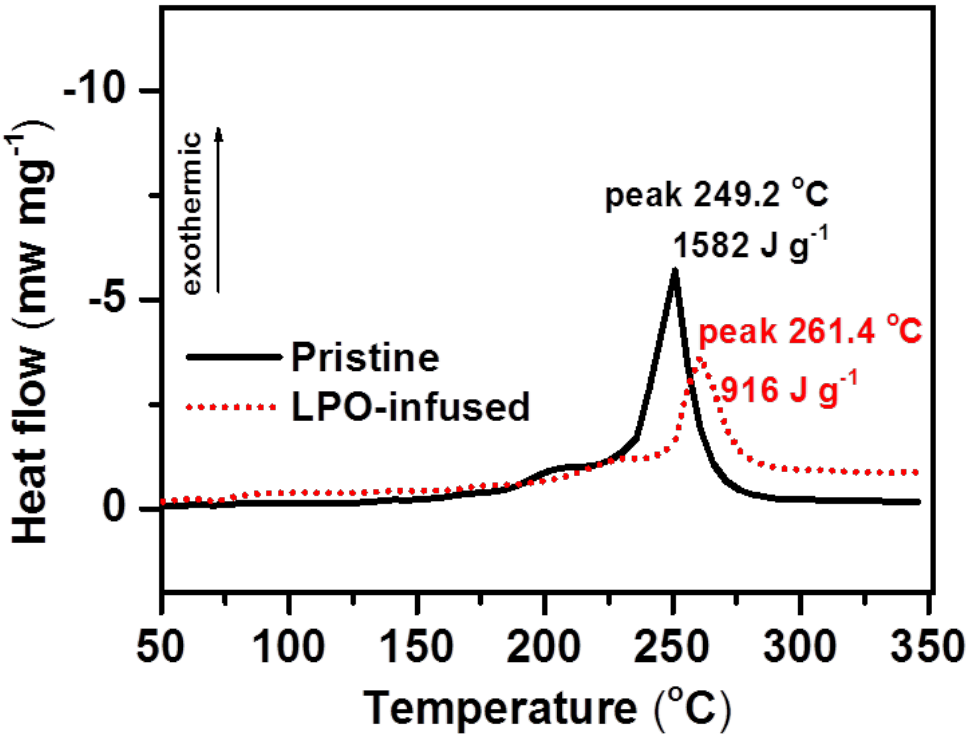
Supplementary Figure 11 | a, STEM-EDS mapping and **b**, EELS to verify the side reaction products at intergranular gaps inside the secondary particle of pristine sample after 200 cycles.



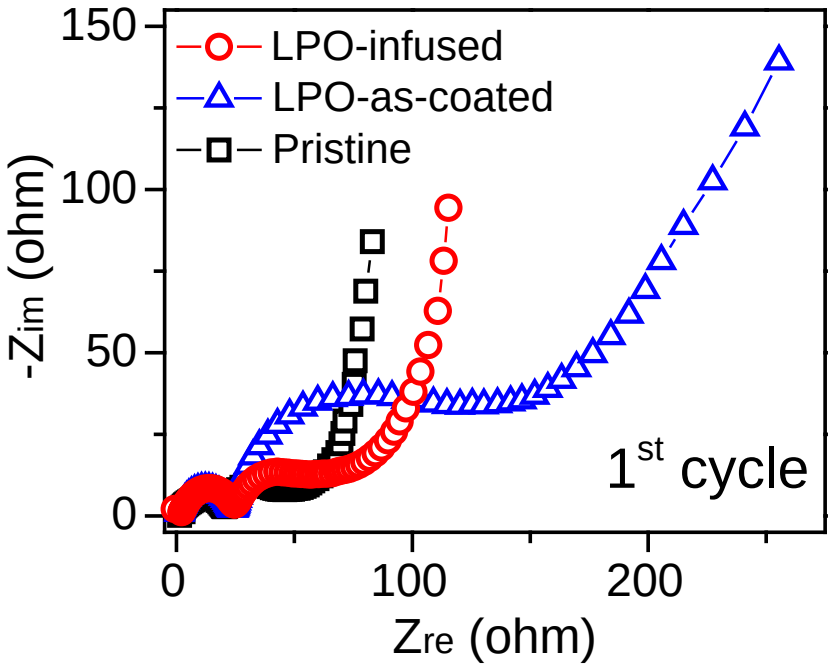
Supplementary Figure 12 | Specific surface area measurement by BET. (a) The specific surface area of pristine sample is 1.006 m^2/g. (b) The specific surface area of LPO-infused sample is 0.2958 m^2/g.



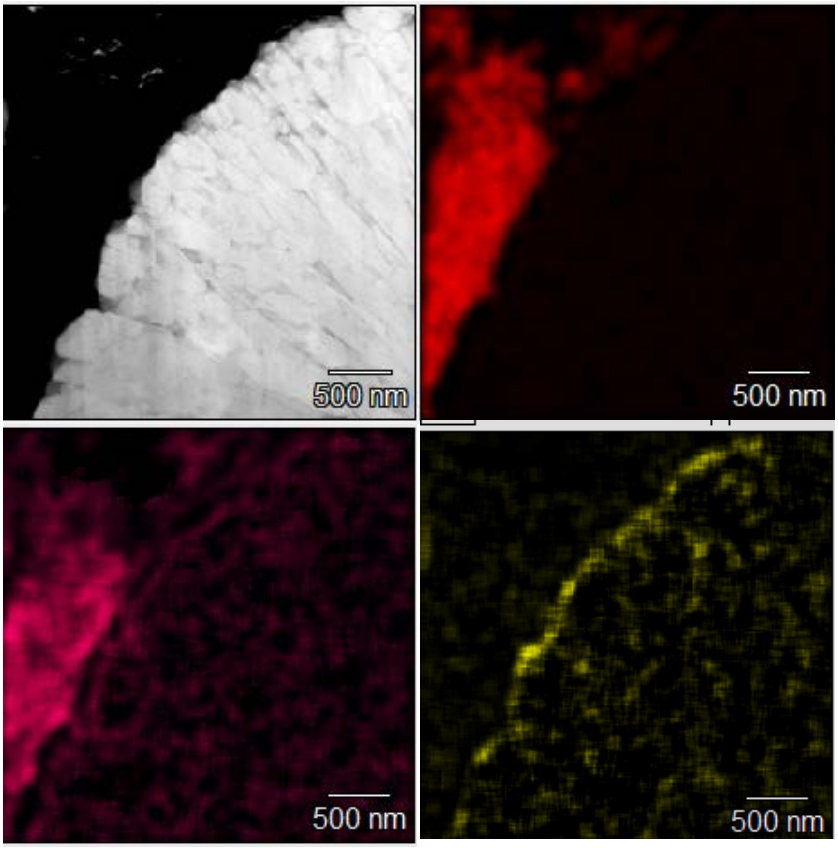
Supplementary Figure 13 | High resolution STEM-HAADF images showing the structure change after cycles. (a, b) pristine sample. (c, d) pristine sample after 200 cycles. (e, f) LPO-infused sample after 200 cycles.



Supplementary Figure 14 | DSC test on pristine and LPO-infused cathode materials. Weight ratios of electrode: 80% active cathode material, 10% super P and 10% PVDF. Both electrodes are charged to 4.5V vs Li metal. The heating rate is 5 °C/min during DSC test.



Supplementary Figure 15 | Nyquist Plots of the pristine, LPO-as-coated, and LPO-infused $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$ cathodes at the charged state of 4.3 V in the first cycle.



Supplementary Figure 16 | EDS mapping on a LPO-coated particle after 200 cycles, which shows few carbon and fluorine inside the secondary particle.