Supporting Information for
The phase-change evolution from surface to bulk of MnO anode upon cycles

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Supplementary Figures

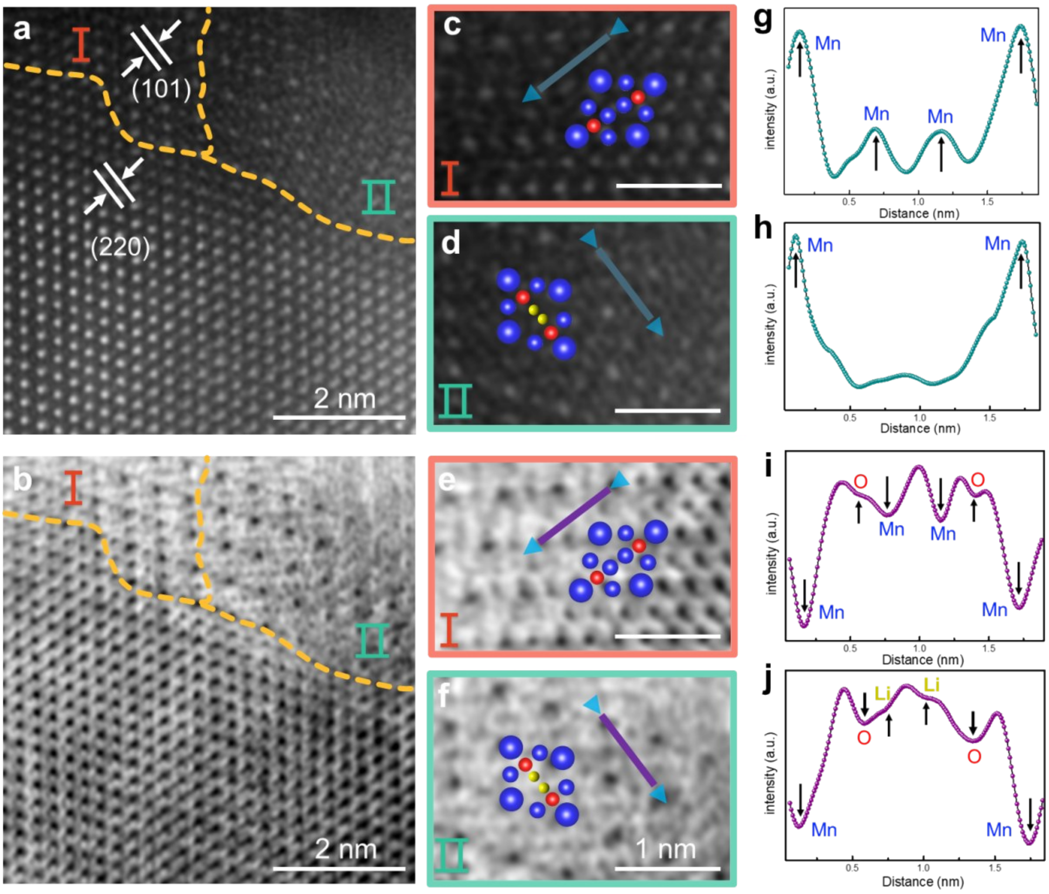

Figure S1 (a b) The annular bright field (ABF) and high-angle annular dark field (HAADF) images of MnO@C anodes discharged to 0.01 V. (c d) enlarged images from region I and region II in Figure a. Figure g and h, the corresponding intensity profiles in Figure c and d. Figure e and f, the enlarged images from region I and region II of ABF image in Figure b, Figure i and j, the corresponding intensity profiles in figure e and f. In Figure c, (d, e, f), the arrow directions represent the intensity profile directions. The blue spheres represent Mn atoms, red spheres represent O atoms, and yellow spheres represent Li atoms, respectively.

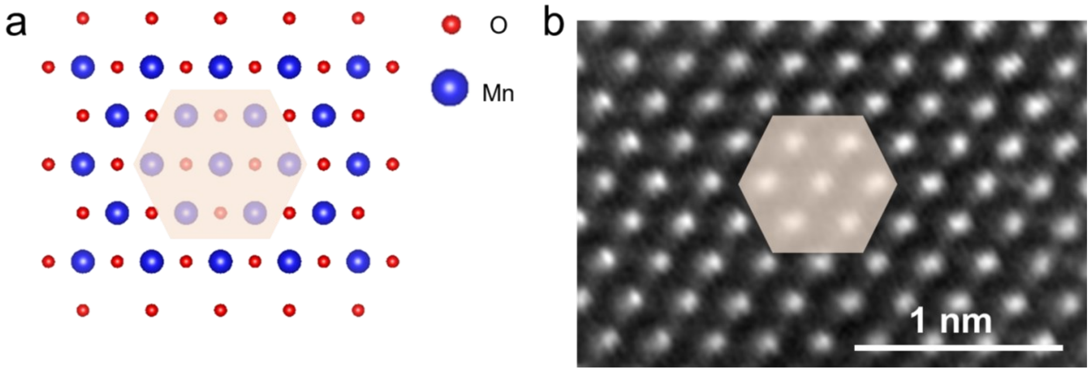

Figure S2 MnO@C anodes crystal structure and HAADF images along the [101] crystallographic. (a) Atomic structural model of MnO@C sample. (b) HAADF image of the MnO@C sample. The blue spheres represent Mn atoms, red spheres represent O atoms.

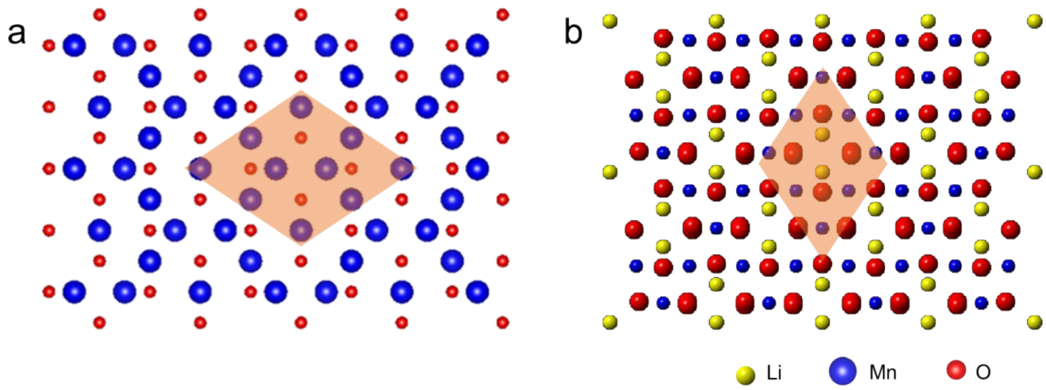

Figure S3 (a)Atomic structural model of the surface Mn_3O_4 along the [100] crystallographic. (b) Atomic structural model of the surface $LiMn_2O_4$ along the [110] crystallographic. The blue spheres represent Mn atoms, red spheres represent O atoms, and yellow spheres represent Li atoms, respectively.

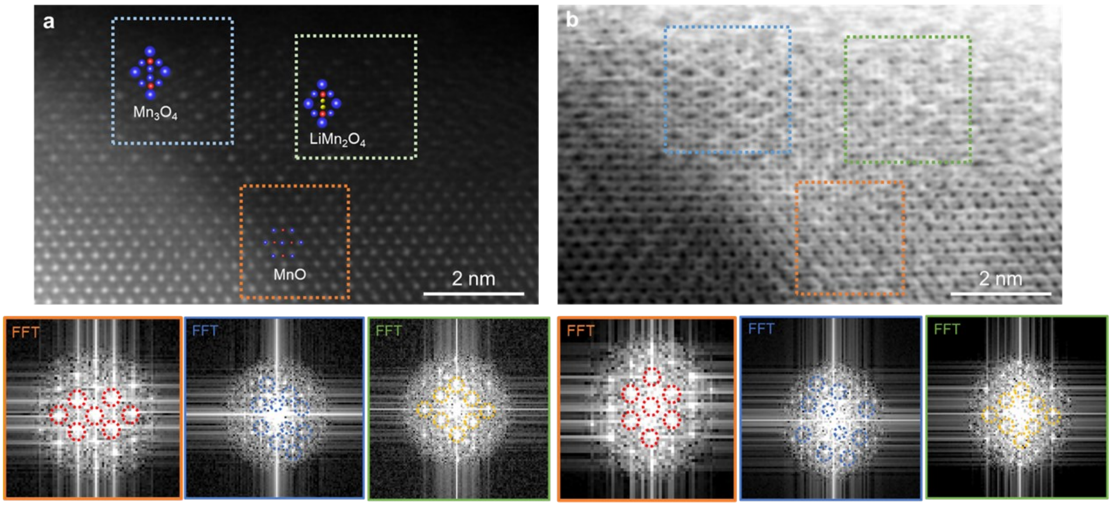

Figure S4 HAADF and ABF images of MnO anode discharged to 0.2 V. (a) HAADF image and the corresponding FFT patterns. (b) ABF image and the corresponding FFT patterns.

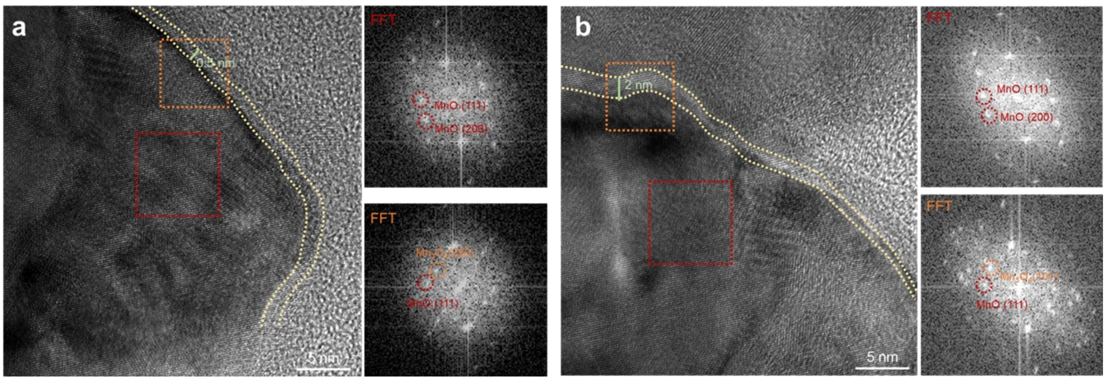

Figure S5 (a) HRTEM image of MnO anode discharged to 0.2 V and the corresponding FFT patterns of different regions. (b) HRTEM image of MnO anode discharged to 0.01 V and the corresponding FFT patterns of different regions.

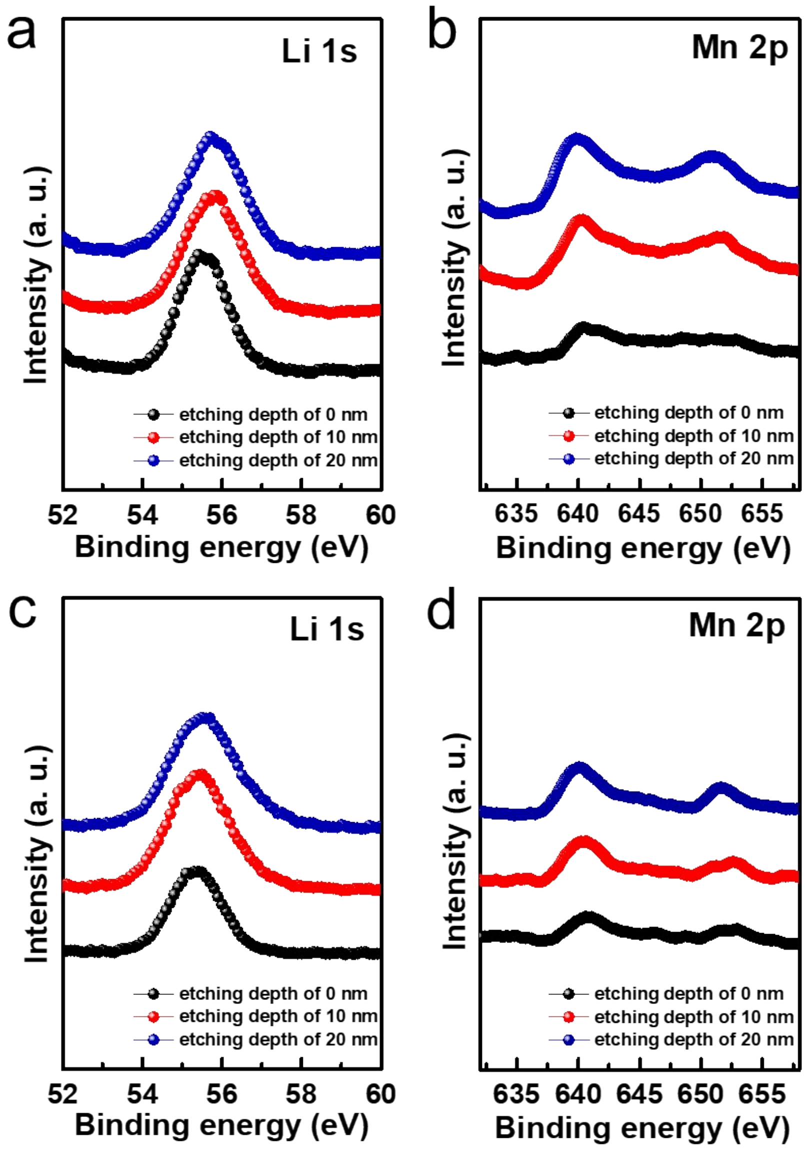

Figure S6 XPS spectra for etching different depth of Li 1s and Mn 2p. (a, b) show Li 1s and Mn 2p of etching depth of 0 nm, 10 nm and 20 nm for MnO anode discharged to 0.2 V. (c, d) show Li 1s and Mn 2p of etching depth of 0 nm, 10 nm and 20 nm for MnO anode discharged to 0.01 V.

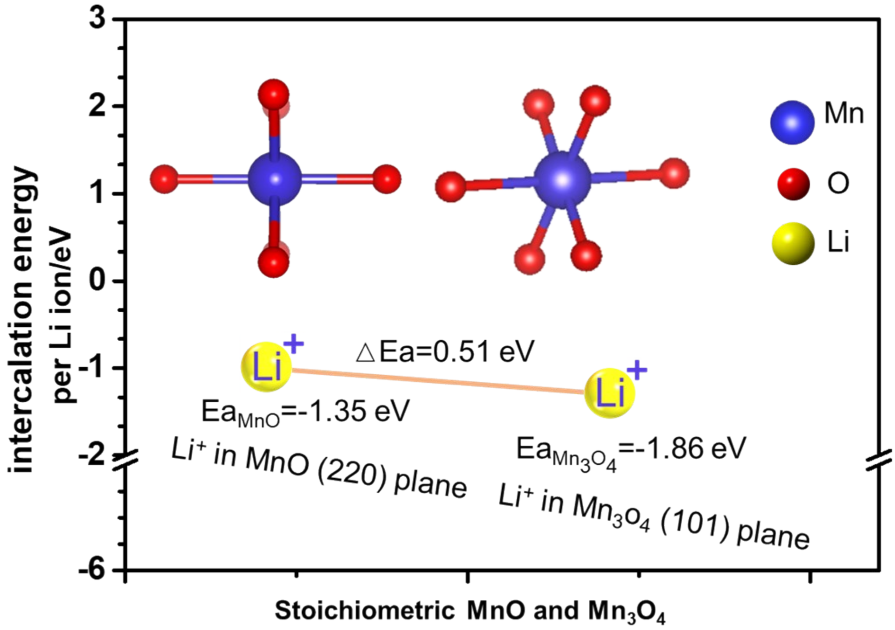

Figure S7 Schematic diagram of Li-ion adsorption energy in $MnO_{(220)}$ plane and in $Mn_3O_{4(101)}$ plane.

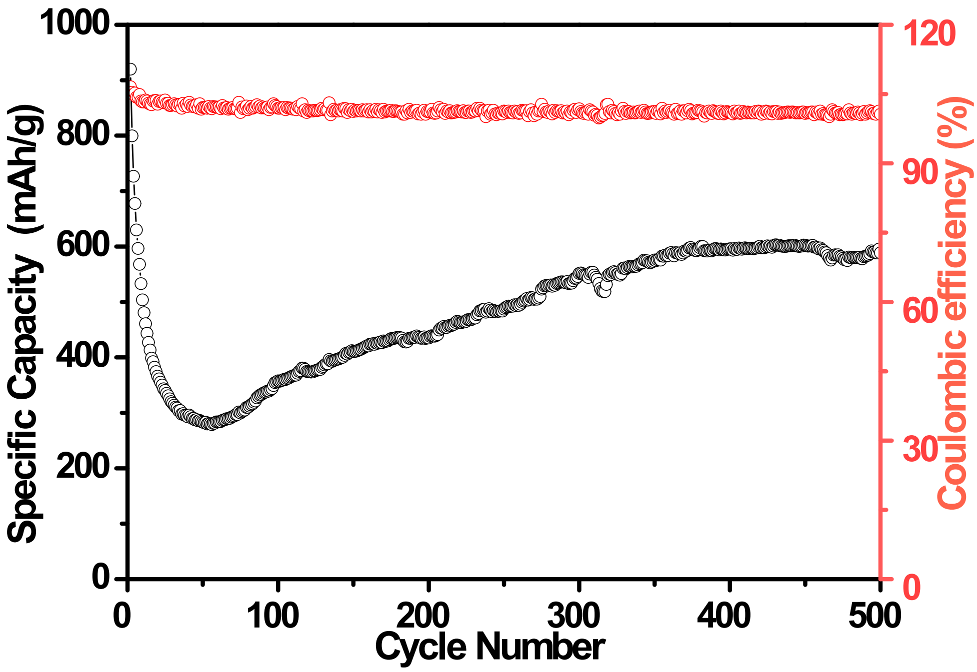

Figure S8 The cycling performances of MnO@C anode at 500 mA g^{-1} current density.

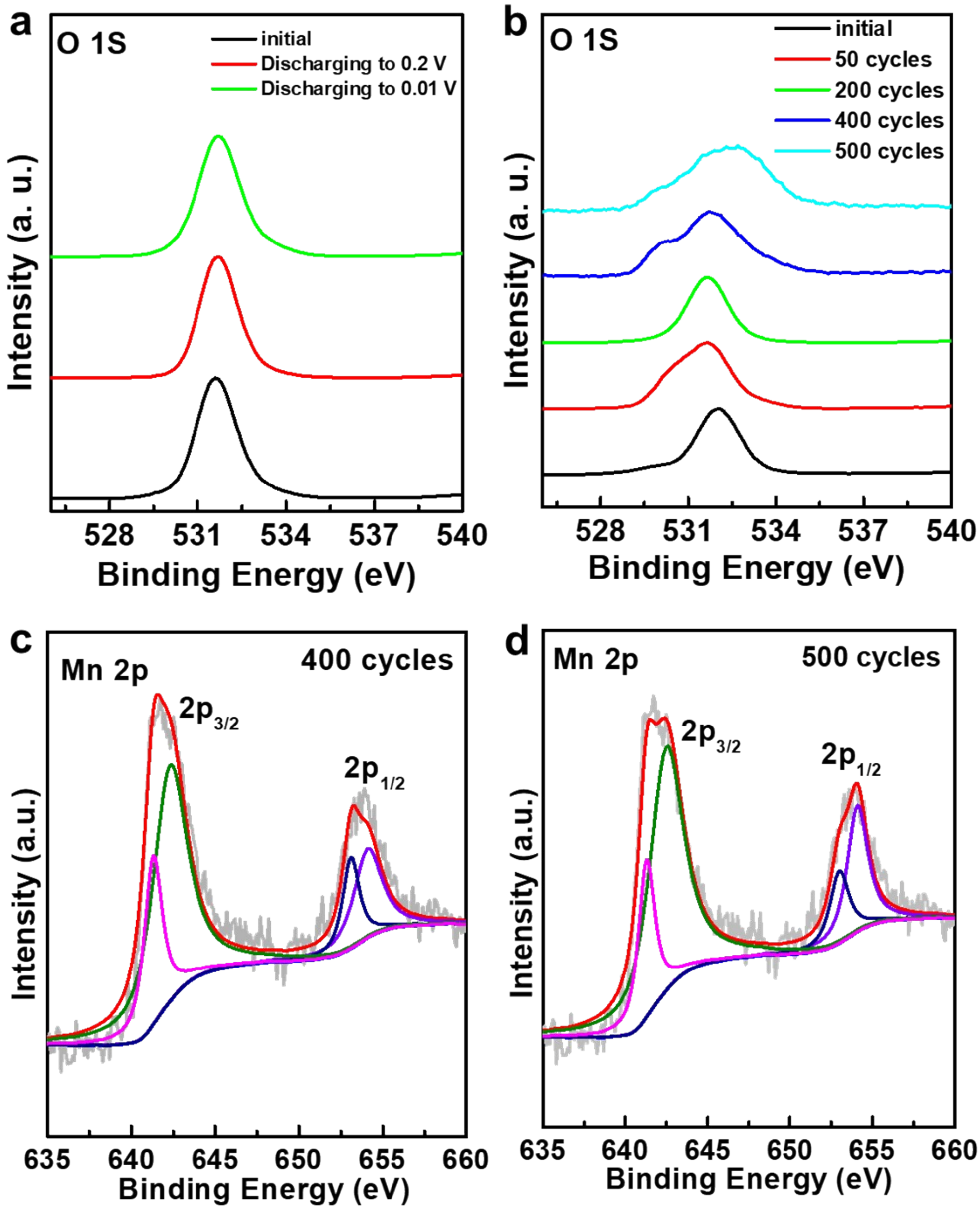

Fig.S9 (a) XPS spectra for initial MnO anode, discharged to 0.2 V and discharged to 0.01 V during the first cycle of O 1s, (b) XPS spectra for initial MnO anode, after 50 cycles, after 200 cycles, after 400 cycles and 500 cycles of O 1s, (c) XPS spectra of Mn 2p after 400 cycles. (d) XPS spectra of Mn 2p after 500 cycles.

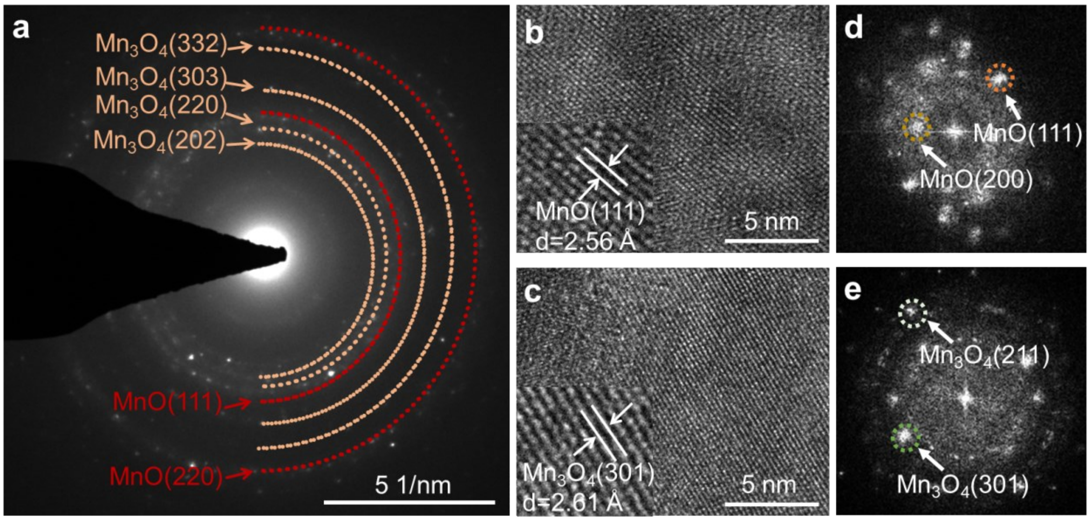

Figure S10 SAED patterns and HRTEM images of anodes after 200 cycles. (a) SAED patterns of MnO anode after 200 cycles. (b c), HRTEM images of anodes after 200 cycles. (d e) the corresponding FFT patterns of HRTEM images in b and c, respectively.

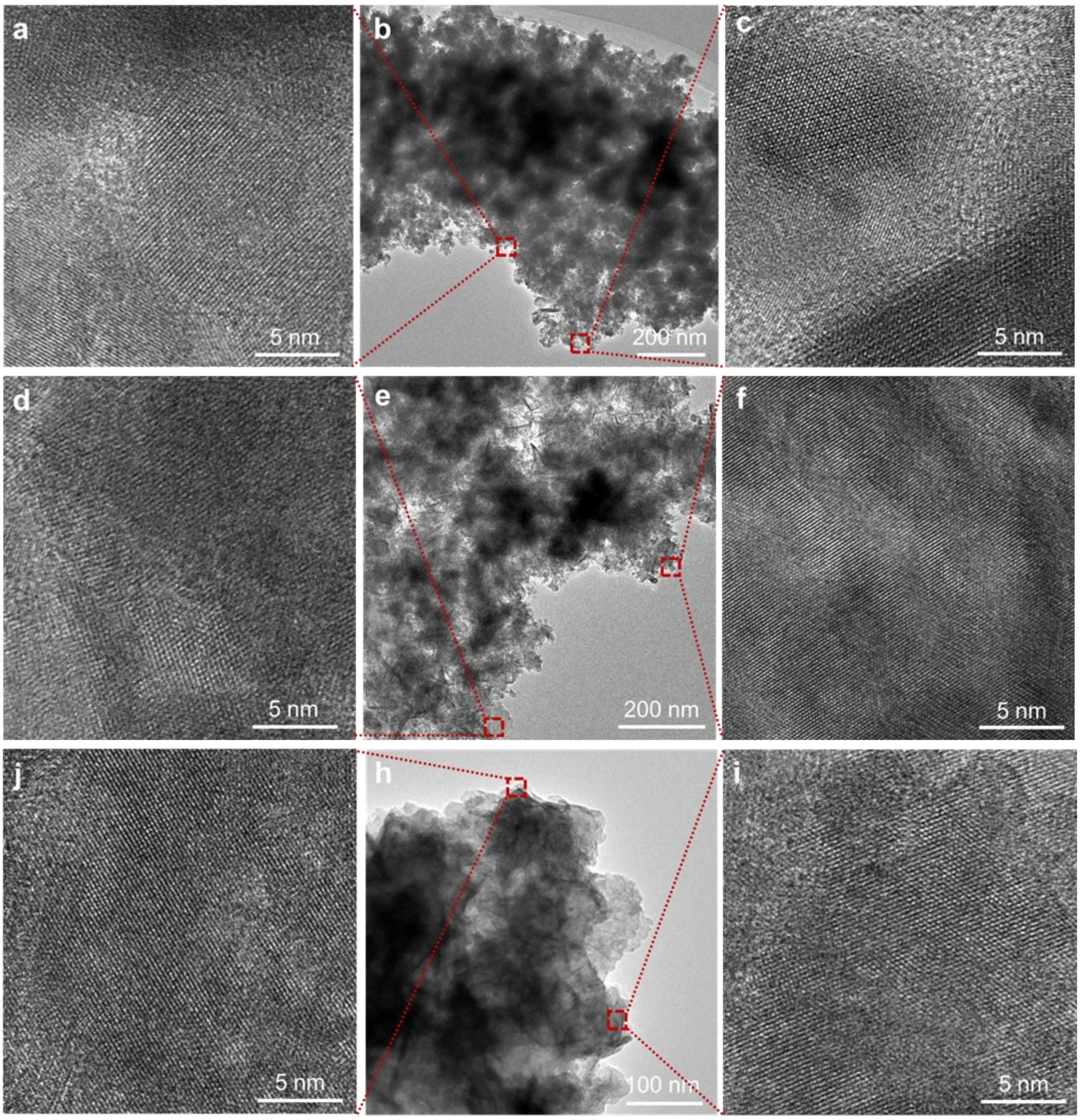

Figure S11 b, e and h, Low magnification images and HRTEM images of anodes after 50, 100 and 200 cycles. (a d j), HRTEM images of MnO. (c) HRTEM image of MnO_2. (f i) HRTEM images of Mn_3O_4.

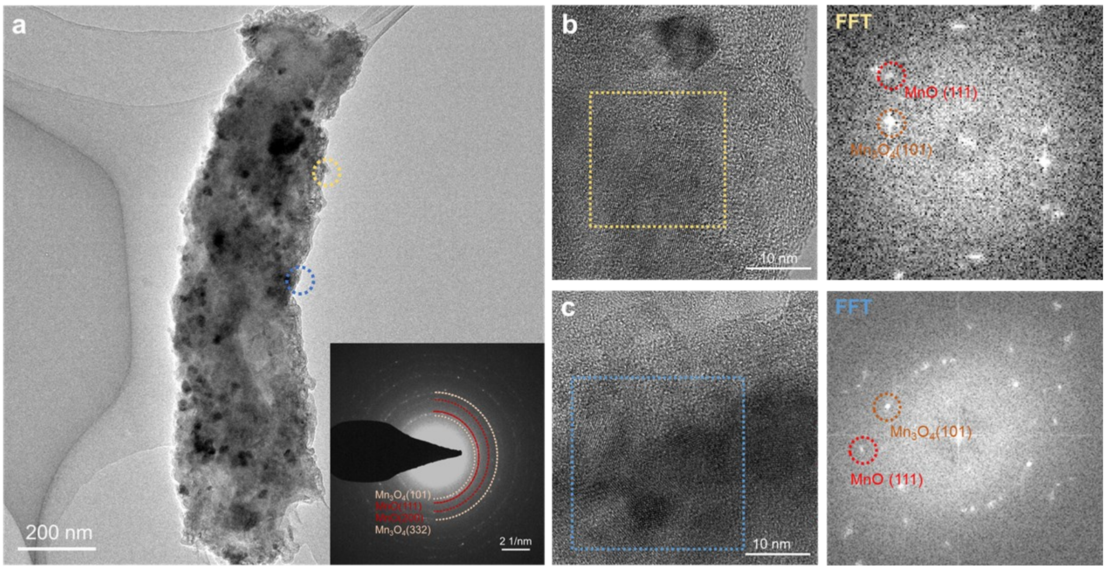

Figure S12 (a) Low magnification morphology image and SAED pattern of MnO anode after 500 cycles, (b) HRTEM image obtained from the area of the yellow box and the corresponding to FFT pattern, (c) HRTEM image obtained from the area of the blue box and the corresponding to FFT pattern.

Table S1 The contents of Mn with various valence

The proportion of Mn valence		
Initial	Mn^{2+}	100%
50 cycles	Mn^{2+} Mn^{3+}	52.05% 47.95%
100 cycles	Mn^{2+} Mn^{3+}	63.51% 36.49%
200 cycles	Mn^{2+} Mn^{3+}	38.28% 61.72%
400 cycles	Mn^{2+} Mn^{3+}	29.68% 70.32%
500 cycles	Mn^{2+} Mn^{3+}	28.71% 71.29%