Supplementary information for

Unraveling the critical role of Zn-phyllomanganates in zinc ion batteries

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This includes supplementary Fig. S1 to S8.

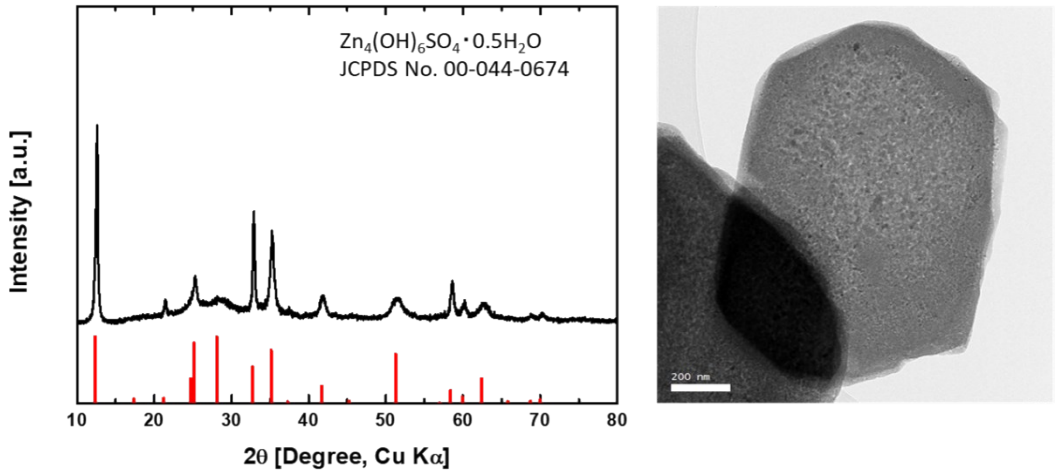

Fig. S1 X-ray diffraction pattern and TEM image of zinc hydroxide sulfate synthesized in this work. The stick XRD pattern represents zinc hydroxide sulfate hydrate ($Zn_4(OH)_6SO_4 \cdot 0.5H_2O$, JCPDS No. 00-044-0674).

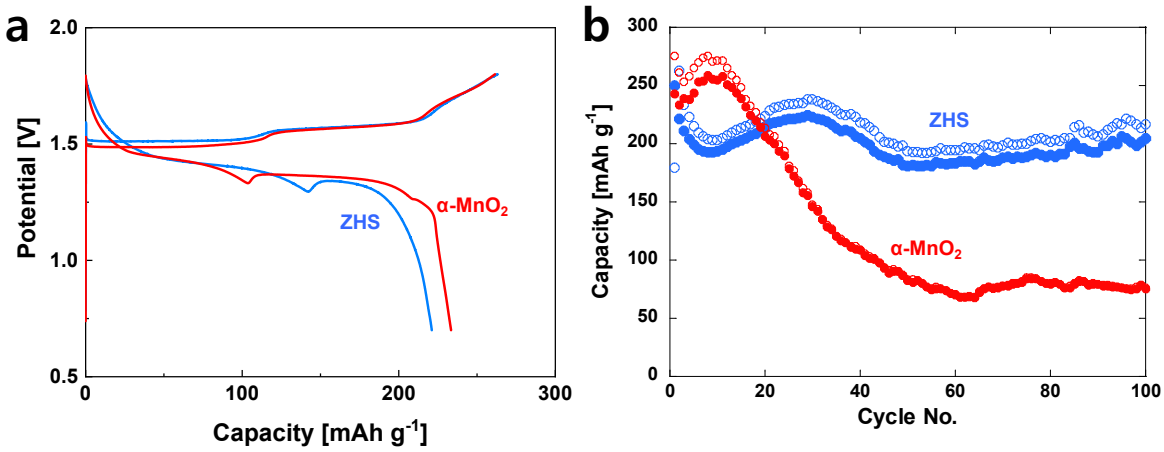

Fig. S2 (a) Charge-discharge profiles and (b) cycling performances up to 100 cycles of the battery cells with α -MnO_2 and zinc hydroxide sulfate hydrate (ZHS) cathode materials. The current rates applied were 70 mA g^{-1} for ZHS, and 30.5 mA g^{-1} for α-MnO_2, respectively. Open and fill circles in (b) represent the charge and discharge capacities, respectively.

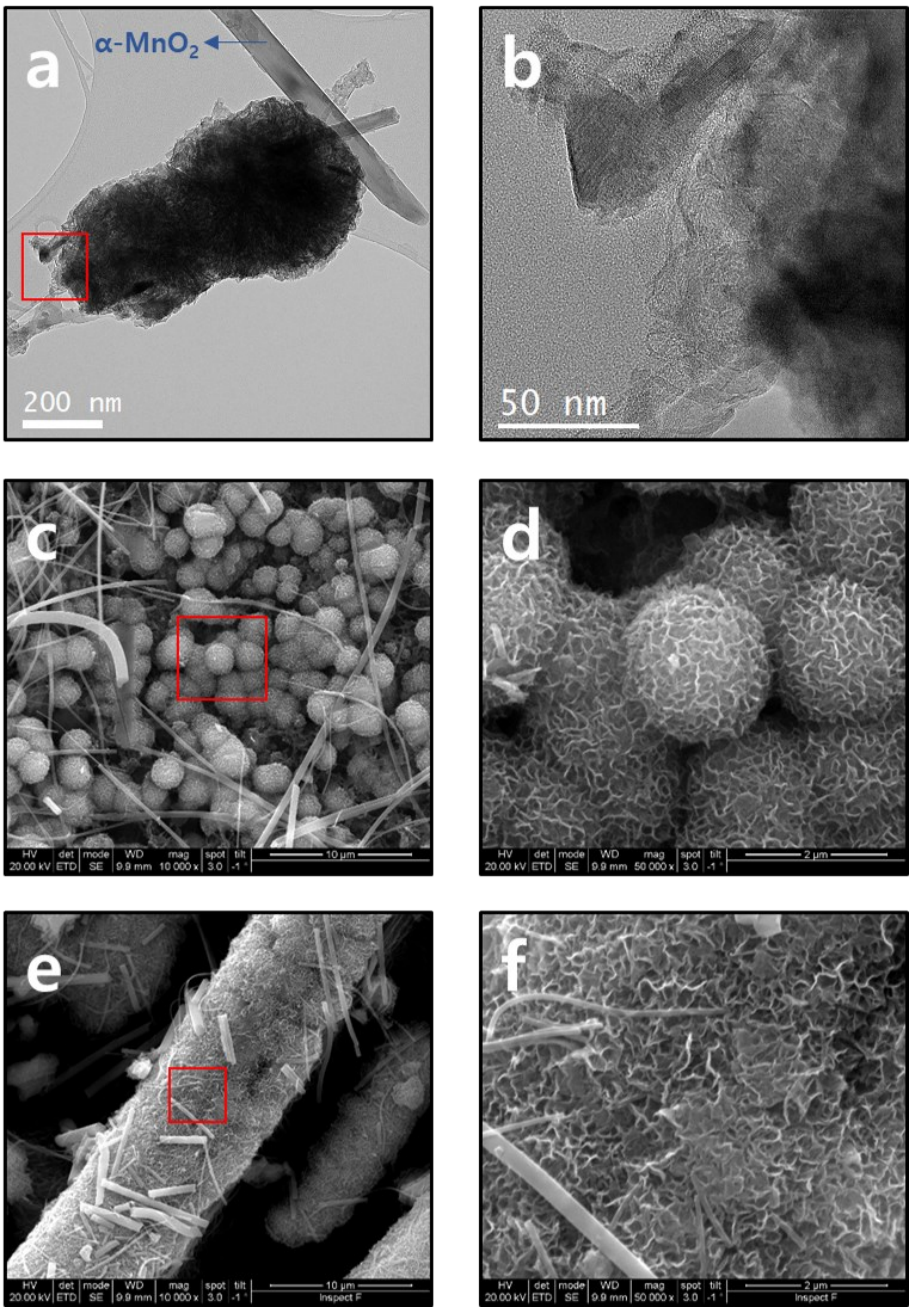

Fig. S3 The morphology of (a), (b) α-MnO_2, (c), (d) ZHS and (e), (f) carbon paper after the 1st charge process. (b), (d), and (f) represent images in higher magnification centered at red square in (a), (c), and (e), respectively.

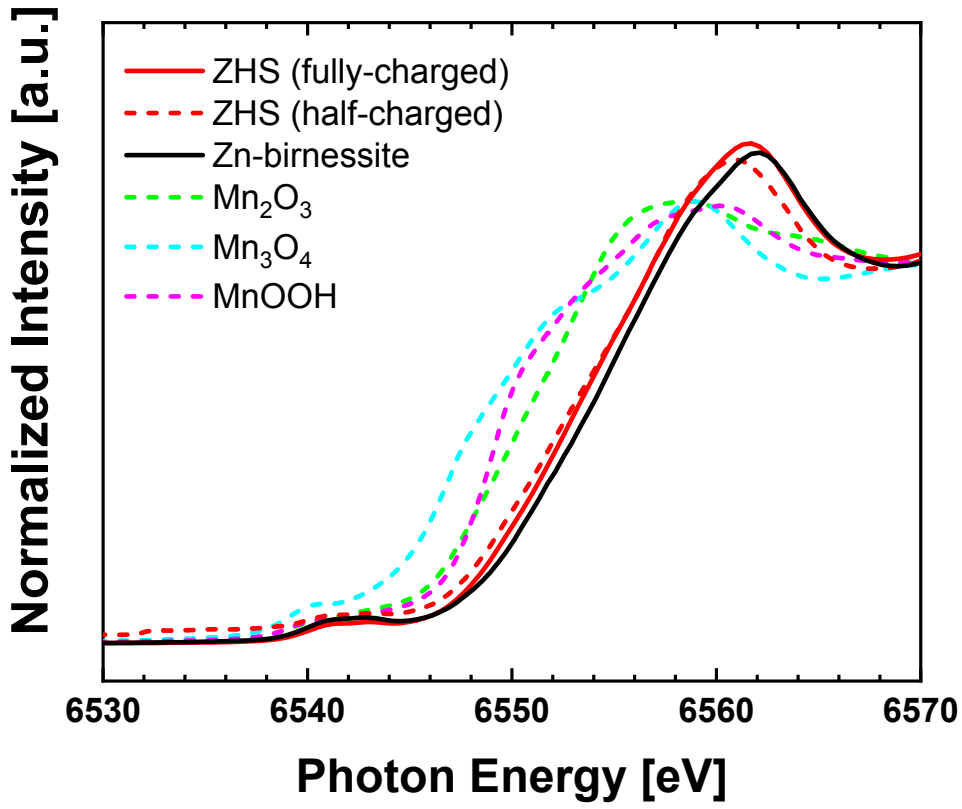

Fig. S4 Mn K-edge X-ray absorption spectra for the half- and fully-charged electrodes for ZHS, and reference spectra for the materials of interests including Zn-birnessite, Mn_2O_3, Mn_3O_4, and MnOOH.

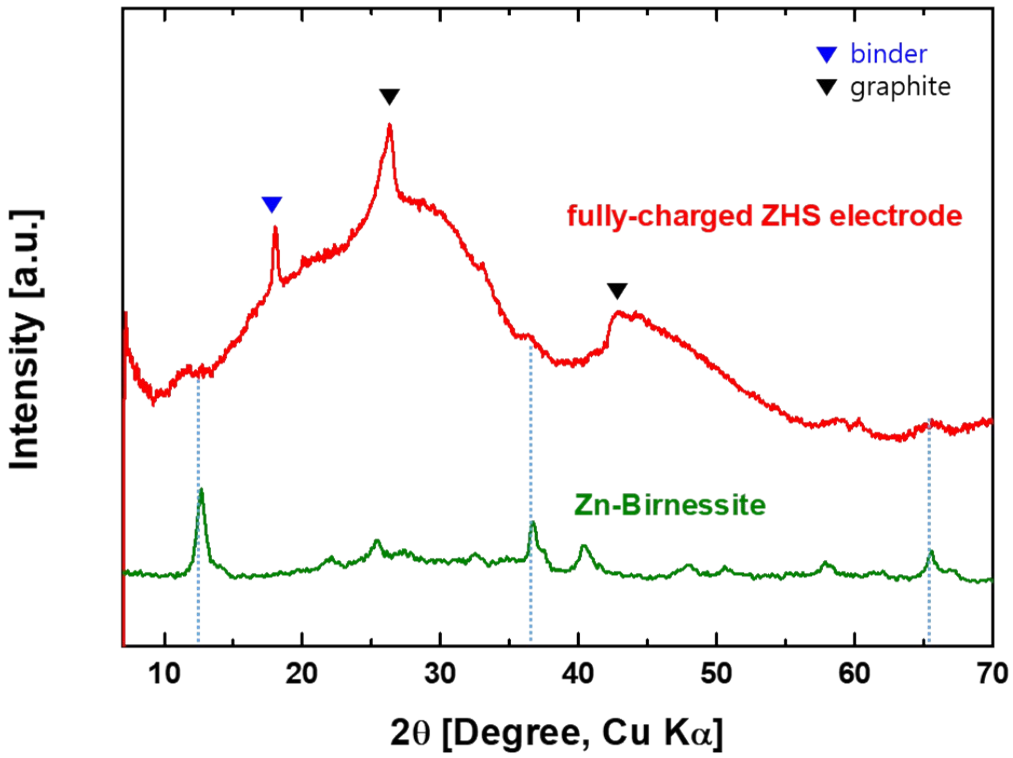

Fig. S5 Comparison of the in-situ XRD pattern of the fully-charged ZHS electrode (red), and XRD pattern of Zn-birnessite (green). The broad peaks at 12.7°, 36.1°, and 65.6° in the fully-charged ZHS electrode could be indexed to those of Zn-birnessite.

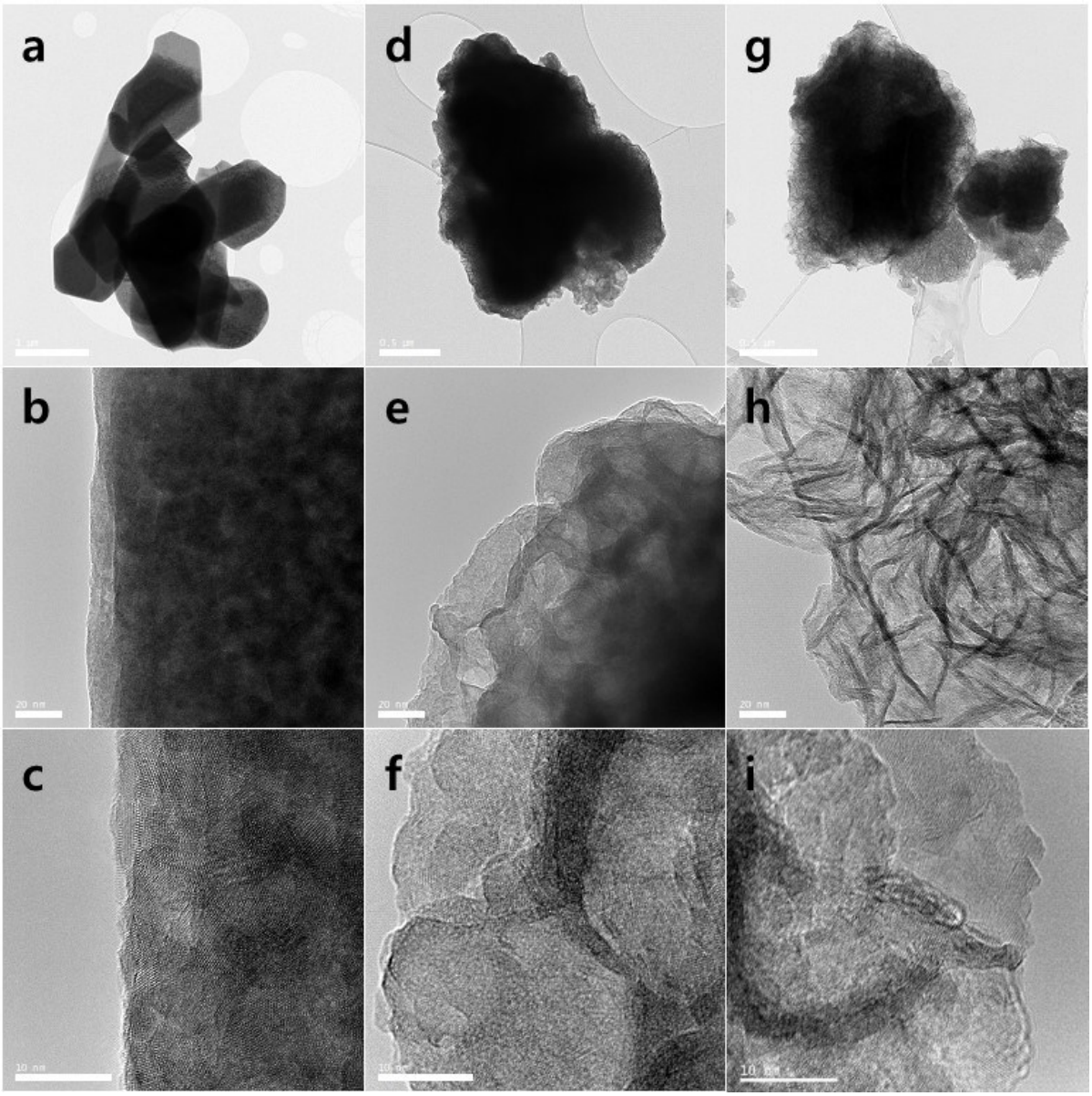

Fig. S6 High-resolution transmission electron microscopic (HR-TEM) images for (a,b,c) the pristine ZHS synthesized, (c,d,f) products from the half-charged, and (g,h,i) the fully-charged ZHS electrodes. No distinct crystalline phases with long-range order were observed from the products in the half- and fully-charged electrodes.

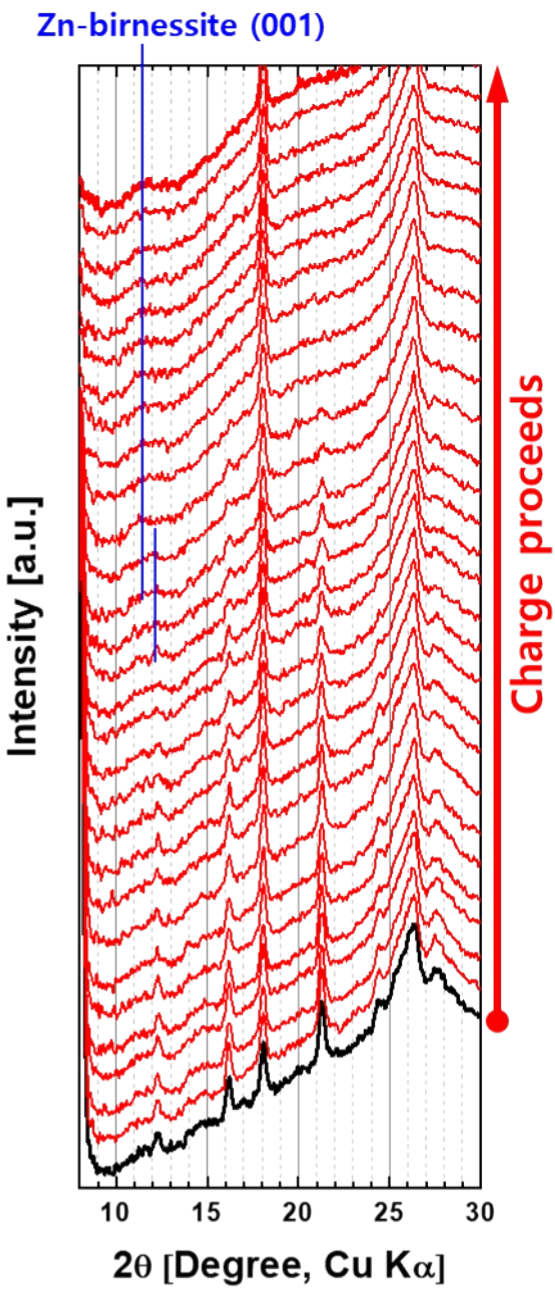

Fig. S7 A shift of (001) reflection of Zn-phyllomanganate formed during the first charging process to lower angle from the in situ XRD patterns of ZHS electrode. This could indicate the layer expansion from 7.25 to 7.69 Å as charge proceeded.

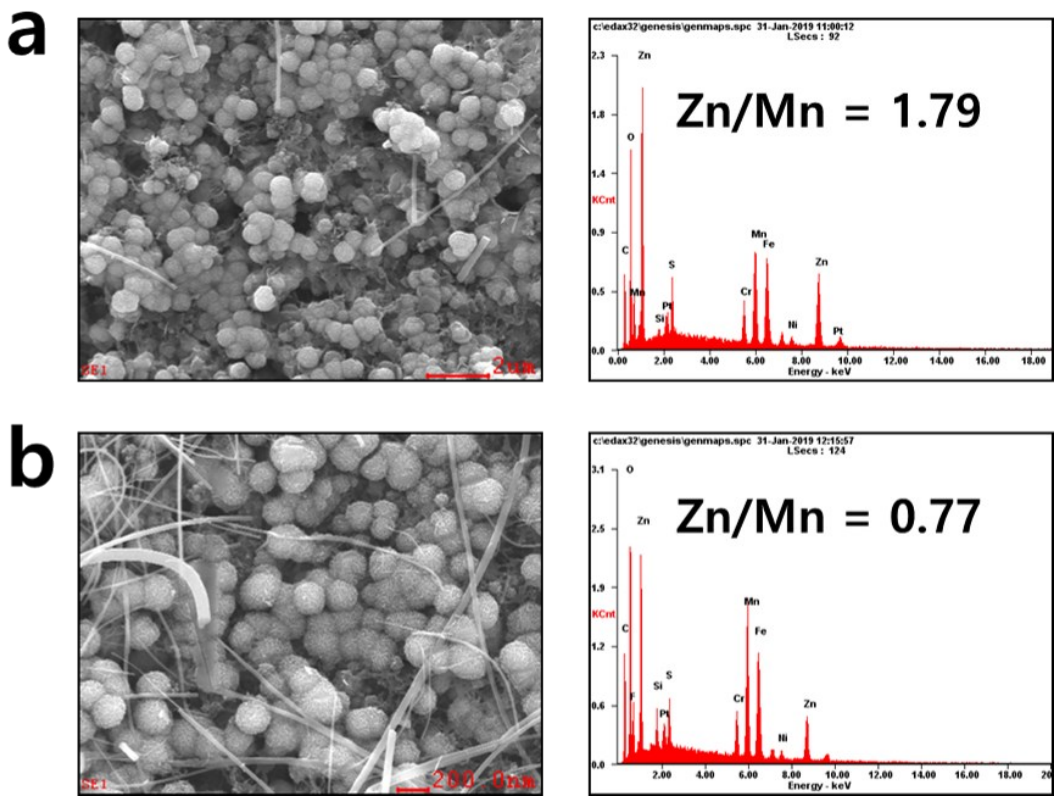

Fig. S8 The morphology and the elemental analysis of MnO_2 particles in-situ formed at (a) the half- and (b) the fully-charged states.