

Supporting Information

Elucidating zinc-ion battery mechanisms in freestanding carbon electrode architectures decorated with nanocrystalline ZnMn₂O₄

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Table S1. Elemental Analysis of ZnMn₂O₄@CNF.

Element	Method ^a	Result
Carbon	GLI Procedure ME-14	36.41%
Manganese	GLI Procedure ME-70	26.5%
Sodium	GLI Procedure ME-70	0.0479%
Zinc	GLI Procedure ME-70	11.2%

^a analysed using Galbraith Laboratories protocols

Calculation of wt. % ZnMn₂O₄ in CNF from elemental analysis:

$$\frac{0.112g\ Zn}{1g\ sample} * \frac{1mol\ Zn}{65.38g} * \frac{2mol\ Mn}{1mol\ Zn} * \frac{54.94g}{1mol\ Mn} + \frac{0.188g\ Mn}{1g\ sample} = 18.8\% \text{ Mn}$$

$$\frac{0.112g\ Zn}{1g\ sample} * \frac{1mol\ Zn}{65.38g} * \frac{4mol\ O}{1mol\ Zn} * \frac{16g}{1mol\ O} + \frac{0.110g\ O}{1g\ sample} = 11\% \text{ O}$$

$$\rightarrow 18.8\% \text{ Mn} + 11.2\% \text{ Zn} + 11\% \text{ O} = 41 \text{ wt.}\% \text{ ZnMn}_2\text{O}_4\text{@CNF}^*$$

**Based on the assumption that all zinc in the sample exists in the form of ZnMn₂O₄, as no other crystalline phase is observed via X-ray diffraction*

Eqn S1: %Mn unassociated with ZnMn₂O₄

$$= 26.5\% \text{ Mn measured} - 18.8\% \text{ Mn associated with ZnMn}_2\text{O}_4 = 7.7\%$$

Eqn S2: % of Zn in pores for reaction

Moles Zn²⁺ required for reaction:

$$\frac{224 \text{ mA h}}{g_{Total}} * \frac{0.01 \text{ g}_{Total}}{\text{electrode}} * \frac{1 \text{ A}}{1000 \text{ mA}} * \frac{3600 \text{ s}}{1 \text{ h}} * \frac{1 \text{ mol } e^{-}}{96485 \text{ C}} * \frac{0.5 \text{ mol Zn}^{2+}}{1 \text{ mol } e^{-}} = 4.2 \times 10^{-5}$$

Moles Zn²⁺ inside pores:

$$\frac{0.44 \text{ cm}^3}{g_{Total}} * \frac{0.01 \text{ g}_{Total}}{\text{electrode}} = 0.0044 \text{ cm}^3 = 4.4 \times 10^{-6} \text{ L} * \frac{1 \text{ mol ZnSO}_4}{L} = 4.4 \times 10^{-6}$$

% of required Zn²⁺ inside pores

$$\frac{4.4 \times 10^{-6} \text{ mol Zn}^{2+} \text{ inside pores}}{4.2 \times 10^{-5} \text{ mol Zn}^{2+} \text{ required}} * 100 = 10.5 \%$$

Eqn. S3: Concentration of dissolved Mn²⁺ inside pores

41 wt. % ZnMn₂O₄ in the electrode

Electrode mass: 0.01 g

Pore volume: 0.0044 cm³ = 4.4 × 10⁻⁶ L

% of electrode area internally

Geometric area of electrode: 0.000127 m²

Specific surface area of electrode: 260 m² g⁻¹ * 0.01 g = 2.6 m²

$$\frac{2.6 \text{ m}^2 - 0.000127 \text{ m}^2}{2.6 \text{ m}^2} * 100 = 99 \%$$

Since 99% of the surface area is expressed internally, essentially all of the ZnMn₂O₄ mass exists in the interior of the electrode, so if all of the ZnMn₂O₄ dissolved, the [Mn²⁺] dissolved inside pores would be:

$$\frac{0.41 \text{ g ZnMn}_2\text{O}_4}{1 \text{ g}_{Total}} * \frac{0.01 \text{ g}_{Total}}{\text{electrode}} * \frac{1 \text{ mol ZnMn}_2\text{O}_4}{239.25 \text{ g}} * \frac{2 \text{ mol Mn}}{1 \text{ mol ZnMn}_2\text{O}_4} * \frac{\text{pore vol}}{4.4 \times 10^{-6} \text{ L}} = 7 \text{ M Mn}$$

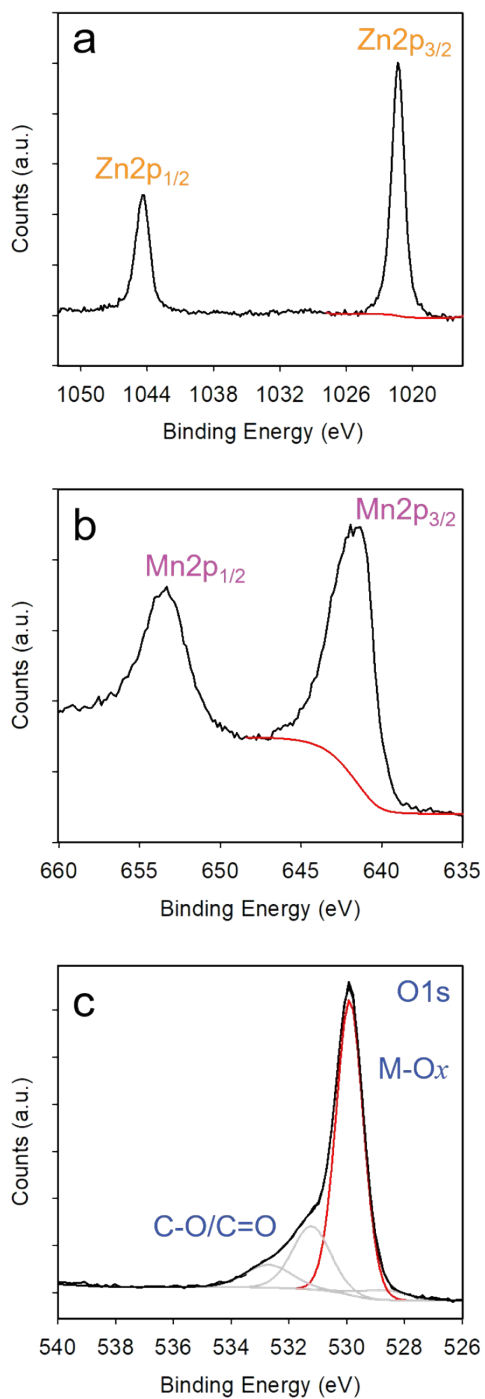


Fig. S1 X-ray photoelectron spectra of (a) Zn 2p, (b) Mn 2p, and (c) O 1s of uncycled ZnMn₂O₄@CNF paper.

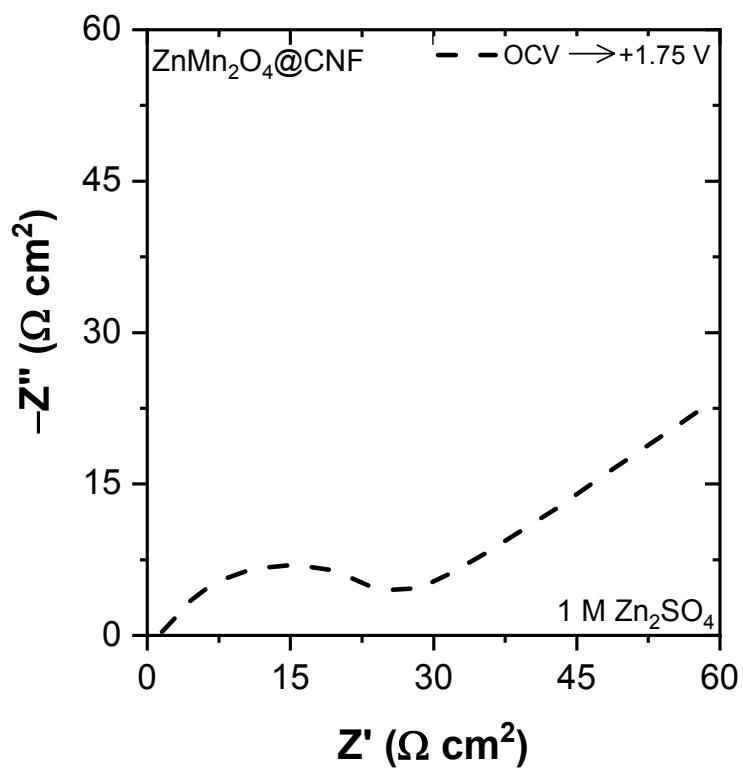


Fig. S2 Nyquist plot of $\text{ZnMn}_2\text{O}_4@\text{CNF}$ after conditioning at 1.75 V for 30 min after a voltage step from open-circuit voltage in 1 M ZnSO_4 .

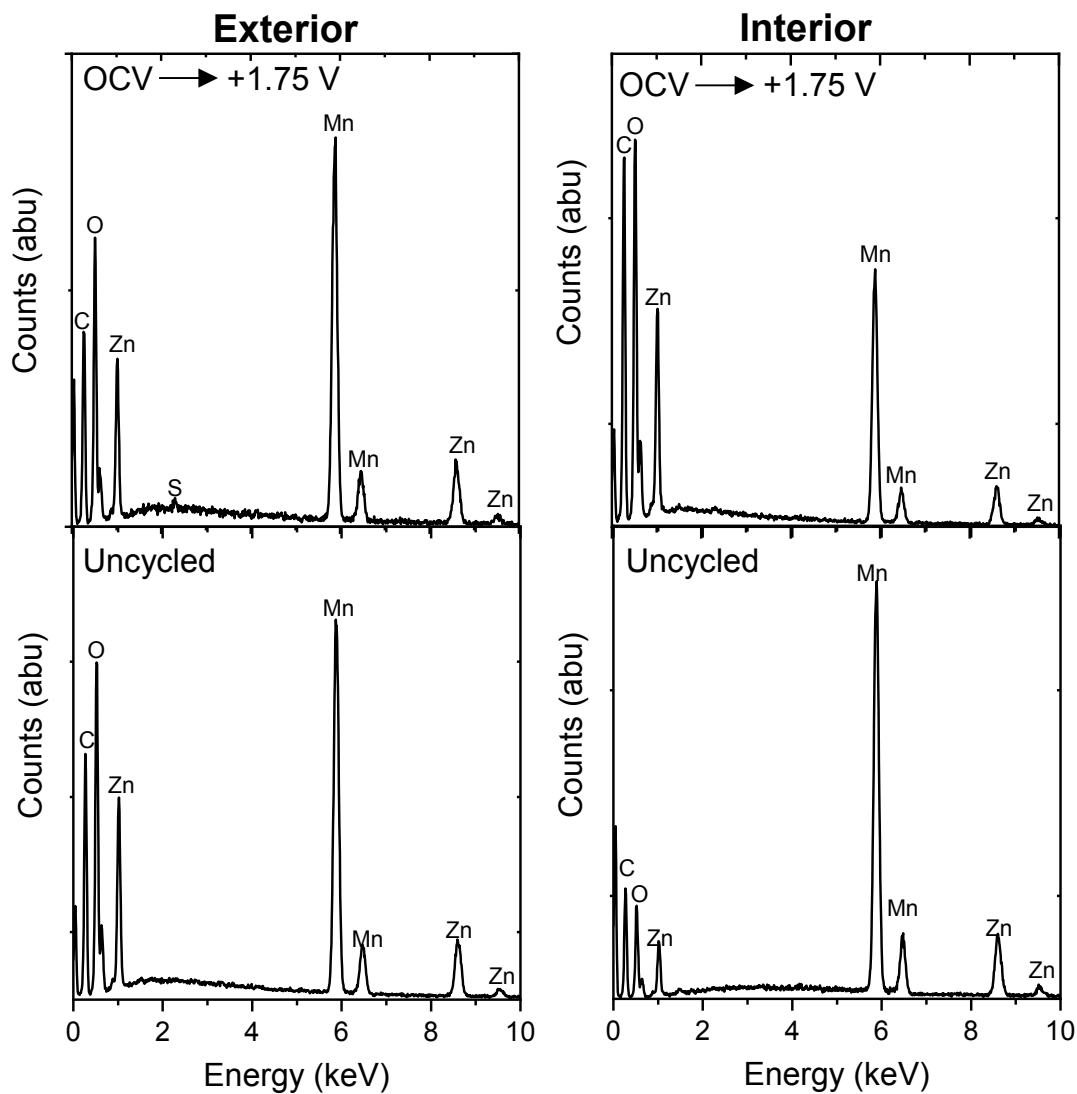


Fig. S3 Energy-dispersive X-ray spectra for the (left) exterior and (right) interior surfaces of (bottom row) uncycled $\text{ZnMn}_2\text{O}_4@\text{CNF}$ and (top row) after conditioning at 1.75 V for 30 min after scanning directly from OCV).

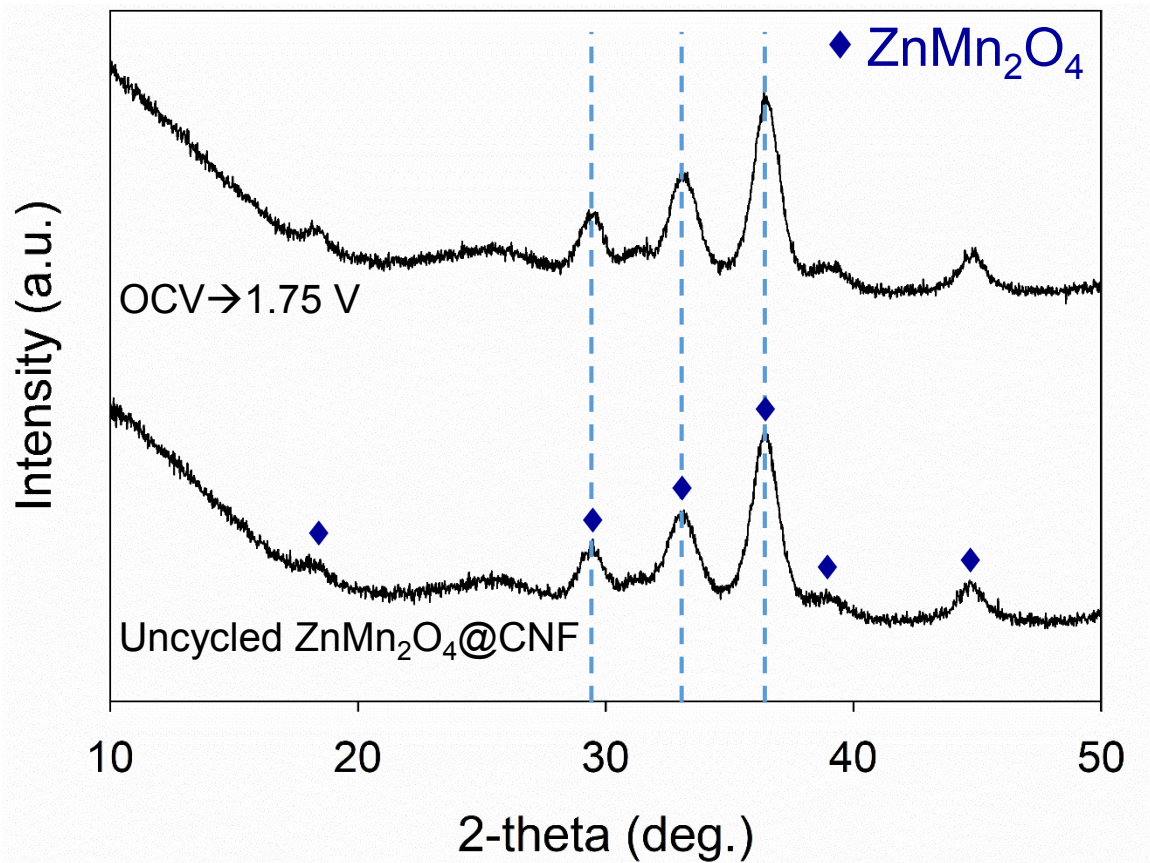


Fig. S4 X-ray diffraction patterns of uncycled ZnMn₂O₄@CNF and after conditioning at 1.75 V for 30 min directly from OCV.

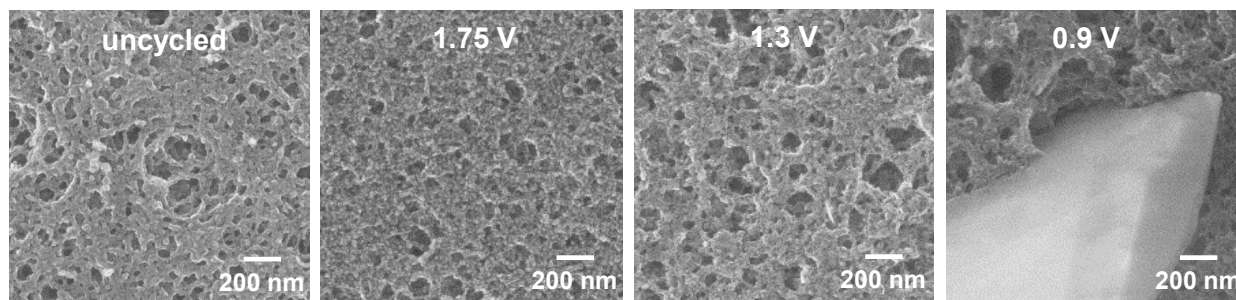


Fig. S5 Scanning electron micrographs of the exterior surface of ZnMn₂O₄@CNFs after conditioning at specified voltages for 30 min in 1 M ZnSO₄.

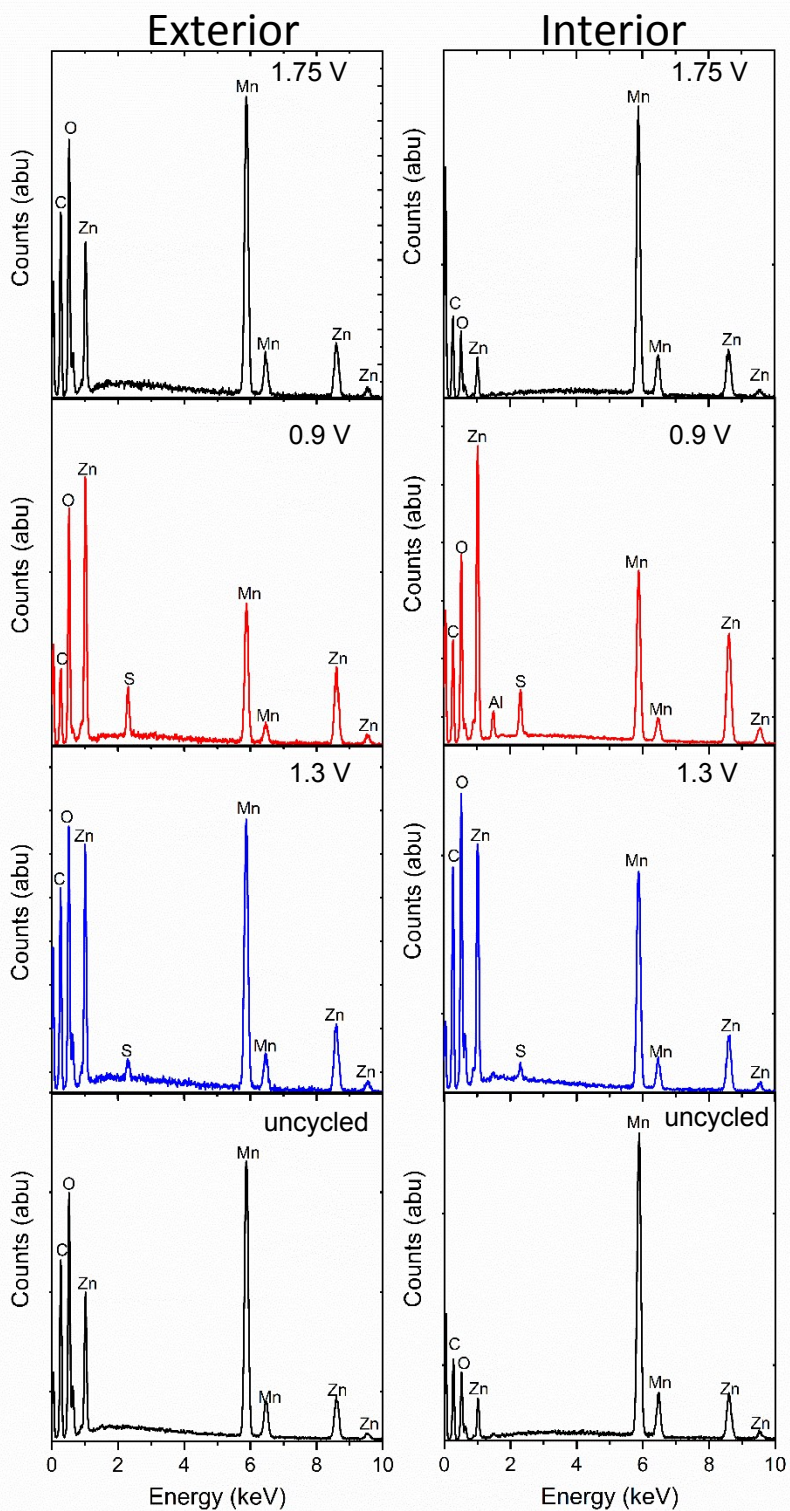


Fig. S6 Energy-dispersive X-ray spectra of the exterior (left) and interior (right) surfaces of ZnMn₂O₄@CNF as a function of applied voltage in 1 M ZnSO₄.

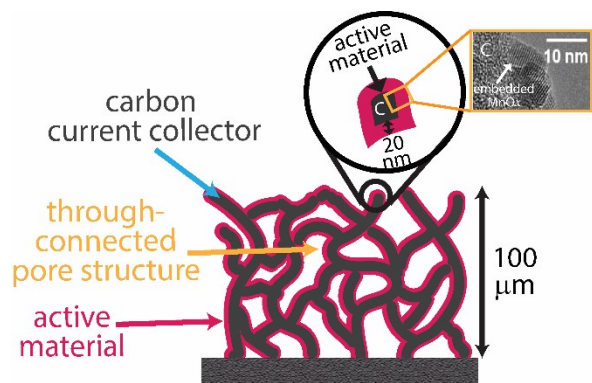


Fig. S7 Schematic of the 3D multifunctional electrode architecture.

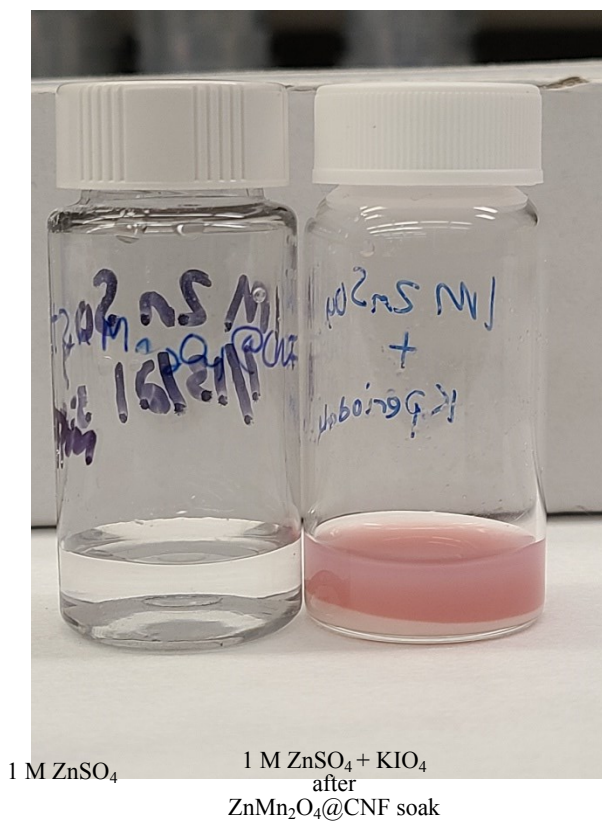


Fig. S8 Optical image of 1 M ZnSO_4 after soaking $\text{ZnMn}_2\text{O}_4@\text{CNF}$ for 13 days (left) and after adding excess potassium periodate (right). The magenta hue arises from the presence of Mn^{7+} generated from the oxidation of soluble Mn^{2+} by KIO_4 .