Co-intercalation strategy for simultaneously boosting two-electron conversion and bulk stabilization of Mn-based cathodes in aqueous zinc-ion batteries

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Experimental Section

Material synthesis

All chemicals were purchased from Sigma-Aldrich.

Synthesis of NCMO nanomaterials: NCMO was synthesized by a facile coprecipitation method. Solution A was prepared by dissolving 4 mmol of manganese (II) nitrate tetrahydrate in 10 mL of deionized water, solution B was prepared by dissolving 3 mmol of copper nitrate in 10 mL of deionized water, solution C was prepared by 27.5 mmol of NaOH in 10 mL of deionized water, and solution D was a mixed solution of 6 mL of H_2O_2 (30 wt%) and 45 mL of deionized water, respectively. Solution C was first sonicated for 20 min while solutions A and B were stirred for 10 min. Then, solution B and C were added to solution A quickly and stirred for an additional 5 minutes. After that, solution D was quickly poured into the mixture of solution A, B and C with vigorous magnetic stirring for another 10 minutes. A black precipitate formed immediately in the solution, after which the solution was kept in an ice bath for 48 hours to form solution E. After sufficient ageing, solution E was centrifuged at 4500 r/min for 10 minutes and the resulting brown-black powder was freeze-dried for a further 48 hours, at which point the NCMO nanomaterial was obtained. As a comparative sample, NMO was synthesized in the same way which was reported in previous work.

Materials Characterization

The change in crystal structure following PEDOT intercalation was investigated via XRD (Rigaku, miniFlex600) using Cu-K α radiation ($\lambda = 0.70$ nm) in the range of 5° to 40° (2 θ) and Mo-K α radiation ($\lambda = 0.15$ nm) in the range of 5° to 70° (2 θ). The morphologies of the samples were examined using a field emission scanning electron microscope (FE-SEM, FEI, Verios G4 UC) equipped with an EDS attachment. The samples were coated with platinum prior to SEM analysis. For TEM (JEOL, JEM2100F), samples were dispersed in acetone and loaded onto a holey carbon grid for imaging. XPS was performed using a K-Alpha+ (Thermo Fisher Scientific Messtechnik) to observe the oxidative state at different voltages. Imaging Processing and Data Analysis: The micro-CT (ZEISS Xradia 620 Versa with 40x lens) projections

were reconstructed using a filtered-back projection algorithm (XMReconstructor, Carl Zeiss Inc.). The reconstructed micro-CT datasets were imported into Avizo 2020.2 (ThermoFisher) for further segmentation and quantification. A median filter was applied to increase the signal to noise ratio. The pristine material, imaged by micro-CT, were segmented (based on grayscale values) into three phases consisting of active materials (NMO), carbon nanotubes and pores.

Electrochemical Measurement

The slurry was prepared by mixing the active materials (NCMO, NMO, and ZHS), carbon black (Super P, TIMCAL Graphite & Carbon), and poly(vinylidene fluoride) (PVDF, M.W. 534000, Sigma-Aldrich) at a weight ratio of 7:2:1 using N-methyl-2pyrrolidone (NMP); the mixture was then coated on carbon paper using automatic coating machine. After drying in a vacuum oven at 60 °C for 24 h, cathodes with ≈ 1-10.9 mg cm⁻² of the active materials were achieved. CR2032 coin cells were assembled by a traditional method in an open-air system using glass-fibers (Whatman, GF/A) and metallic Zn foils as separators and anodes, respectively. Additionally, 2 M ZnSO₄, as well as 2 M ZnSO₄ and 0.2 M MnSO₄ were used as the electrolyte. The electrolyte for ZHS full cells were 2 M ZnSO₄, 2 M ZnSO₄ and 0.2 M MnSO₄ as well as 2 M ZnSO₄, 0.2 M MnSO₄ and 0.1 M CuSO₄. The electrolyte of the proton full cell is H₂SO₄ whose pH value is adjusted to be the same as that of 2M ZnSO₄. The coin cells were tested using a WBCS 3000 automatic battery cycler (WonA Tech, Korea) at 25 °C. The current density and specific capacity were calculated using only the weight of the active material. CV tests were performed using a ZIVE SP1 potentiostat analyzer (WonA Tech, Korea) at 25 °C. CV tests were performed at various scan rates (0.8 to 1.9 V versus Zn²⁺/Zn). EIS tests were performed using a ZIVE SP1 impedance analyzer (WonA Tech, Korea) in the frequency range of 10^{5} – 10^{-1} Hz.

Computational methods

In the present study, we use the Vienna ab initio simulation package (VASP)^[1] based on DFT and the projector-augmented-wave (PAW) pseudopotential approach.^[2] Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) functional^[3] and Hubbard correction^[4] with U_{eff} 5.00 eV are used. The cutoff energy for plane-wave basis is set high enough at 800 eV, and the magnetic moment of each Mn atom is initially set at $\pm 3.00 \ \mu_B$ corresponding to Mn. We carry out geometrical optimizations with the unit-cell relaxations. For the k-points, we use a Γ -centered grid with $12 \times 12 \times 4$ for MnO₂. The tetrahedron method is used for the DOS calculations.^[5]

Abbreviation

Zinc hydroxide sulfate: ZHS Scanning electron microscope: SEM Energy-dispersive X-ray spectroscopy: EDS X-ray micro-Computed Tomography: CT Sodium and copper co-intercalated birnessite manganese oxide: NCMO Sodium-intercalated manganese oxide: NMO



Figure S1. The CT image of NCMO cathode shows a uniform distribution of active material in the electrode.



Figure S2. (a) The flux density heatmap in X direction and (b) the relationship of volume fraction, tortuoisty and fraction of original volume at X-axis.



Figure S3. (a) The flux density heatmap in Y direction and (b) the relationship of volume fraction, tortuoisty and fraction of original volume at Y-axis.



Figure S4. The relationship of Volume fraction, tortuoisty and fraction of original volume at Z-axis.



Figure S5. (a) *Ex-situ* XRD spectra of the NCMO cathode in the full cell at different potentials marked in (b) during the initial cycle (1-5), and the fully discharged (6) and fully charged (7) states after 50 cycles.



Figure S6. Changes in the valence states of Mn and Cu elements during charge and discharge are determined by high resolution *ex-situ* XPS spectra of (a, b) Mn 2p, (c, d) Mn 3s, and (e, f) Cu 2p in full discharge and full charge, respectively.



Figure S7. Galvanostatic charge and discharge profiles of 1^{st} cycle for NMO and NCMO full cell in the electrolyte of 2 M H₂SO₄ electrolyte without Zn²⁺.



Figure S8. Cycle performance of NCMO and NCMO cathodes at a current density of 0.5 A g^{-1} in 2 M H_2SO_4 electrolyte without Zn^{2+} .



Figure S9. Galvanostatic charge and discharge profiles of (a) 1st, (b) 10th and 50th, and (c) 100th cycles for NMO full cell in the electrolyte of 2 M ZnSO₄.



Figure S10. Galvanostatic charge and discharge profiles of (a) 1^{st} , (b) 10^{th} and 50^{th} , and (c) 100^{th} cycles for NCMO full cell in the electrolyte of 2 M ZnSO₄.



Figure S11. Galvanostatic charge and discharge profiles of (a) 1^{st} , (b) 10^{th} and 50^{th} , and (c) 100^{th} cycles for NMO full cell in the electrolyte of 2 M ZnSO₄ and 0.2 M MnSO₄.



Figure S12. Galvanostatic charge and discharge profiles of (a) 1^{st} , (b) 10^{th} and 50^{th} , and (c) 100^{th} cycles for NCMO full cell in the electrolyte of 2 M ZnSO₄ and 0.2 M MnSO₄.



Figure S13. CV curves for the (a) first three cycles at a scan rate of 0.5 mV s⁻¹ after activation and (b) first five cycles a scan rate of 0.3 mV s⁻¹ after activation of NCMO full cell.



Figure S14. (a) SEM and (b) EDS mapping of NCMO cathode after 100 cycles at a current density of 0.1 mA g⁻¹, with the scale bars of 5 μ m.



Figure S15. Cycle performance of ZHS at a current density from 0.1 A g^{-1} in the electrolyte of 2 M ZnSO₄.



Figure S16. Cycle performance of ZHS at a current density from 0.1 A g^{-1} in the electrolyte of 2 M ZnSO₄ and 0.2 M MnSO₄.



Figure S17. Cycle performance of ZHS at a current density from 0.1 A g^{-1} in the electrolyte of 2 M ZnSO₄, 0.2 M MnSO₄ and 0.1 M CuSO₄.

Electrochemical impedance spectroscopy (EIS) Equivalent Circuit Fitting

The ion transport properties within the electrodes were investigated by EIS over the frequency range from 100 kHz to 100 mHz. Each of the Nyquist plots in Figure 5g exhibits a quasi-vertical curve in the low-frequency region, indicating a nearly ideal surface behavior of all the electrodes. A clear difference of these electrodes is shown in the high-frequency region, where a shorter 45° Warburg transition region and a smaller diameter of semicircle can reveal a lower charge transfer resistance and more efficient diffusion of the electrolyte within the electrodes.



Figure S18. The equivalent circuit for EIS fitting.

R_s: Combined internal resistance, including the interfacial contact resistance of the material with current collector, the ohmic resistance of electrolyte and the intrinsic resistance of current collector.

 \mathbf{R}_{ct} : Interfacial charge transfer resistance, representing the resistance of electrochemical reactions at the electrode surface.

W₀: Warburg element, describing the transfer and diffusion of the electrons and electrolyte ions in the pores of the electrode materials.

CPE: Constant phase element.

C_{Isf}: Element account for the low-frequency surface capacitance.

R_{leak}: Leakage resistance at low frequency.



Figure S19. EIS test of NCMO and NMO full cells, showing a better conductivity of NCMO cathode.

References

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