Supplementary Information

Approaching Convergence in the Electrochemical Mechanism of Aqueous Zn–MnO_2 Sustainable Batteries

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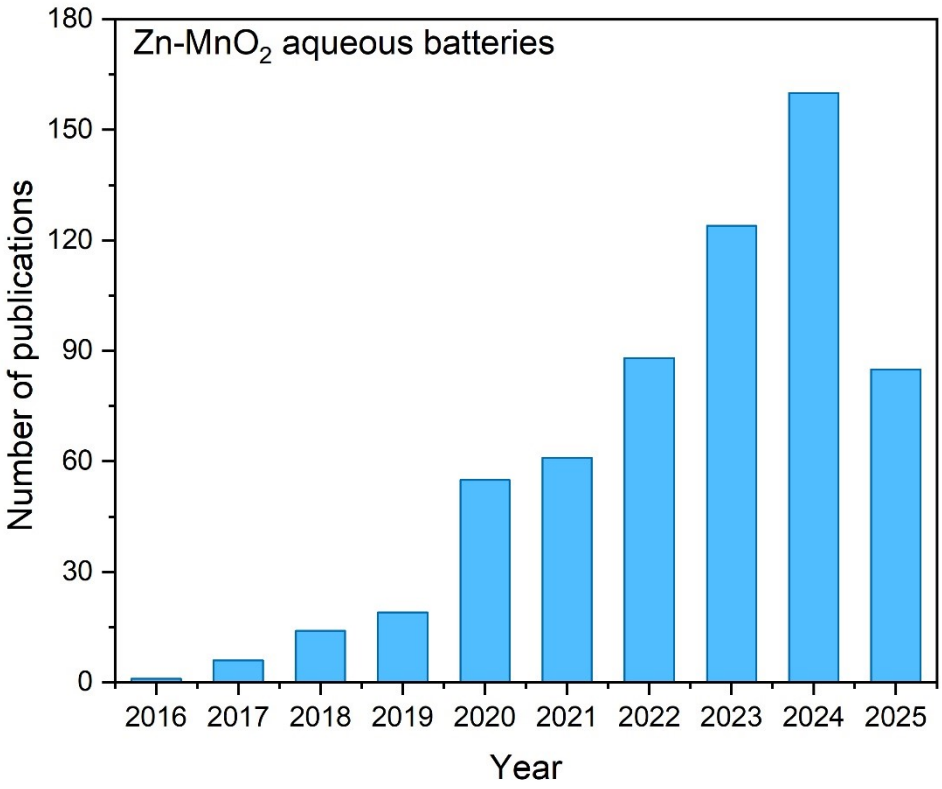

Figure S1. Number of publications of the Zn-MnO_2 aqueous batteries in the past one decade (Source: Scopus search on "Aqueous Zn-MnO_2 batteries". Total number of publications, in the past one decade, are found to be 574, excluding 49 preprints available in the literature.

Table 1. Various selected reported electrochemical mechanisms in Zn–MnO_2 AZIBs through operando and non-operando techniques.

Battery structure[ref.] Period:2012-2022	Electrochemical mechanism (Type of analysis)	Year
α-MnO_2||Zn[1]	Zn^{2+} (de)intercalation (non-operando)	2012
α-MnO_2||Zn[2]	Zn^{2+}intercalation (non-operando)	2014
γ-MnO_2||Zn[3]	Zn^{2+} (de)intercalation (operando)	2015
α-MnO_2||Zn[4]	H^+ conversion reaction (non-operando)	2016
ε-MnO_2||Zn[5]	Co-insertion of H^+ and Zn^{2+} ions (non-operando)	2017
layered-MnO_2||Zn[6]	Zn^{2+}intercalation (operando)	2018
δ-MnO_2||Zn[7]	Intercalation–conversion reaction (non-operando)	2019
α-MnO_2||Zn[8]	Intercalation–conversion reaction (non-operando)	2019
α, δ-MnO_2||Zn[9]	MnO_2-Mn^{2+} deposition–dissolution with trace of Zn^{2+}/H^+ intercalation (non-operando)	2020
α-MnO_2||Zn[10]	H^+ -insertion with trace of Zn^{2+} insertion (operando)	2020
α-MnO_2||Zn[11]	MnO_2-Mn^{2+} deposition–dissolution without intercalation (non-operando)	2021
EMD (47%)δ-MnO_2||Zn[12]	Multi-phase formations; deposition-dissolution, insertion (operando)	2021
$Zn_4SO_4(OH)_6.nH_2O$ ||Zn[13]	Deposition–dissolution of parasitic phase of $Zn_4SO_4(OH)_6.nH_2O$ without intercalation (operando)	2022
α-MnO_2||Zn[14]	Exclusive H^+ intercalation (non-operando)	2022
α-MnO_2||Zn[15]	MnO_2-Mn^{2+} deposition–dissolution with $ZnMn_3O_7$ layer formation during charge reaction (operando)	2022
γ-MnO_2||Zn[16] (CMD/EMD)	MnO_2-Mn^{2+} electrodeposition–dissolution with reversible deposition-dissolution of ZHS, respectively, on discharge regions I and II, with with almost identical first and remaining electrochemical charge-discharge traces	2022
Period:2023-2024*		
β-MnO_2||Zn[17]	Dissolution–deposition reaction with (ir)reversible Zn-Mn complex formation during charge (operando)	2023
α-MnO_2||Zn[18]	Multi-stage Mn dissolution–conversion (via. $Zn_4SO_4(OH)_6.nH_2O$ assisted Mn dissolution–deposition with Zn-ion inserted layered Zn_xMnO_2 formation during charge reaction (operando)	2023
α-MnO_2||Zn[19]	Exclusive MnO_2-Mn^{2+} deposition–dissolution (non-operando)	2024
δ- MnO_2||Zn[20]	Formation of irreversible Zn_xMnO_2 (formed before charge-discharge) H^+ intercalation and Mn^{2+} dissolution	2024

	(operando)	
α-MnO_2||Zn[21]	$HMnO_2$ with $Zn_4SO_4(OH)_6$. nH_2O causing from MnO_2 and MnOOH dissolution with H^+ consuming (operando)	2024

* Not including reportes of known (explored) mechanisms

Simulation Method

The possible dissolution phenomenon of Mn atoms was investigated using ab initio molecular dynamics (AIMD) simulations implemented in the Vienna Ab Initio Simulation Package (VASP) software. The calculations employed the projector-augmented wave (PAW) method and the Perdew-Burke-Ernzerhof (PBE) functional within the framework of generalized gradient approximation (GGA)[22-26]. The plane-wave energy cutoff was set to 500 eV. The Brillouin zone was sampled using the Γ-point scheme, and electronic smearing was handled using the Gaussian smearing method with a smearing width 0.1 eV. The AIMD simulations were performed using the Nose-Hoover thermostat at an elevated constant temperature of 800 K (MnOOH) and 1200 K ($ZnMn_2O_4$ and MnO) throughout the simulation[27, 28]. The dynamics were propagated using the velocity Verlet integrator with a time step of 1 fs, and the simulations were run for 1000 steps, corresponding to 1 ps of simulation time. About 72 hours of computing time was used for each calculation on Volta Supercomping facilities at Next Generation Batteries Lab, Chonnam National University. The vacuum region was set to exceed 12 Å. The van der Walls dispersion interactions DFT-D3 method with Becke-Johnson damping function were employed in the simulation[29].

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