## Polyoxometalate Driven Dendrite-free Zinc Electrode by Synergy

## Mechanisms of Cation and Anion Cluster Regulation

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## **Results and Discussion**



**Figure S1.** (a) Ball-and-stick presentations of  $[Mo_7O_{24}]^{6-}$  anion cluster. (Mo: blue, O: gray) (b) Polyhedral representation of  $[Mo_7O_{24}]^{6-}$  anion cluster.



Figure S2. Electrolytes containing different amount of NMO.



Figure S3. IR spectra of NMO powder and NMO adsorbed on the Zn foil.

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NMO Powder		NMO on Zn foil			
Peak (cm <sup>-1</sup> )		Peak (cm <sup>-1</sup> )			
564, 682	Мо <sup>үл</sup> -О-Мо <sup>үл</sup>	622, 781	Mo <sup>v</sup> -O-Mo <sup>v</sup>		
843, 887	Mo <sup>VI</sup> Ot	844, 885	Mo <sup>VI</sup> Ot		
902, 994	Mo <sup>VI</sup> =Ot	996	Mo <sup>VI</sup> =Ot		
		920	Mo <sup>v</sup> =Ot		

Table S1. The infrared characteristic absorption peak.



Figure S4. SEM images of zinc foil after immersing in the electrolyte added with  $18 \text{ mM} (\text{NH}_4)_2 \text{SO}_4$  for 5 hours.



Figure S5. Voltage-time profiles at a current density of 10 mA  $cm^{-2}$  with a fixed capacity of 1 mAh  $cm^{-2}$ .



**Figure S6.** Cycling performance of Zn symmetric cells using electrolyte without or with NMO additives at current densities of 2 mA  $cm^{-2}$  with a fixed capacity of 4 mAh  $cm^{-2}$ .



**Figure S7.** Cycling curves of Zn symmetric cells in electrolytes with different amounts of NMO additives at current densities of 10 mA cm<sup>-2</sup> with a fixed capacity of 1 mAh cm<sup>-2</sup>.



**Figure S8.** Cycling curves of Zn symmetric cells in blank electrolyte and electrolytes with NMO additive and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> additive, respectively.



**Figure S9.** Cyclic voltammetry (CV) curves of the Zn/NVO full cells using blank electrolytes at  $1 \text{ mV s}^{-1}$ .



Figure S10. Discharge/charge curves of Zn/NVO full cells from 2000 mA  $g^{-1}$  to 4000 mA  $g^{-1}$  using blank electrolytes.



Figure S11. The equivalent circuits corresponding to figure 5d.

	NMO	Error (%)	Blank	Error (%)
R <sub>e</sub>	5.057	3.225	2.181	3.422
$R_{ m f}$	4.266	9.343	8.323	21.74
$R_{ m ct}$	307.3	4.168	473.3	11.18
Sum	316.6		483.8	

Table S2. The fitting results of the simulated equivalent circuit.

Main materials	Current density and areal capacity	Cycle	Reference
(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>7</sub> O <sub>24</sub> ]·4H <sub>2</sub> O	10 mA cm <sup>-2</sup> 1 mAh cm <sup>-2</sup>	568 cycles	This work
Zn-X zeolite nanoparticles and Nafion	1 mA cm <sup>-2</sup> 10 mAh cm <sup>-2</sup>	50 cycles	[20]
Diethyl ether	1 mA cm <sup>-2</sup> 1 mAh cm <sup>-2</sup>	90 cycles	[22]
Carbon nanotubes	1 mA cm <sup>-2</sup> 2 mAh cm <sup>-2</sup>	50 cycles	[23]
Polyacrylamide	$2 \text{ mA cm}^{-2}$ $4 \text{ mAh cm}^{-2}$	70 cycles	[24]
Metallic indium (In)	1 mA cm <sup>-2</sup> 1 mAh cm <sup>-2</sup>	250 cycles	[25]
Polyamide coating layer	10 mA cm <sup>-2</sup> 10 mAh cm <sup>-2</sup>	38 cycles	[26]
NaTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	1 mA cm <sup>-2</sup> 1 mAh cm <sup>-2</sup>	125 cycles	[27]
ZIF-8	10 mA cm <sup>-2</sup> 10 mAh cm <sup>-2</sup>	200 cycles	[31]
TiO <sub>2</sub>	1 mA cm <sup>-2</sup> 1 mAh cm <sup>-2</sup>	75 cycles	[33]
Faceted titanium dioxide	1 mA cm <sup>-2</sup> 1 mAh cm <sup>-2</sup>	230 cycles	[35]

 Table S3. Comparison of the electrochemical performance of Zn anode in aqueous electrolytes with previous work.

MXene	1 mA cm <sup>-2</sup> 1 mAh cm <sup>-2</sup>	150 cycles	[36]
RGO	1 mA cm <sup>-2</sup> 2 mAh cm <sup>-2</sup>	50 cycles	[37]