

SUPPORTING INFORMATION

Reverse Voltage Pulse Deposition of Porous Polyaniline/Mn-Co Sulfide Composite Cathode Material for Modified Zn-ion Hybrid Supercapacitor

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Supplementary Figures

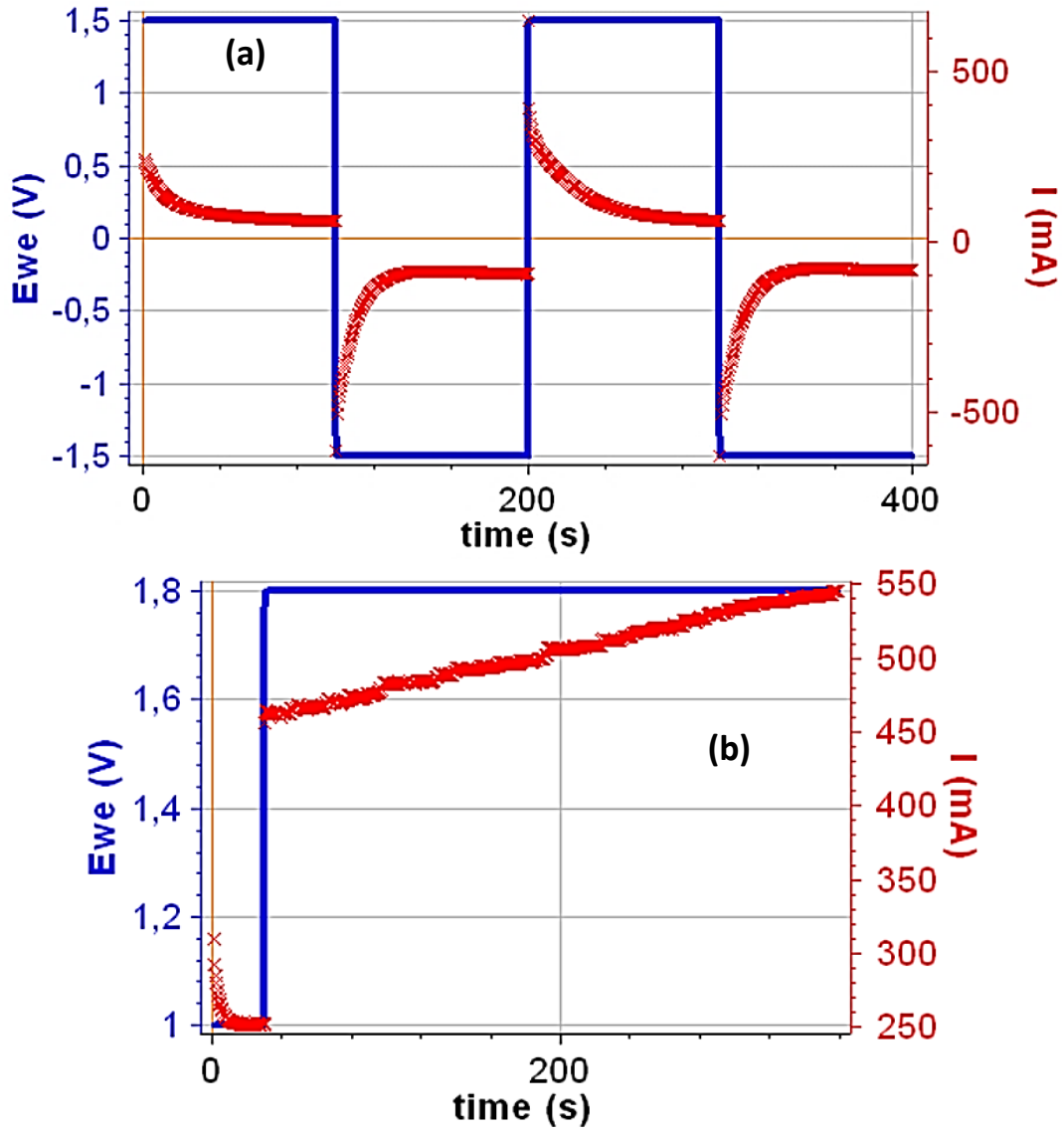


Fig. S1. Potential and current graphs of electrodeposition method (a) and electroplating method (b).

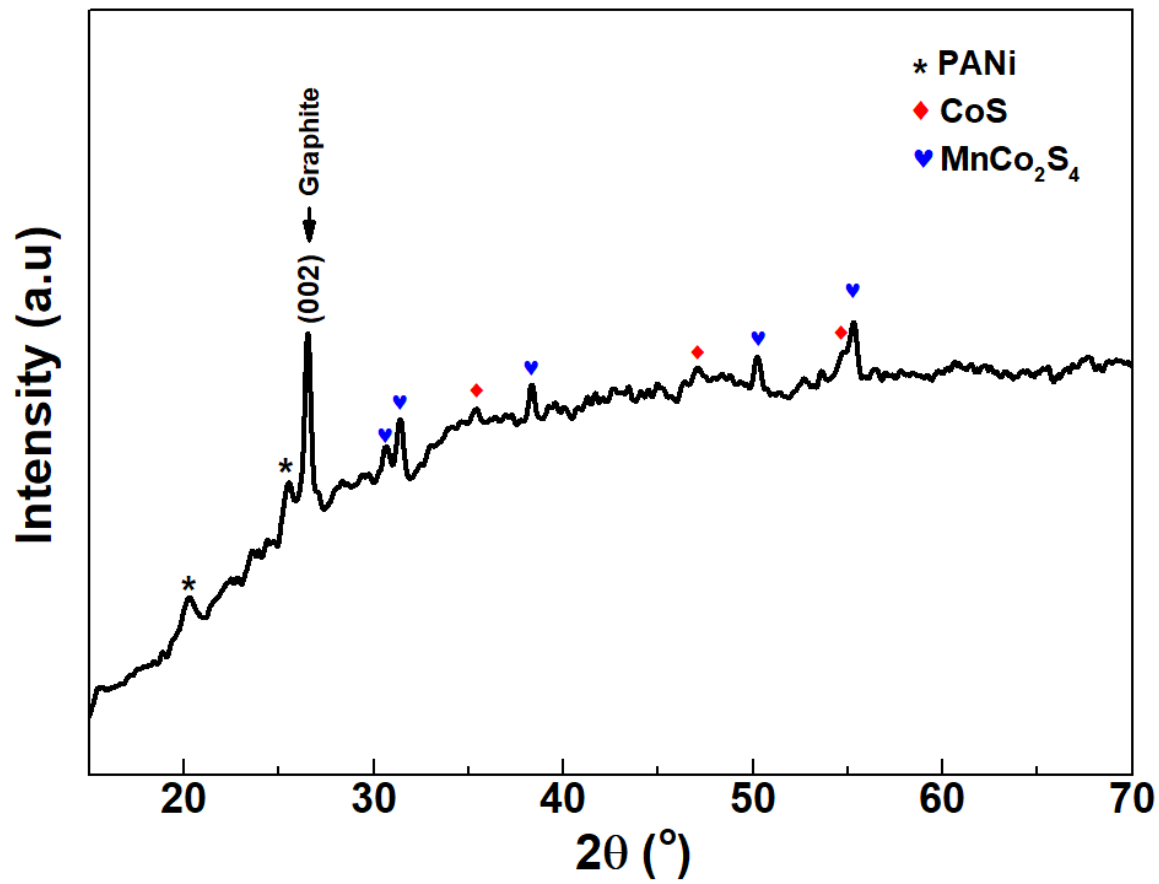


Fig. S2. XRD pattern of MCS/PANI electrode.

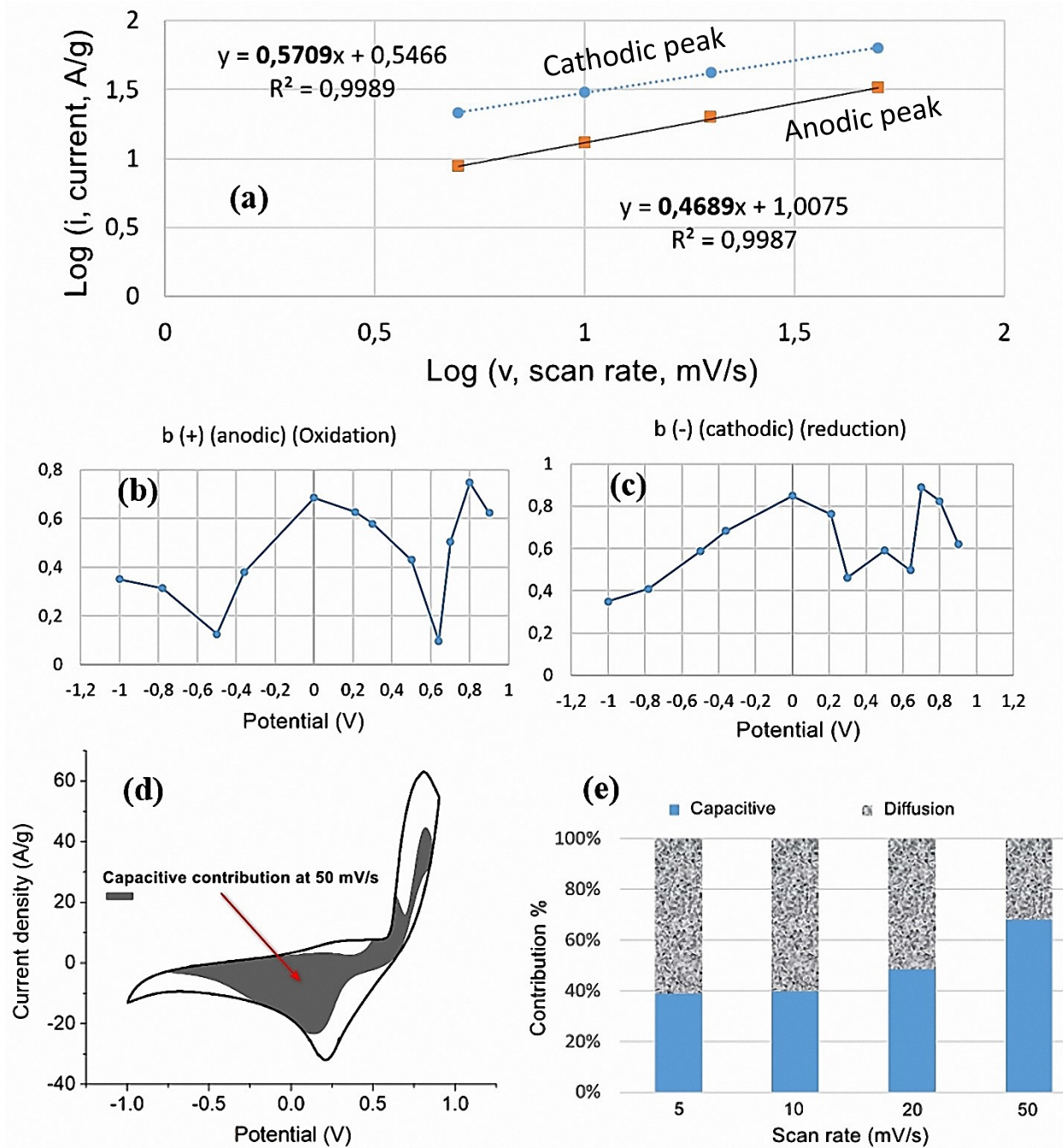


Fig. S3. Log I (A/g) vs log v (mV/s) (a), b factor vs some potential value (b,c), CV curve with capacitive contribution at scan rate of 50 mV/s (d) and the percentages of capacitive and diffusion contributions at different scan rates (e).

Supplementary Tables

Table S1. Electrochemical performance and synthesis methods of different transition metal sulfides-based electrodes

Materials	Method	Electrolyte	Working Potential (V)	Specific capacitance	Reference
<i>MCS-PANi</i>	<i>Electrodeposition (Reverse Voltage Pulse)</i>	<i>ZnSO₄ 1M and MnSO₄ 0.1M</i>	<i>-1 to 0.9</i>	<i>1048.8 F/g (at CV scan rate of 5 mV/s)</i>	<i>This work</i>
MnCoS	CVD	6M KOH	-0.2 to 0.6	1938 F/g (at 5 A/g)	[S1]
MnCoS	Hydrothermal	3M NaOH	0 to 0.4	992 F/g (at 1 A/g)	[S2]
Ni-Co-Zn-S	Hydrothermal	3.5M KOH	0 to 0.5	825 F/g (at 1 A/g)	[S3]
Zn-Ni-Co-S-rGO	Electrodeposition (CV)	2M KOH	0 to 0.6	1302 F/g (at 0.5 A/g)	[S4]
FeCoS-rGO-PPy	Electrodeposition (Const V)	3M KOH	-0.1 to 0.55	3178 F/g (at 2 A/g)	[S5]
NiCo ₂ S ₄ – C quantum dot	Hydrothermal	2M KOH	0 to 0.5	124.4 mAh/g (at 2 A/g)	[S6]
Zn-Co-S	Hydrothermal	6M KOH	-0.5 to 0.4	578.6 F/g (at 1 A/g)	[S7]
FeS _x	Hydrothermal	1M Na ₂ SO ₄	-0.95 to 0	730.52 mF/cm ² (at 1 mA/cm ²)	[S8]
MnCo ₂ S ₄	Hydrothermal	1M KOH	0 to 1 V	1980 F/g (at 1 A/g)	[S9]
MnCo ₂ S ₄	Solvothermal	3 M KOH	0 to 0.4	780.8 mF/cm ² (at 1 mA/cm ²)	[S10]

Table S2. Electrochemical performance of various electrodes for ZHSCs

Cathode	Anode	Electrolyte	Working Potential (V)	Capacitance	Energy density	Durability, stability	Ref
<i>MCS-PANi/graphite paper</i>	<i>hierarchical micro-flower-like Zn</i>	<i>ZnSO₄ 1M and MnSO₄ 0.1M</i>	<i>0 to 2</i>	<i>1048.8 F/g (at CV scan rate of 5 mV/s)</i>	<i>216 Wh/kg at a power density of 4610 W/kg</i>	<i>98,3 % after 11232 cycles (50 A/g)</i>	<i>This work</i>
Flower-like carbon	Zn foam	ZnSO ₄ (aq)	0.1–1.8	132 mAh/g (1 A/g)	117.5 Wh/kg	90% after 10,000 cycles (5 A/g)	[S11]
Carbon sponge	nano Zn foil	Zn(CF ₃ SO ₃) ₂ + AN	0–1.8	226 F/g (0.1 A/g)	91.5 Wh/kg	Nearly 100% after 60,000 cycles (10 A/g)	[S12]
S-doped 3D PC	Zn foil	ZnSO ₄ (aq)	0.2–1.8	123.8 mAh/cm ³ (0.2 A/g)	162.6 Wh/kg	96.8% after 18,000 cycles (10 A/g)	[S13]
P-doped PC	Zn foil	ZnSO ₄ (aq)	0.1–1.8	143.7 mAh/g (1 A/g)	129.3 Wh/kg	92% after 10,000 cycles (5 A/g)	[S14]
Graphene Hydrogel (GH)	Zn foil	ZnSO ₄ (aq)	0.2–1.8	99.3 mAh/g (0.2 A/g)	76.2 Wh/kg	90% after 10,000 cycles (15 A/g)	[S15]
3D Mxene-rGO aerogel	Zn foil	ZnSO ₄ (aq)	0.2–1.6	128.6 F/g (0.4 A/g)	34.9 Wh/kg	95% after 75,000 cycles (5 A/g)	[S16]
2D/2D LDH/V2CTx MXene	Zn plate	ZnSO ₄ + MnSO ₄ (aq)	0.9–1.85	372.9 mAh/g (0.2 A/g)	368.7 Wh/kg	95.7% after 600 cycles (1 A/g)	[S17]

3D graphene@PANI	Zn foil	ZnSO ₄ (aq)	0.4–1.6	154 mAh/g (0.1 A/g)	205 Wh/kg	80.5% after 6000 cycles (0.1 A/g)	[S18]
Few-layer phosphorene	Zn plate	Zn(CF ₃ SO ₃) ₂ + LiTFSI-PAM	0.8–2.2	304 F/g (0.2 A/g)	315.6 Wh/kg	Nearly 100% after 5000 cycles (0.5 A/g)	[S19]
Few-layer siloxene	Zinc plate	Zn(CF ₃ SO ₃) ₂ + LiTFSI	0–1.8	6.86 mF/cm ² (0.05 mA/cm ²)	10.66 mJ/cm ²	94.3% after 16,000 cycles (0.05 mA/cm ²)	[S20]

Supplementary References

- [S1] M. Yu, X. Li, Y. Ma, R. Liu, and J. Liu, Nanohoneycomb-like manganese cobalt sulfide/three dimensional graphene-nickel foam hybrid electrodes for high-rate capability supercapacitors. *Appl. Surf. Sci.* 396, (2017) 1816.
- [S2] Y. Zhao, Z. Shi, H. Li, and C.-A. Wang, Designing pinecone-like and hierarchical manganese cobalt sulfides for advanced supercapacitor electrodes. *J. Mater. Chem. A* 6, (2018) 12782–12793.
- [S3] V. Vignesh and R. Navamathavan, Spherical-Like Ball-by-Ball Architecture of Ni-Co-Zn-S Electrodes for Electrochemical Energy Storage Application in Supercapacitors, *J. Electrochem. Soc.* 164, (2017) 434.
- [S4] U. Evariste, G. Jiang, B. Yu, Y. Liu, Z. Huang, Q. Lu, and P. Ma, 34, 2445 (2019).
- [S5] A. Karimi, I. Kazeminezhad, L. Naderi, and S. Shahrokhian, Construction of a ternary nanocomposite, polypyrrole/Fe-Co sulfide-reduced graphene oxide/nickel foam, as a novel binderfree electrode for high-performance asymmetric supercapacitors. *J. Phys. Chem. C* 124, (2020) 4393.
- [S6] Y. Zhu, J. Li, X. Yun, G. Zhao, and P. Ge, Graphitic carbon quantum dots modified nickel cobalt sulfide as cathode materials for alkaline aqueous batteries. *Nano-Micro Lett.* 12, (2020) 18.
- [S7] X. Yu, W. Zhang, L. Liu, and Y. Fautrelle, High magnetic fieldengineered bunched Zn-Co-S yolk-shell balls intercalated within S, N Codoped CNTs/graphene films for free-standing supercapacitors. *ACS Appl. Mater. Interf.* 1, (2020) 12.
- [S8] K.K. Upadhyay, T. Nguyen, T.M. Silva, M.J. Carmezim, M.F. Montemor, Pseudocapacitive behaviour of FeS_x grown on stainless steel up to 1.8 V in aqueous electrolyte, *J. Energy Storage* 26 (2019) 100949.
- [S9] P.M. Anjana, S.R. Sarath Kumar, R.B. Rakhi, MnCo₂S₄ nanoflowers directly grown over nickel foam as cathode for high-performance asymmetric hybrid supercapacitors, *Journal of Energy Storage*, 61 (2023) 106672.
- [S10] M. Fu, Q. Zhuang, H. Yu, W. Chen, MnCo₂S₄ nanosheet arrays modified with vermicular polypyrrole for advanced free-standing flexible electrodes, *Electrochimica Acta*, 447 (2023) 142167.

- [S11] H.L. Fan, S.X. Zhou, Q.Y. Li, G.M. Gao, Y.R. Wang, F. He, G.Z. Hu, X. Hu, Hydrogen-bonded frameworks crystals-assisted synthesis of flower-like carbon materials with penetrable meso/macropores from heavy fraction of bio-oil for Zn-ion hybrid supercapacitors, *J. ColloidInterface Sci.* 600 (2021) 681–690.
- [S12] H. Zhou, C. Liu, J.C. Wu, M. Liu, D. Zhang, H. Song, X. Zhang, H. Gao, J. Yang, D. Chen, Boosting the electrochemical performance through proton transfer for the Zn-ion hybrid supercapacitor with both ionic liquid and organic electrolytes, *J. Mater. Chem. A* 7 (2019) 9708–9715.
- [S13] D. Wang, S. Wang, Z. Lu, S-doped 3D porous carbons derived from potassium thioacetate activation strategy for zinc-ion hybrid supercapacitor applications, *Int. J. Energy Res.* 45 (2021) 2498–2510.
- [S14] H.L. Fan, S.X. Zhou, Q.F. Chen, G.M. Gao, Q.F. Ban, Z.X. Xu, F. He, G.Z. Hu, X. Hu, Phosphorus in honeycomb-like carbon as a cathode boosting pseudocapacitive properties for Zn-ion storage, *J. Power Sources* 493 (2021) 229687.
- [S15] Y. Zhu, X. Ye, H. Jiang, J. Xia, Z. Yue, L. Wang, Z. Wan, C. Jia, X. Yao, Controlled swelling of graphene films towards hierarchical structures for supercapacitor electrodes, *J. Power Sources* 453 (2020) 227851.
- [S16] Q. Wang, S. Wang, X. Guo, L. Ruan, N. Wei, Y. Ma, J. Li, M. Wang, W. Li, W. Zeng, MXene-reduced graphene oxide aerogel for aqueous zinc-ion hybrid supercapacitor with ultralong cycle life, *Adv. Electron. Mater.* 5 (2019) 1900537.
- [S17] Y. Zhang, J. Cao, J. Li, Z. Yuan, D. Li, L. Wang, W. Han, Self-assembled cobaltdoped NiMn-layered double hydroxide (LDH)/V₂CTx MXene hybrids for advanced queous electrochemical energy storage properties, *Chem. Eng. J.* 430 (2022) 132992.
- [S18] J.W. Han, K. Wang, W.H. Liu, C. Li, X.Z. Sun, X. Zhang, Y.B. An, S. Yi, Y.W. Ma, Rational design of nano-architecture composite hydrogel electrode towards high performance Zn-ion hybrid cell, *Nanoscale* 10 (2018) 13083–13091.
- [S19] Z. Huang, A. Chen, F. Mo, G. Liang, X. Li, Q. Yang, Y. Guo, Z. Chen, Q. Li, B. Dong, C. Zhi, Phosphorene as cathode material for high-voltage, anti-self-discharge zinc ion hybrid capacitors, *Adv. Energy Mater.* 10 (2020) 2001024.
- [S20] Q. Guo, Y. Han, N. Chen, L. Qu, Few-layer siloxene as an electrode for superior high-rate zinc ion hybrid capacitors, *ACS Energy Lett.* 6 (2021) 1786–1794.