Supplementary Information (SI) for Sustainable Energy & Fuels.

Supporting Information

Mn-doped Cobalt oxide dodecahedron nanocages as an efficient bifunctional electrocatalyst for zinc-air batteries

Sai Vani Terlapu, Ranjit Bauri*

Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai 600036, India

*Corresponding author, Email: rbauri@iitm.ac.in

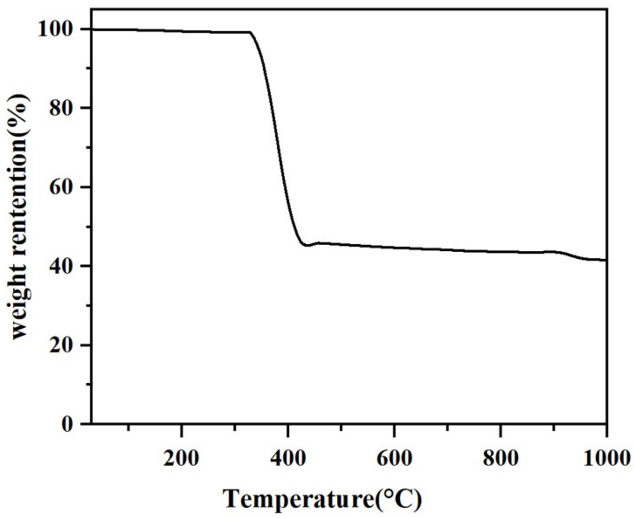

Fig. S1. TGA profile of Co-Mn-ZIF sample in air atmosphere

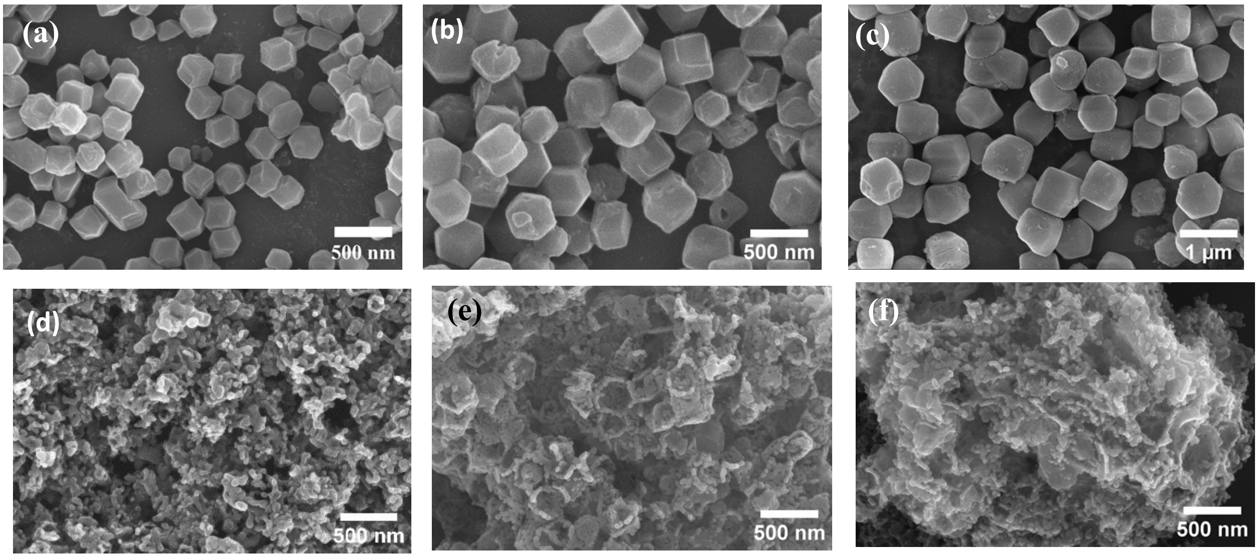

Fig.S2.SEM images of (a) Co-ZIF, (b) Mn-Co-ZIF-0.5, (c) Mn-Co-ZIF-2, (d) Co_3O_4, (e) Mn-Co_3O_4-0.5, and (f) Mn-Co_3O_4-2.

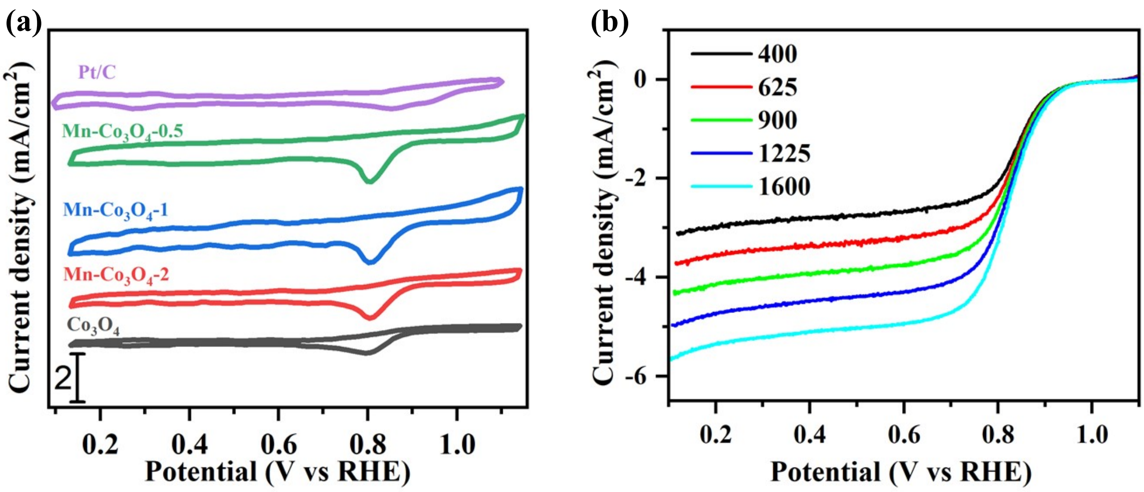

Fig.S3. (a) CV curves of all the studied catalysts in oxygen-saturated KOH electrolyte, (b) LSV curves of Mn-Co_3O_4-1 at various rotation speeds.

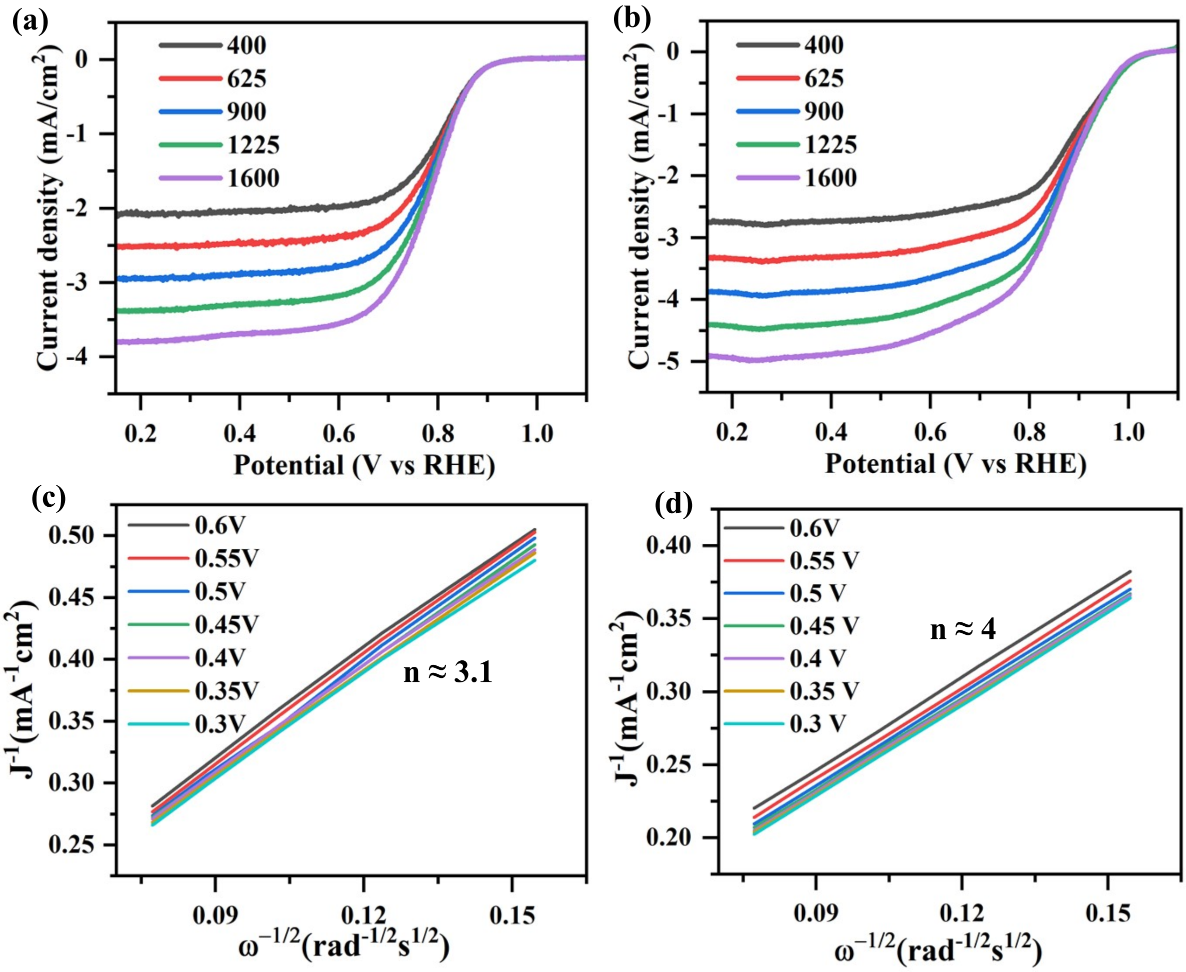

Fig. S4. LSV curves of (a) Co_3O_4 and (b) Pt/C at various rotation speeds, corresponding K-L plots of (c) Co_3O_4 and (d) Pt/C.

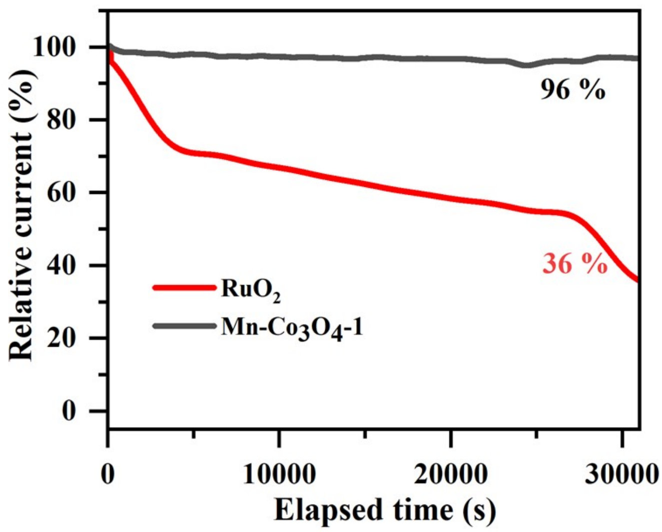

Fig.S5. Chronoamperometric test of RuO_2 and Mn-Co_3O_4-1 under OER conditions.

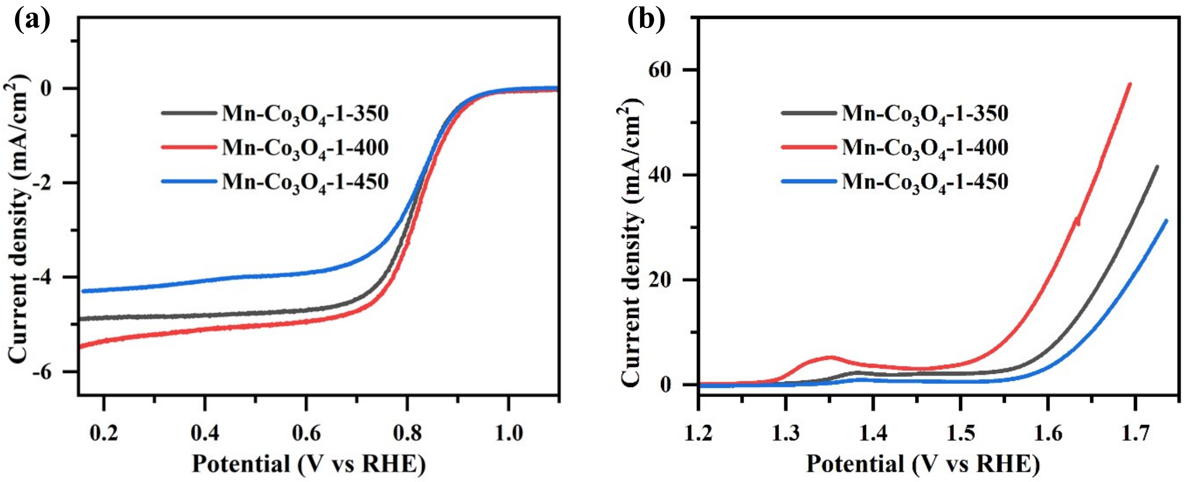

Fig. S6. LSV curves of Mn-Co_3O_4-1 catalyst at various temperatures for (a) ORR and (b) OER.

Table.S1. Summary of the ORR/OER bifunctional performance of cobalt metal-based electrocatalysts reported in literature

Electrocatalyst	**$E_{1/2}$(vs. RHE)**	**$E_{j=10}$ (vs. RHE)**	**ΔE(V)**	**Ref.**
Mn-Co_3O_4-1	0.84	1.56	0.71	This work
$ZnCoMnO_4$/N-rGO	0.83	1.68	0.85	1
N-rGO/Co_3O_4	0.8	1.58	0.78	2
NCO-2	0.65	1.505	0.855	3
0.1Ni@Co_3O_4	0.8	1.58	0.78	4
Ce@Co_3O_4/CNFs	0.81	1.61	0.8	5
$NiCo_2O_4$/N-G	0.72	1.595	0.785	6
CoLa-1	0.842	1.531	0.69	7
N-Co_3O_4/N-CNs	0.79	1.584	0.794	8
$NiCo_2O_4$-GO/C	0.74	1.62	0.88	9
5% Cu- Co_3O_4	0.69	1.59	0.9	10
Ni_{oh}- Co_3O_4	0.84	1.62	0.78	11
Co_3O_4-$NiCo_2O_4$/NRGO	0.79	1.62	0.83	12

References:

1 W. Liu, D. Rao, J. Bao, L. Xu, Y. Lei and H. Li, *J. Energy Chem.*, 2021, **57**, 428–435.

2 J. S. Sanchez, R. R. Maça, A. Pendashteh, V. Etacheri, V. A. de la P. O'Shea, M. Castillo-Rodríguez, J. Palma and R. Marcilla, *Catal. Sci. Technol.*, 2020, **10**, 1444–1457.

3 J. Zhao, Y. He, J. Wang, J. Zhang, L. Qiu, Y. Chen, C. Zhong, X. Han, Y. Deng and W. Hu, *Chem. Eng. J.*, 2022, **435**, 134261.

4 Y. Zhang, C. Huang, J. Lu, H. Cao, C. Zhang and X. S. Zhao, *Appl. Surf. Sci.*, 2024, **651**, 159241.

5 X. Sun, T. Xu, W. Sun, J. Bai and C. Li, *J. Alloys Compd.*, 2022, **898**, 162778.

6 Y. Ma, W. Shang, W. Yu, X. Chen, W. Xia, C. Wang and P. Tan, *Energy Fuels*, 2021, **35**, 14188–14196.

7 N. S. Gultom, Y.-C. Zhou and D.-H. Kuo, *J. Colloid Interface Sci.*, 2024, **655**, 394–406.

8 Z. Liu, Y. Cao, S. Wang, Z. Lu, J. Hu, J. Xie and A. Hao, *J. Alloys Compd.*, 2023, **965**, 171479.

9 L. Fu, Y. Yao, J. Ma, Z. Zhang, G. Wang and W. Wei, *Langmuir*, 2024, **40**, 6990–7000.

10 A. Behera, D. Seth, M. Agarwal, M. A. Haider and A. J. Bhattacharyya, *ACS Appl. Mater. Interfaces*, 2024, **16**, 17574–17586.

11 S. Liu, B. Zhang, Y. Cao, H. Wang, Y. Zhang, S. Zhang, Y. Li, H. Gong, S. Liu, Z. Yang and J. Sun, *ACS Energy Lett.*, 2023, **8**, 159–168.

12 Z. Zhu, J. Zhang, X. Peng, Y. Liu, T. Cen, Z. Ye and D. Yuan, *Energy Fuels*, 2021, **35**, 4550–4558.