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Supplementary Information

NiMn Layered Double Hydroxide as Efficient Electrocatalyst for Oxygen Evolution Reaction and its Application in Rechargeable Zn-Air Batteries

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1. EDX mapping of Ni_1Mn_1 and Ni_5Mn_1

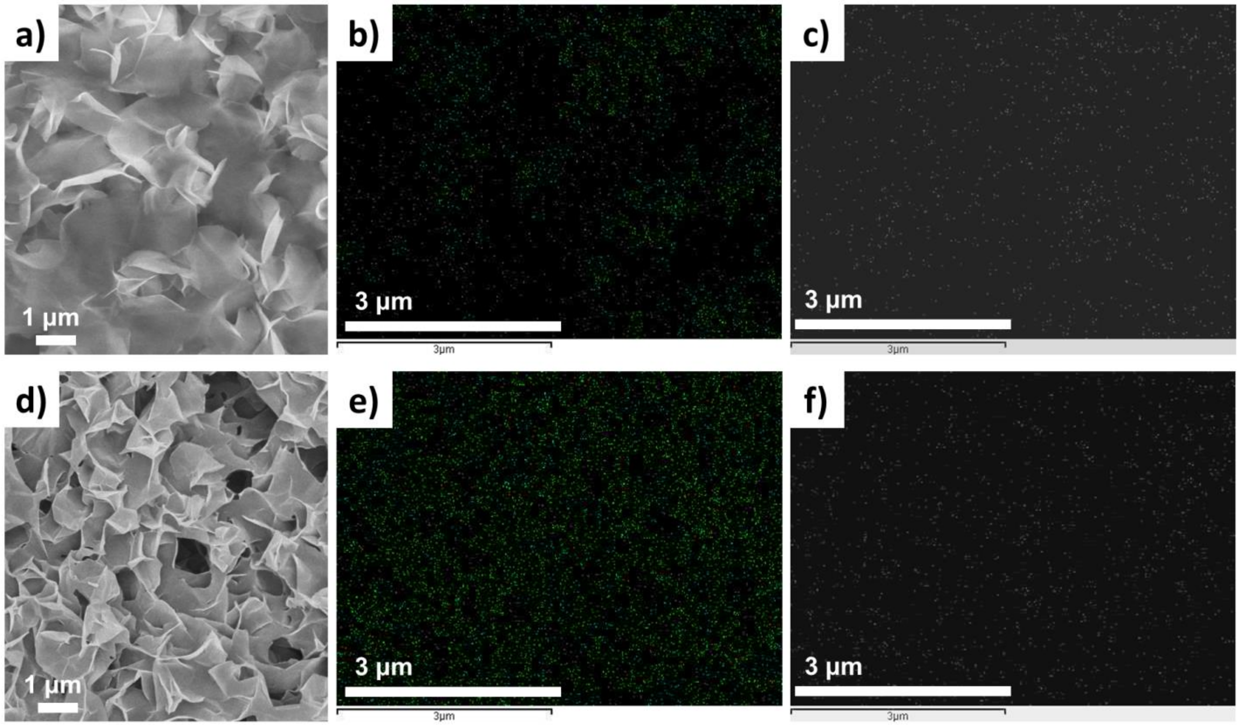

Fig. S1 (a) SEM images of Ni_1Mn_1 and EDX elemental mapping of (b) Ni and (c) Mn in Ni_1Mn_1. (d) SEM images of Ni_5Mn_1 and EDX elemental mapping of (e) Ni and f) Mn in Ni_5Mn_1.

Ni and Mn in NiMn LDHs are atomically well-dispersed throughout the sample rather than forming separate phases, which further support our XRD results.

2. TEM of Ni_1Mn_1 and Ni_5Mn_1

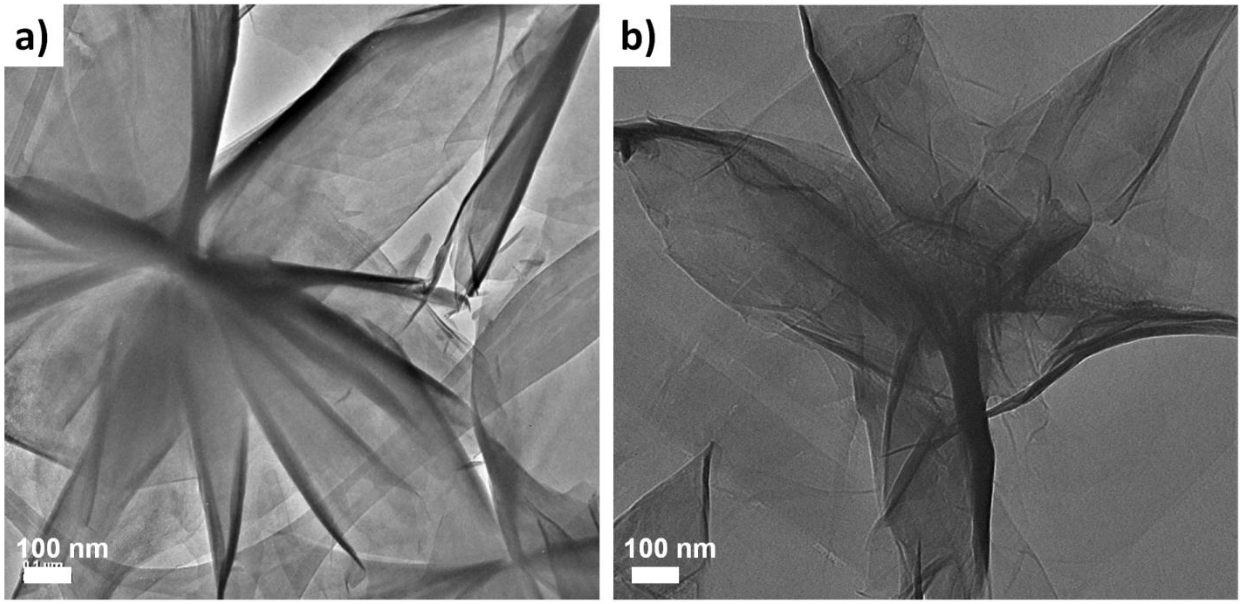

Fig. S2 TEM images of (a) Ni_1Mn_1 and (b) Ni_5Mn_1

3. Characterization of commercial $Ni(OH)_2$

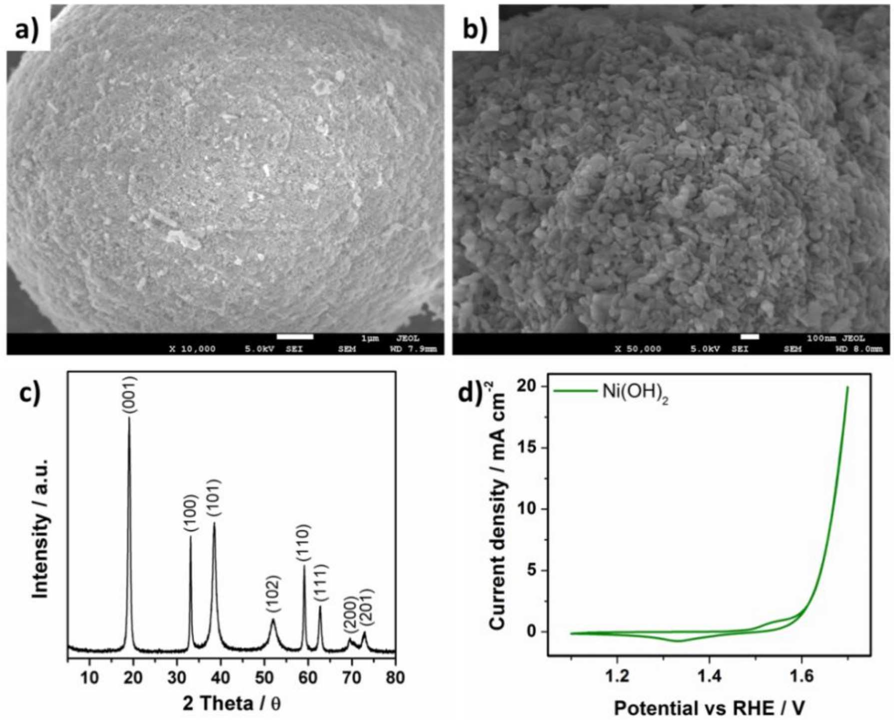

Fig. S3 (a, b) SEM images and (c) XRD pattern commercial $Ni(OH)_2$. (d) RDE Cyclic voltammograms of commercial $Ni(OH)_2$ at scan rate of 5 mV s^{-1} and rotating speed of 1600 rpm in 1 M KOH.

4. **Catalytic activity of 20 wt% Ni_3Mn_1/C, commercial 20 wt% RuO_2/C and 20 wt% Ir/C during oxygen evolution reaction**

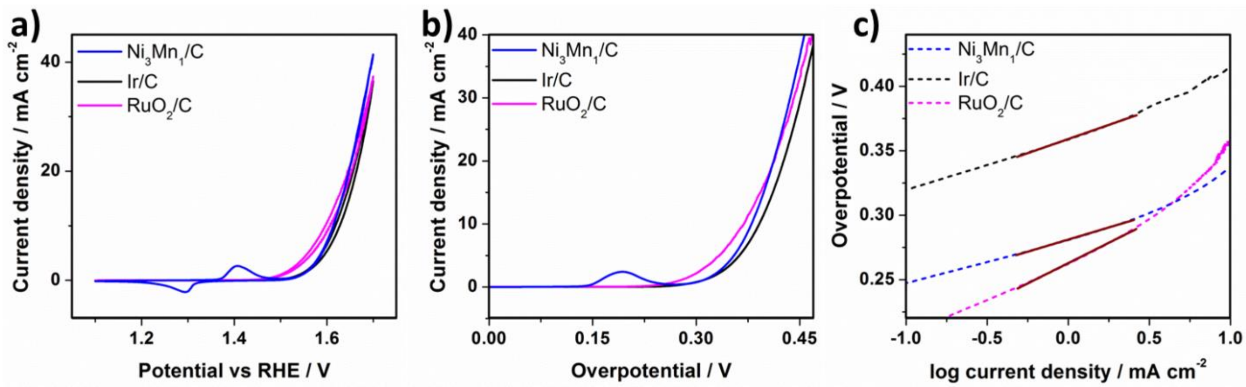

Fig. S4 (a) Cyclic voltammograms and (b) linear scan voltammograms of 20 wt% Ni_3Mn_1/C, commercial 20 wt% Ir/C, and 20 wt% RuO_2 catalysts. (c) Tafel plots (i.e. dash curves) showing the Tafel slope (i.e. solid curve) of the samples.

In order to have fair comparison to 20 wt% Ir/C, we have also tested 20 wt% Ni_3Mn_1/C and 20 wt% RuO_2/C. With 80 wt% of carbon black, the overpotential of RuO_2, Ni_3Mn_1, and Ir are 0.37, 0.38, and 0.39 V, respectively. The Tafel plot of RuO_2/C, Ni_3Mn_1/C and Ir/C are 63, 38, and 44 mV dec^{-1}.

5. **Stability of commercial RuO_2**

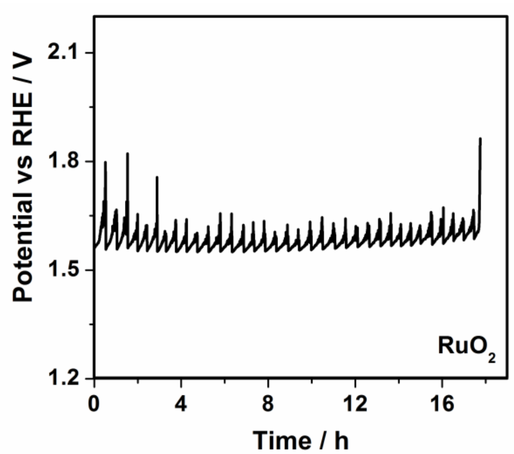

Fig. S5 Stability test of commercial RuO_2 under constant current of 10 mA cm^{-2} at rotating speed of 2500 rpm in 1 M KOH.

Due to the low overpotential of RuO_2 at 10 mA cm^{-2}, O_2 gas generated at the surface of RDE glassy carbon is considerably high causing significant fluctuation in the measured potential.

6. Catalytic activity of Ni_3Mn_1 LDH during oxygen reduction reaction

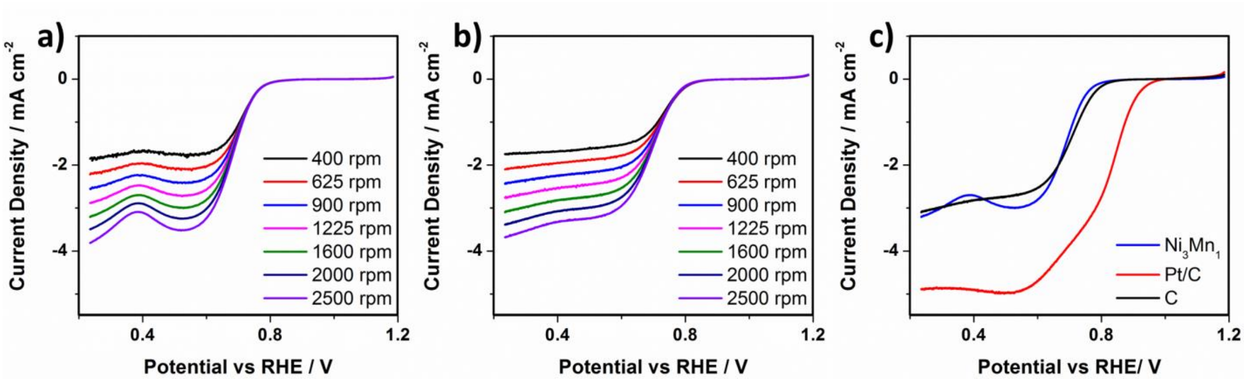

Fig. S6 Linear scan voltammograms of (a) Ni_3Mn_1 and (b) Vulcan carbon black during oxygen reduction reaction at various rotating speeds. (b) Linear scan voltammograms of $Ni_3Mn_{1,}$ commercials Pt/C and Vulcan carbon black during oxygen reduction reaction at rotating speed of 1600 rpm. The measurements were carried out at scan rate of 5 mV s^{-1} in 0.1 M KOH.

A catalyst for oxygen reduction reaction (ORR) is required during the discharge of Zn-air batteries. Carbon black which is present in the carbon paper and catalyst ink of both batteries functions as ORR catalyst. Besides that, NiMn LDHs also show catalytic activity during oxygen reduction reaction in 0.1 M KOH (Fig. S4a). The catalytic activity of Ni_3Mn_1 is inferior than 20 wt % Pt/C and similar to Vulcan carbon black.

7. **Digital image of Zn-air batteries**

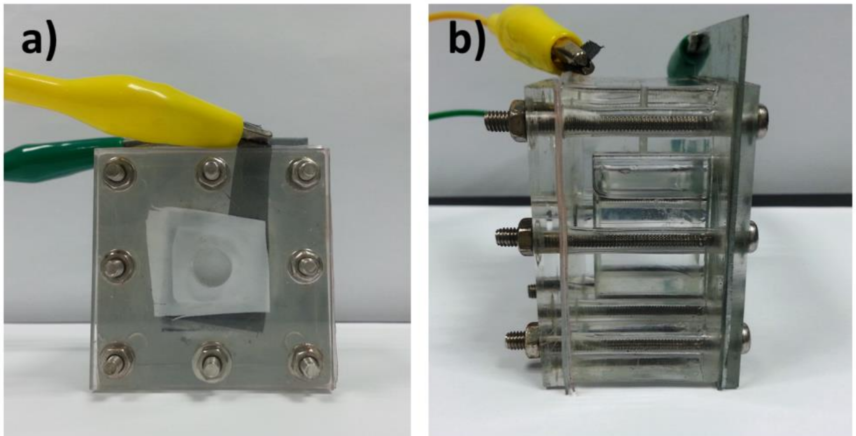

Fig. S7 (a) Front view displaying the carbon paper air cathode. O_2 was supplied through the hole (≈0.79 cm^2); (b) Side view showing electrolyte and zinc plate anode. The cell contains 20 ml of electrolyte. Outer dimension of the cell is 6x6x4 cm^3. The distance between air cathode and Zn-anode is about xx cm. The white color membrane is hydrophobic PTFE membrane which is used to prevent the leakage of the electrolyte during the prolonged cycling test.

8. Ni-based layered double hydroxide as OER catalyst in literature

Table S1. Ni-based layered double hydroxide as OER catalyst in literature

Ref	Catalyst	Overpotential at 10 mA cm^{-2} (V)	Tafel Slope (mV dec^{-1})	Stability / Testing condition
This work	NiMn LDH Ir/C reference RuO_2 reference	0.35 0.39 0.32	40 44 49	16 h / constant current at 10 mA cm^{-2}
1	NiFe LDH	0.35	47	-
2	Exfoliated NiFe LDH NiCo LDH CoCo LDH IrO_2 reference	 0.302 0.334 0.353 0.338	 40 41 45 47	 13 h / constant current at 10 mA cm^{-2}
3	NiFe LDH on Ni foam	0.28	50	10 h / constant potential at 1.6 V (RHE)
4	CoMn LDH /MWCNT NiMn LDH /MWCNT	0.30 0.35	73.6 83.5	12 h / constant current at 10 mA cm^{-2} 9 h / constant current at 10 mA cm^{-2}
5	NiMn LDH NiMn LDH /rGO	0.36 0.26	65 46	1 h / constant current at 5 mA cm^{-2} 2 h / constant current at 5 mA cm^{-2}
6	NiCo LDH on carbon paper	0.37	40	6 h / constant current at 10 mA cm^{-2}
7	NiCo LDH on Ni foam RuO_2 reference	0.42 0.41	113 128	1 h / constant potential at 1.52 V (RHE)
8	NiCoFe LDH on Ni foam	0.23	53	10 h / constant potential at 1.46 V (RHE)
9	NiCo DH/N-graphene on Ni	0.35	614	12 h / constant potential at 1.54 V (RHE)

	foam			
10	NiFe DH/graphene on Ni foam	0.2	40	-

9. Performance of rechargeable Zn-air batteries in literature

Table S2. Performance of rechargeable Zn-air batteries in literature

Ref	OER Catalyst	Initial charging voltage (V)	No. of Cycle	Applied Current (mA cm^{-2})	Change in charging voltage (%)
This work	NiMn LDH	1.98	200	10	5.4
11	MnO_x/carbon paper	2.06	500	7.5	8
12	$LaNiO_3$/N-CNT	2.17	10	17.6	~0
13	CoO/N-CNT/NiFe LDH	1.99	58	10	~0
14	MnO_2/N-CNT	2.6	50	8	5
15	$NiCo_2O_4$	1.8	50	20	2.2
16	Co_3O_4/carbon nanofiber	2.03	55	20	-
17	Co_3O_4/ MnO_2	2.2	60	15	5
18	Co_3O_4	2.15	60	17.6	~0
19	$\alpha MnO_2/LaNiO_3$/CNT	1.95	75	-	4.8
20	$LaNiO_3$/N-CNT	2.15	75	17.6	4.5
21	Ag/MnO_2	2.5	270	5 mA	~0
22	$MnCo_2O_4$/CNT	2.0	64	10	4.9
23	Mn-Co substituted Fe_3O_4/ N-RGO	2.35	75	10	-

References

1. K. Yan, T. Lafleur, J. Chai and C. Jarvis, *Electrochem. Commun.*, 2016**, 62**, 24-28.
2. F. Song and X. Hu, *Nat. Commun.*, 2014**, 5**.
3. Z. Lu, W. Xu, W. Zhu, Q. Yang, X. Lei, J. Liu, Y. Li, X. Sun and X. Duan, *Chem. Commun.*, 2014**, 50**, 6479-6482.
4. G. Jia, Y. Hu, Q. Qian, Y. Yao, S. Zhang, Z. Li and Z. Zou, *ACS Appl. Mater. Interfaces*, 2016.
5. W. Ma, R. Ma, J. Wu, P. Sun, X. Liu, K. Zhou and T. Sasaki, *Nanoscale*, 2016**, 8**, 10425-10432.
6. H. Liang, F. Meng, M. Cabán-Acevedo, L. Li, A. Forticaux, L. Xiu, Z. Wang and S. Jin, *Nano Lett.*, 2015**, 15**, 1421-1427.
7. J. Jiang, A. Zhang, L. Li and L. Ai, *J. Power Sources*, 2015**, 278**, 445-451.
8. Q. Yang, T. Li, Z. Lu, X. Sun and J. Liu, *Nanoscale*, 2014**, 6**, 11789-11794.
9. S. Chen, J. Duan, M. Jaroniec and S. Z. Qiao, *Angew. Chem. Int. Ed.*, 2013**, 52**, 13567-13570.
10. X. Long, J. Li, S. Xiao, K. Yan, Z. Wang, H. Chen and S. Yang, *Angew. Chem.*, 2014**, 126**, 7714-7718.
11. A. Sumboja, X. Ge, F. W. T. Goh, B. Li, D. Geng, T. S. A. Hor, Y. Zong and Z. Liu, *ChemPlusChem*, 2015**, 80**, 1341-1346.
12. D. U. Lee, H. W. Park, M. G. Park, V. Ismayilov and Z. Chen, *ACS Appl. Mater. Interfaces*, 2014**, 7**, 902-910.
13. Y. Li, M. Gong, Y. Liang, J. Feng, J. E. Kim, H. Wang, G. Hong, B. Zhang and H. Dai, *Nat. Commun.*, 2013**, 4**, 1805.
14. Z. Chen, A. Yu, R. Ahmed, H. Wang, H. Li and Z. Chen, *Electrochim. Acta*, 2012**, 69**, 295-300.
15. M. Prabu, K. Ketpang and S. Shanmugam, *Nanoscale*, 2014**, 6**, 3173-3181.
16. B. Li, X. Ge, F. W. T. Goh, T. S. A. Hor, D. Geng, G. Du, Z. Liu, J. Zhang, X. Liu and Y. Zong, *Nanoscale*, 2015**, 7**, 1830-1838.
17. G. Du, X. Liu, Y. Zong, T. S. A. Hor, A. Yu and Z. Liu, *Nanoscale*, 2013**, 5**, 4657-4661.
18. D. U. Lee, J. Scott, H. W. Park, S. Abureden, J.-Y. Choi and Z. Chen, *Electrochem. Commun.*, 2014**, 43**, 109-112.
19. H. Ma and B. Wang, *RSC Adv.*, 2014**, 4**, 46084-46092.
20. Z. Chen, A. Yu, D. Higgins, H. Li, H. Wang and Z. Chen, *Nano Lett.*, 2012**, 12**, 1946-1952.
21. F. W. T. Goh, Z. Liu, X. Ge, Y. Zong, G. Du and T. S. A. Hor, *Electrochim. Acta*, 2013**, 114**, 598-604.
22. X. Ge, Y. Liu, F. W. T. Goh, T. S. A. Hor, Y. Zong, P. Xiao, Z. Zhang, S. H. Lim, B. Li, X. Wang and Z. Liu, *ACS Appl. Mater. Interfaces*, 2014**, 6**, 12684-12691.
23. Y. Zhan, C. Xu, M. Lu, Z. Liu and J. Y. Lee, *J. Mater. Chem. A*, 2014**, 2**, 16217-16223.