Electronic Supplementary Information

Spent alkaline battery-derived manganese oxides as efficient oxygen electrocatalysts for Zn-air batteries

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Fig. S1. Flow chart of spent ZMB dismantling process in obtaining the cathode material.

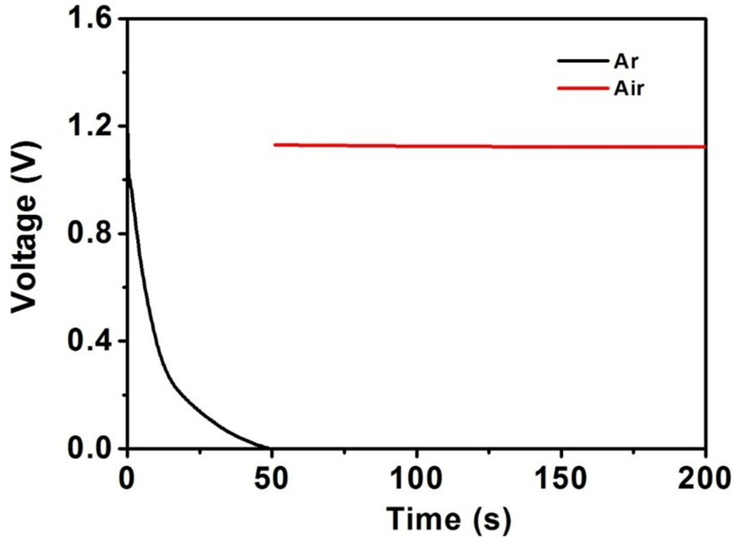

Fig. S2. The electrochemical profiles of zinc air batteries in Ar atmosphere and subsequent ambient air atmosphere to confirm the electrocatalytic performance of the Treated-AL-CA catalyst.

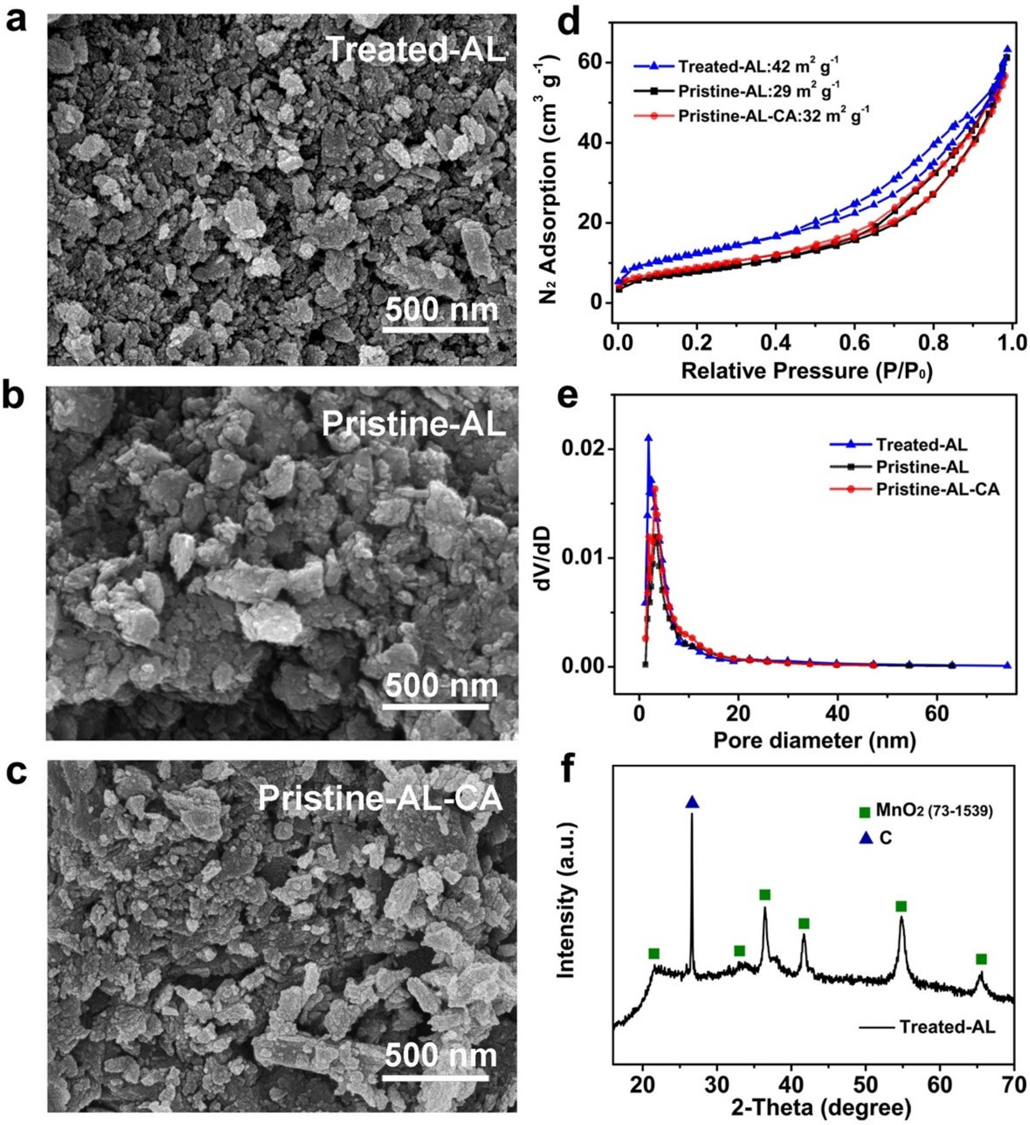

Fig. S3. SEM images of the (a) Treated-AL, (b) Pristine-AL and (c) Pristine-AL-CA. (d) N_2 adsorption/desorption isotherm measured at 77 K with (e) the corresponding pore size distribution. (f) XRD pattern of the Treated-AL sample.

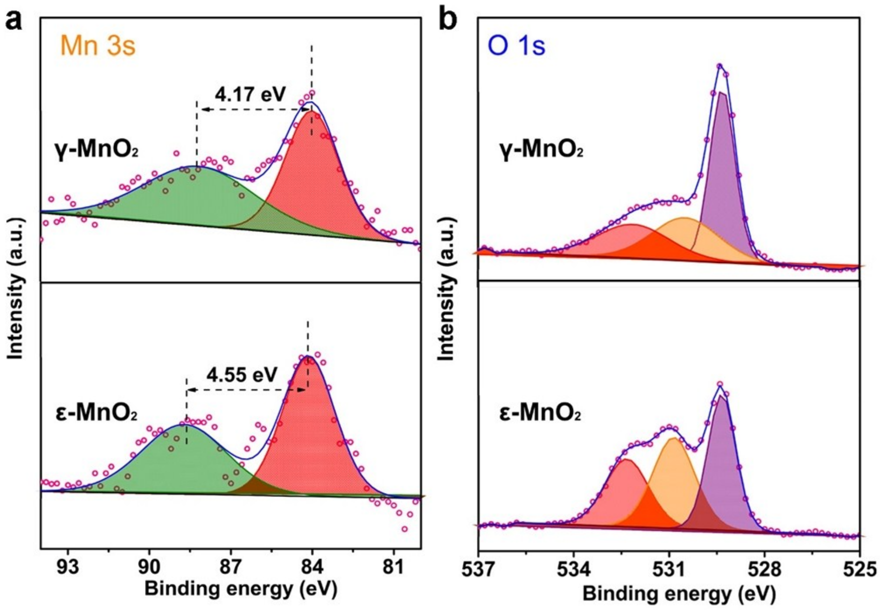

Fig. S4 XPS spectra of (a) Mn 3s and (b) O 1s for γ-MnO_2 and ε-MnO_2.

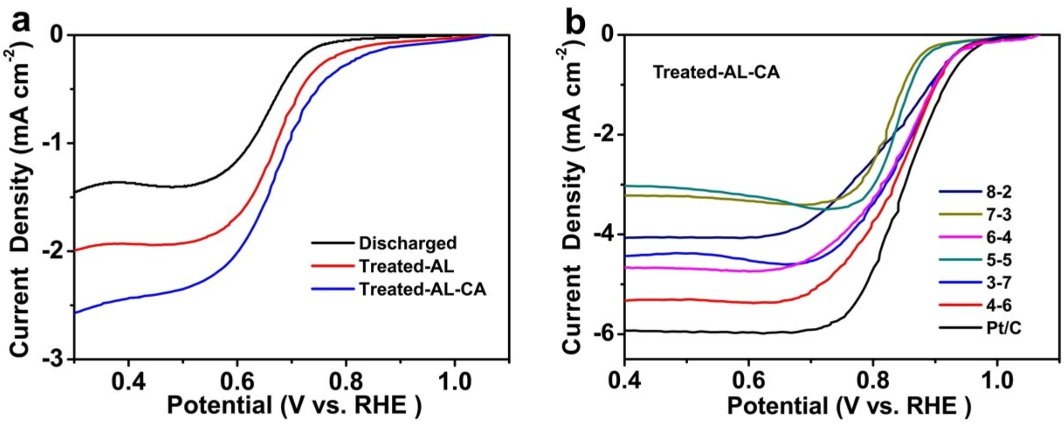

Fig. S5. (a) ORR activities of MnO_2 electrodes at different states in primary Zn-MnO_2 battery: the discharged electrode without (Discharged) and with post-treatment (Treated-AL and Treated-AL-CA). (b) ORR curves of Treated-AL-CA sample with varied sample:carbon ratios. The plots were measured at a rotation speed of 1600 rpm in 0.1 M KOH using a scan rate of 5 mV s^{-1}. The curve of 20% Pt/C is included for comparison.

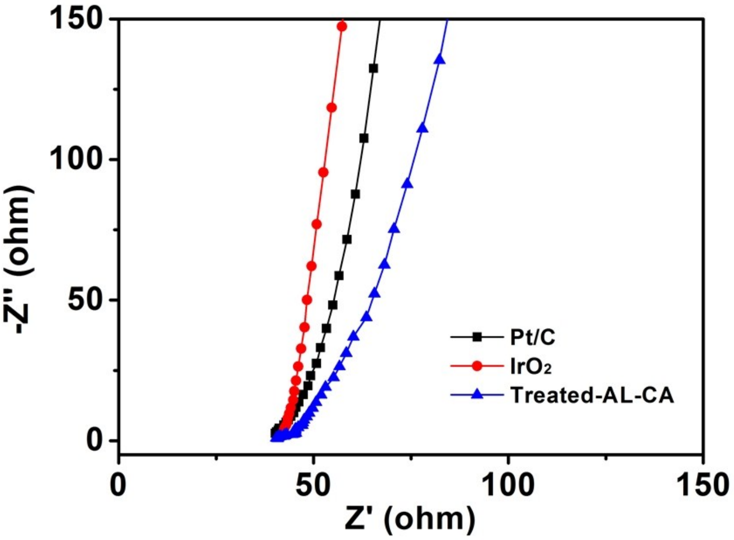

Fig. S6. Electrochemical impedance spectroscopies of Pt/C, IrO_2 and Treated-AL-CA at open circuit potential.

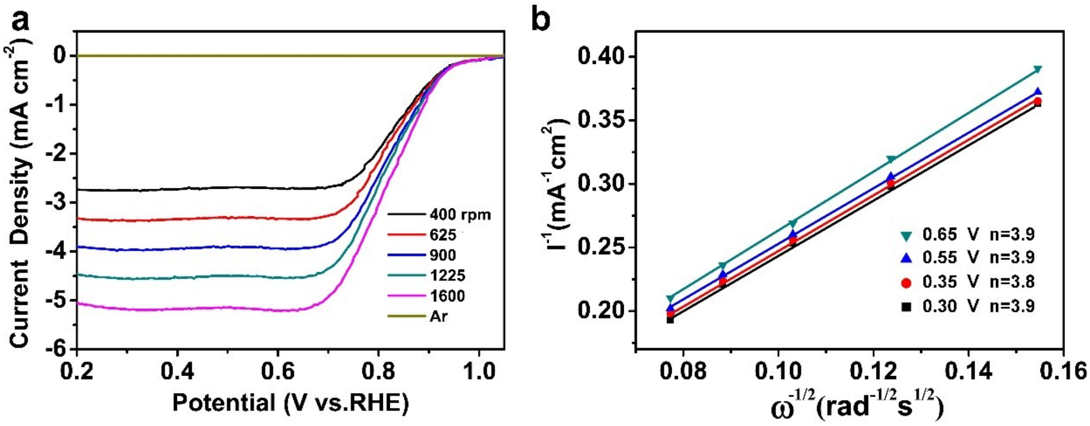

Fig. S7. (a) LSVs of Treated-AL-CA recorded in Ar- and O_2-saturated 0.1 M KOH solution. (b) Koutechy-Levich curves of Treated-AL-CA at various potentials.

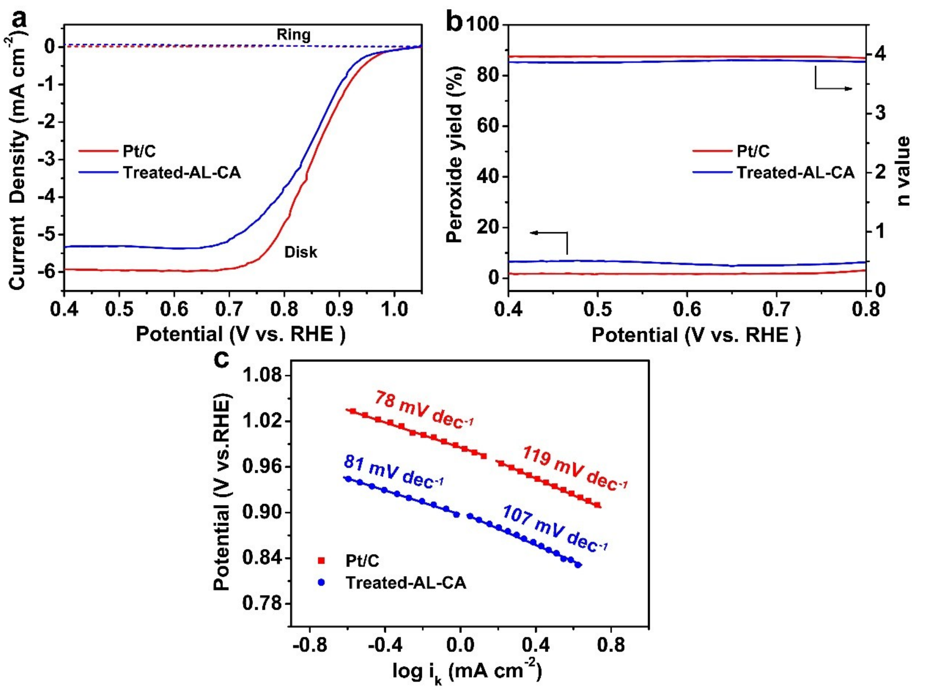

Fig. S8. (a) The polarization plots of Treated-AL-CA and Pt/C recorded at 1600 rpm in O_2-saturated 0.1 M KOH solution. (b) the electron transfer number (dotted line) and percentage of peroxide (solid line). (c) Tafel plots of Treated-AL-CA and Pt/C at different potentials.

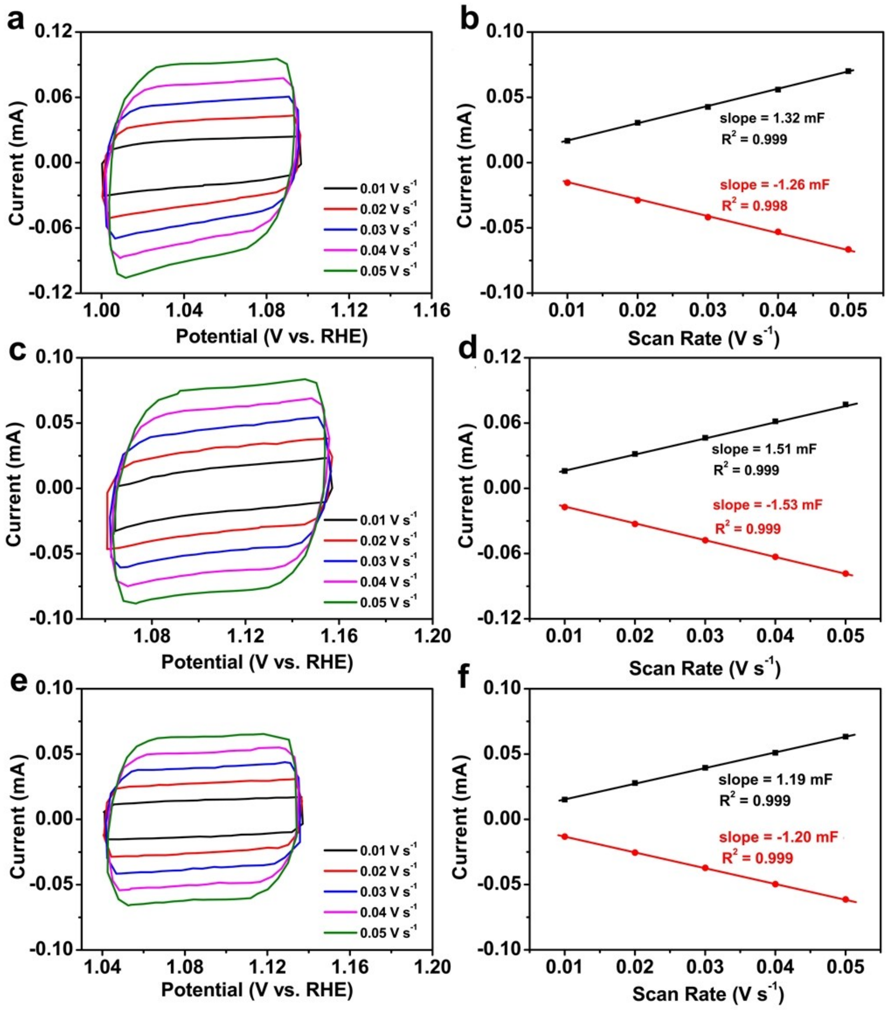

Fig. S9. Double-layer capacitance measurements for evaluating ECSA of Treated-AL-CA (a,b), Pt/C (c,d) and IrO_2 (e,f) from cyclic voltammetry in Ar-saturated 0.1 M KOH in non-faradaic region.

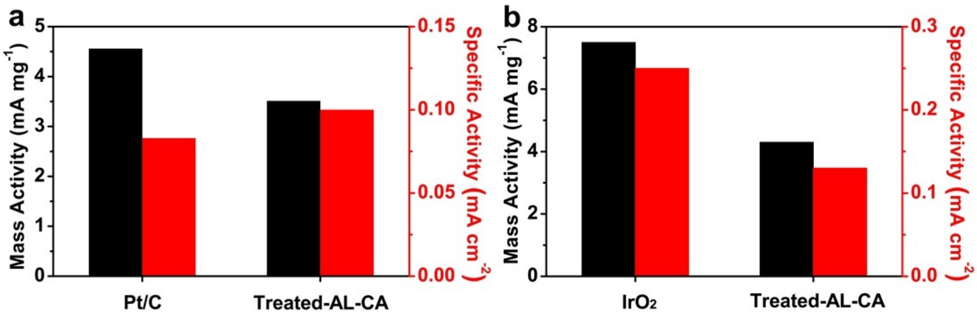

Fig. S10. (a) ORR mass activity and specific activity of Pt/C and Treated-AL-CA at 0.9 V. (b) OER mass activity and specific activity of IrO_2 and Treated-AL-CA at 1.65 V.

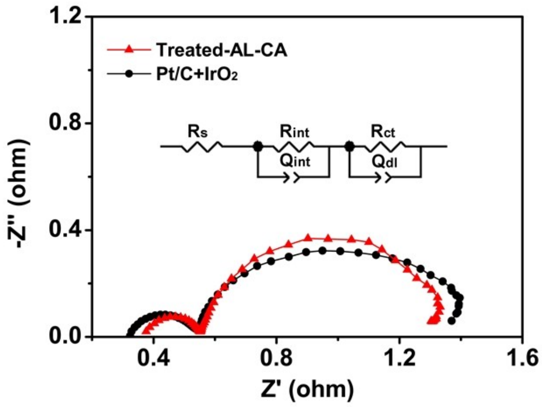

Fig. S11. Nyquist plots obtained from EIS measurements using Treated-AL-CA and Pt/C+IrO_2 air electrode in Zn-air batteries. The Nyquist plots of Treated-AL-CA and Pt/C+IrO_2 are composed of two semicircles, which can be fitted to the given equivalent circuit model with elements of R_s (solution resistance), R_{int} (solid-electrolyte interface resistance), R_{ct} (charge transfer resistance), and Q_{int}/Q_{dl} (constant phase elements).[1]

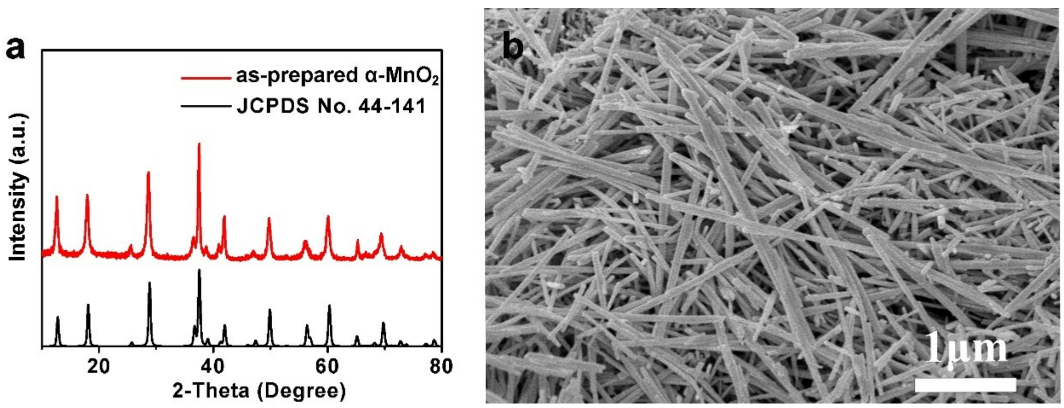

Fig. S12. (a) XRD patterns and (b) SEM image of the prepared α-MnO_2 nanowires.

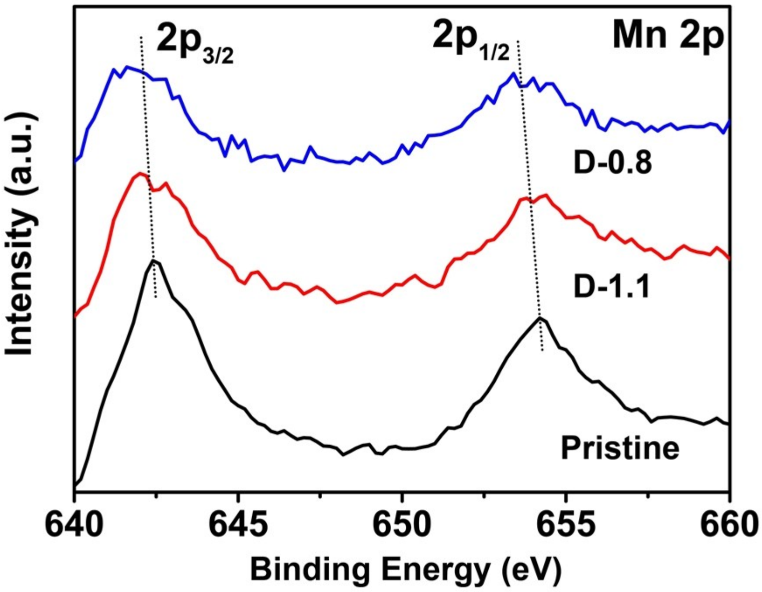

Fig. S13. XPS spectra of Mn 2p of the α-MnO_2 cathodes at different discharge states.

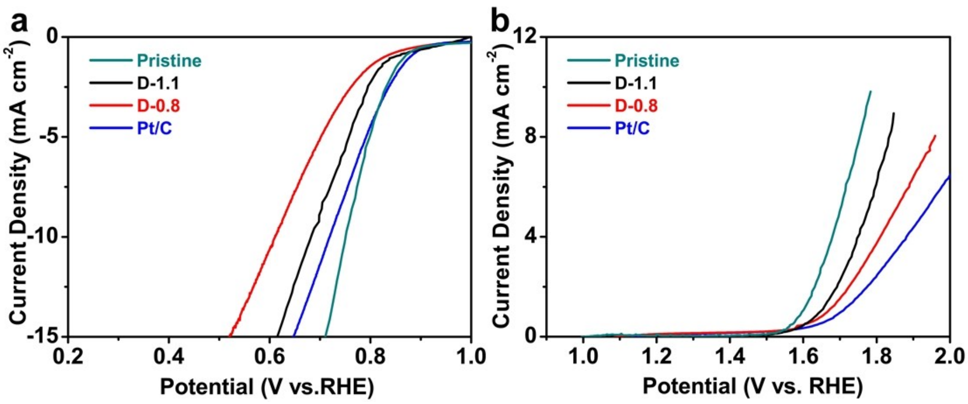

Fig. S14. (a) ORR and (b) OER voltammograms of the cathodes at different discharge states measured at O_2-saturated 0.1 M KOH with a scan rate of 5 mV s^{-1}. Curves of commercial 20% Pt/C catalysts are also shown for comparison.

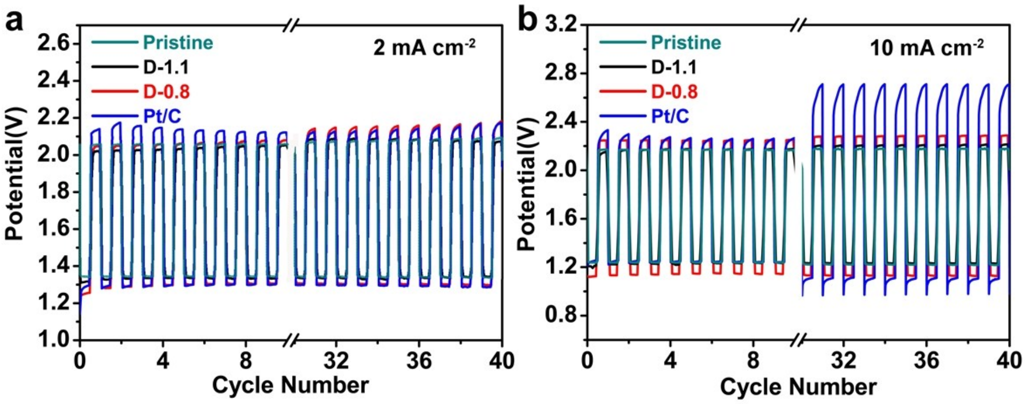

Fig. S15. Charge/discharge cycling curves of the rechargeable ZABs using α-MnO_2-resulted cathodes at current densities of 2 and 10 mA cm^{-2} in fixed cycle periods of 30 min and 10 min per cycle, respectively. The electrochemical performance of ZABs utilizing the commercial 20% Pt/C catalysts is also involved.

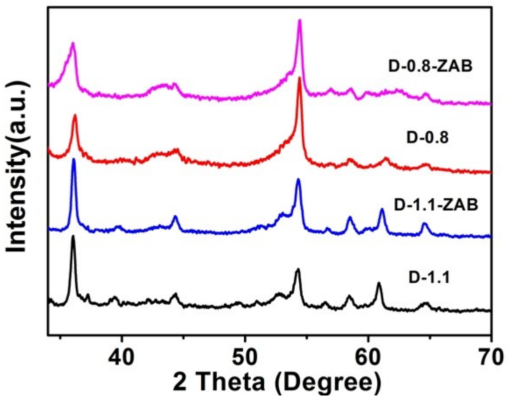

Fig. S16. XRD patterns of the electrodes before (D-1.1, D-0.8) and after (D-1.1-ZAB, D-0.8-ZAB) the Zn-air battery testing.

Table S1. Comparison of the electrocatalytical ORR activity with reported representative manganese oxides.

Sample	E_{onset} (V)	E_{half} (V)	Rotating Speed (rpm)	Ref.
ε-MnO_2/Vulcan C	0.94	0.85	1600	This work
ε-MnO_2/MOF(Fe)	0.84	0.64	1600	2
α-MnO_2 hierarchical stars	0.84	0.72	1600	3
α-MnO_2 nanowires	0.94	0.72	1600	4
β-MnO_2	0.84	0.69	1600	5
MnO_2 nanofilm	0.94	0.85	1600	6
Amorphous MnO_x on KB	0.82	0.75	3200	7

Table S2. The value of the equivalent circuit elements based on the EIS measurements of Treated-AL-CA and Pt/C+IrO_2 electrodes in rechargeable zinc-air battery.

element	Treated-AL-CA	Pt/C+IrO_2
R_s (Ω)	0.37	0.32
R_{int} (Ω)	0.15	0.21
R_{ct} (Ω)	0.84	0.88
Q_{int} (S s^n)	1.00	0.91
Q_{dl} (S s^n)	0.86	0.82

References:

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