

Supplementary information

Bifunctional hydrous RuO₂ nanocluster electrocatalyst embedded in carbon matrix for efficient and durable operation of rechargeable zinc-air batteries

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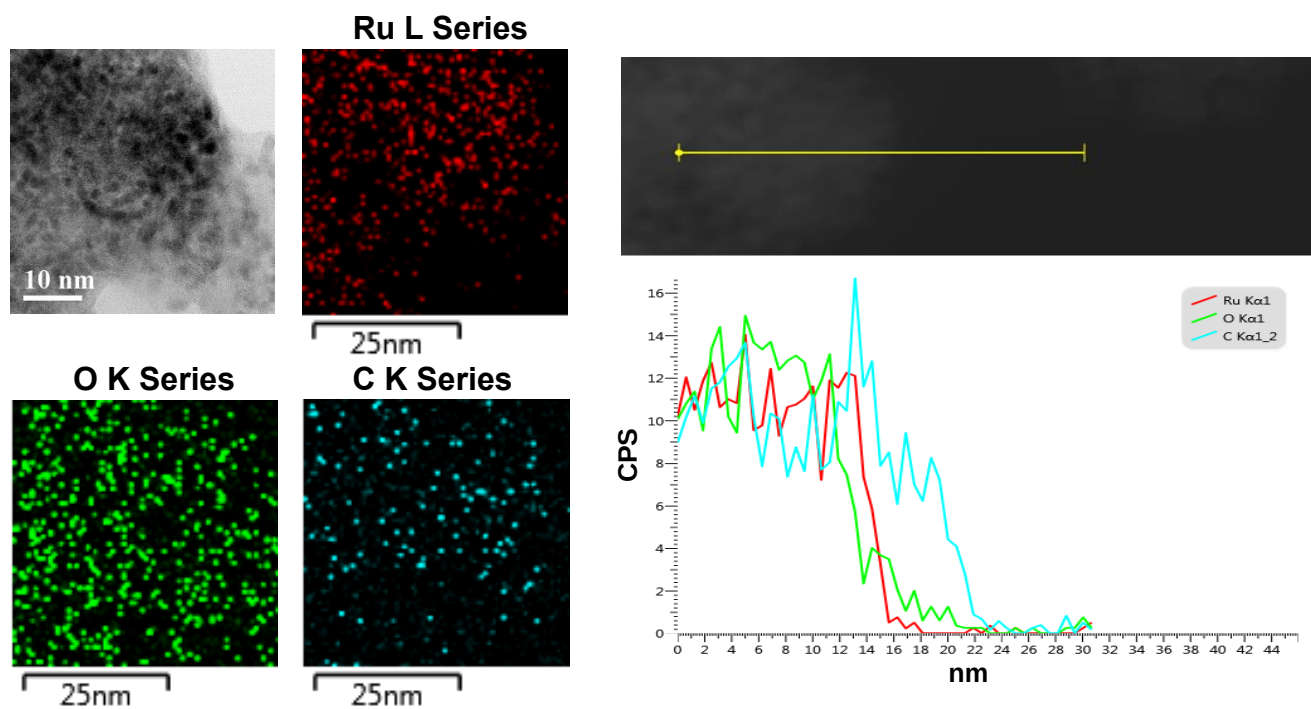


Figure S1. Scanning transmission electron microscopy (STEM) image, energy-dispersive X-ray spectroscopy (EDS) mapping of Ru, O and C and line mapping.

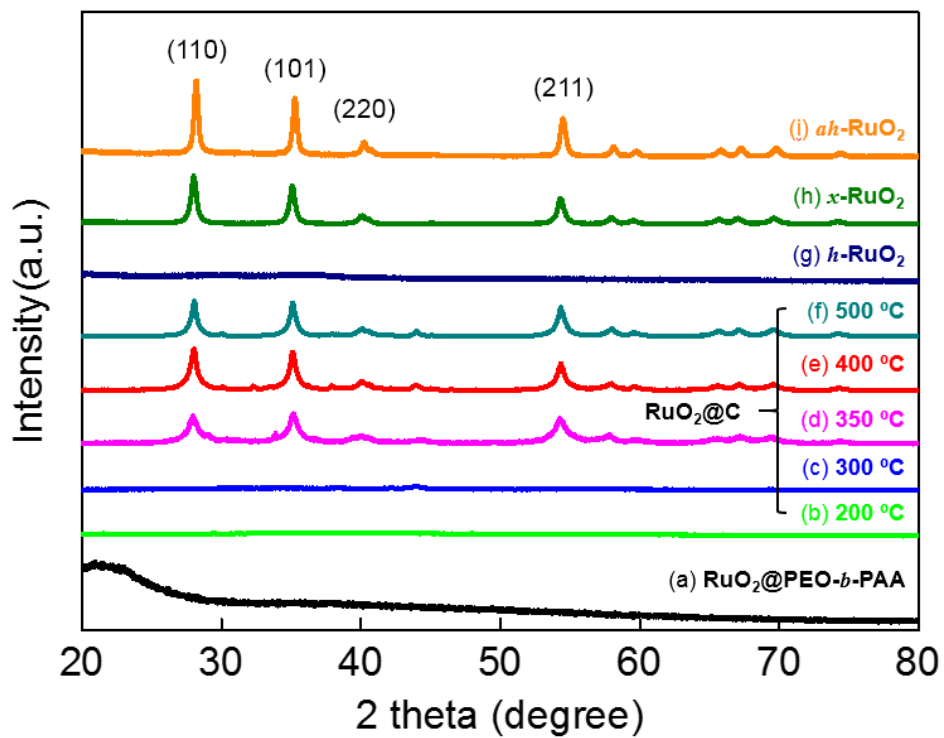


Figure S2. XRD patterns. (a) $\text{RuO}_2@\text{PEO-}b\text{-PAA}$. (b to f) $\text{RuO}_2@\text{C}$ obtained after annealing $\text{RuO}_2@\text{PEO-}b\text{-PAA}$. The annealing temperatures were indicated. (g) $h\text{-RuO}_2$ = hydrous RuO_2 (x = high in $\text{RuO}_2 \cdot x\text{H}_2\text{O}$). (h) $x\text{-RuO}_2 = h\text{-RuO}_2$ thermally treated at 400 °C. (i) $ah\text{-RuO}_2$ = anhydrous RuO_2 (x approaching 0 in $\text{RuO}_2 \cdot x\text{H}_2\text{O}$).

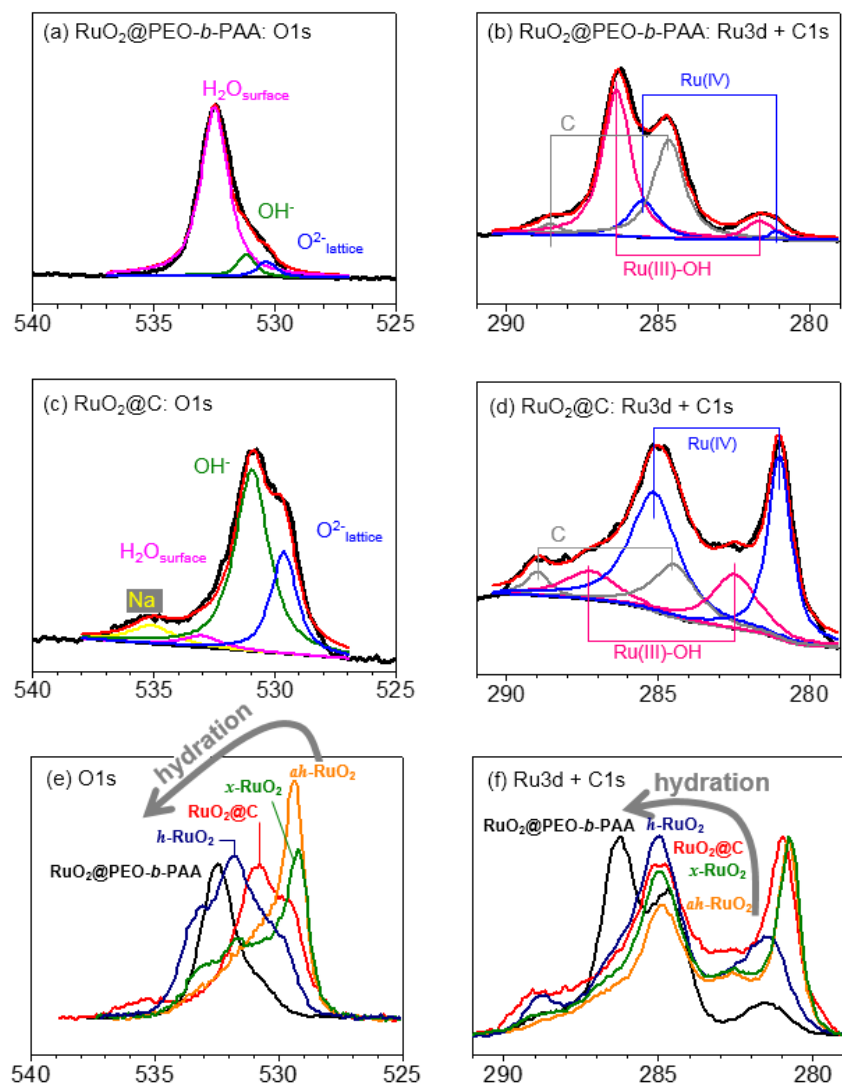


Figure S3. X-ray photoelectron spectra. Abscissa = binding energy (eV), ordinate = intensity in arbitrary unit. (a and b) O1s (a) and Ru3d + C1s (b) spectra of RuO₂@PEO-*b*-PAA after drying. (c and d) O1s (c) and Ru3d + C1s (d) spectra of RuO₂@C obtained by annealing RuO₂@PEO-*b*-PAA at 400 °C. 3 component spectra were used for deconvoluting O1s spectra: lattice oxygen (O²⁻) at 530.4 eV; hydroxyl group (OH⁻) at 531.2 eV; and surface-bound water (H₂O) at 532.5 eV. 6 component spectra were used for deconvoluting Ru3d and C1s spectra: Ru (IV) indicating RuO₂ at 281.0 and 285.5 eV; Ru(III) of hydrous Ru(III)-OH at 281.7 and 286.4 eV; C 1s at 284.6 and 288.5 eV. (e and f) O1s (e) and Ru3d + C1s (f) spectra of RuO₂@PEO-*b*-PAA, RuO₂@C, *ah*-RuO₂, *h*-RuO₂ and *x*-RuO₂.

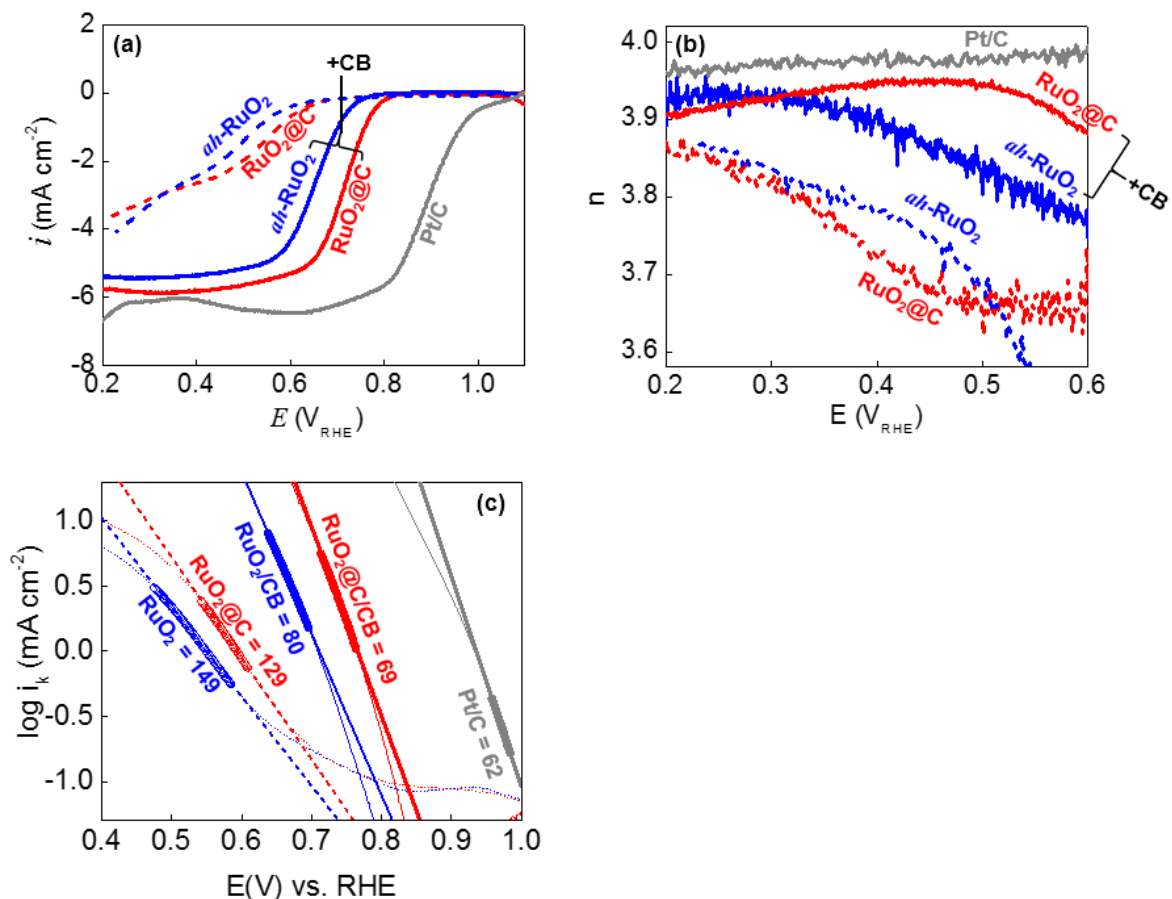


Figure S4. ORR in O₂-saturated 0.1 M KOH (aq). (a) ORR polarization curves at 1600 rpm and 10 mV s⁻¹. (b) Electron transfer number (n). (c) Tafel plots. Mass-transfer-corrected currents (i_k) were used. Tafel slopes (b) were indicated in mV dec⁻¹.

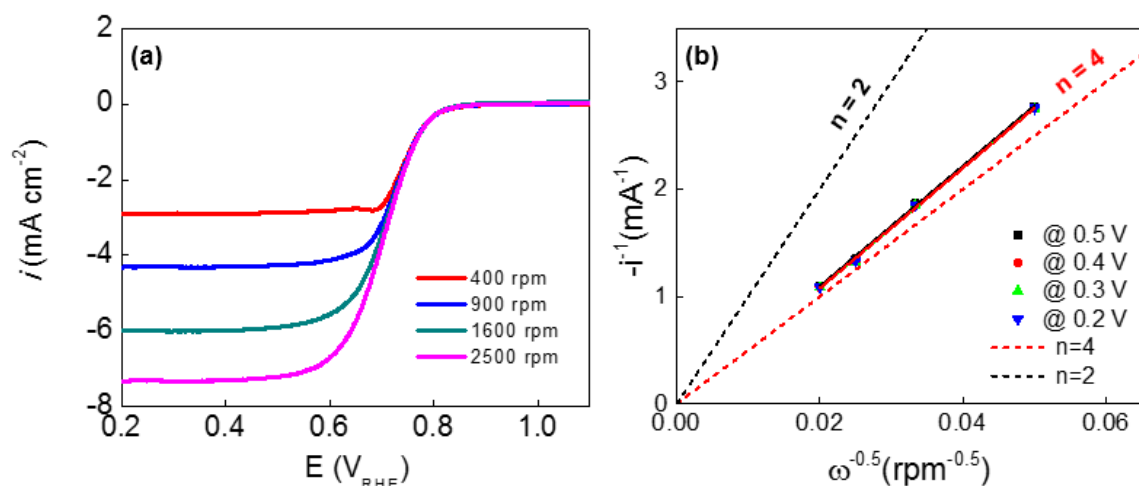


Figure S5. (a) ORR polarization curves of RuO₂@C/CB at various rotating speeds. (b) Koutecky-Levich plots of ORR on RuO₂@C/CB at various potentials. Dashed lines indicated the lines for two and four electron transfer cases ($n = 2$ and 4). The data for the dashed lines were calculated by Koutecky-Levich equation with the following values of parameters: bulk concentration of oxygen (C_{O^*}) = 1.21 mol m⁻³, diffusivity of oxygen (D_{O}) = 1.87×10⁻⁹ m²·s⁻¹ and kinematic viscosity (ν) = 1 × 10⁻⁶ m² s⁻¹.

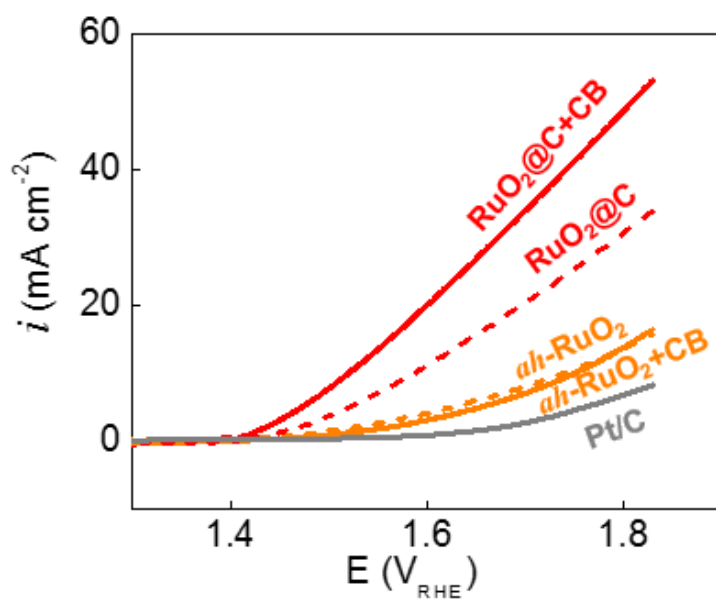


Figure S6. OER in N_2 -saturated 0.1 M KOH (aq). OER polarization curves at 1600 rpm in the first potential sweep cycles at 10 mV s^{-1} .

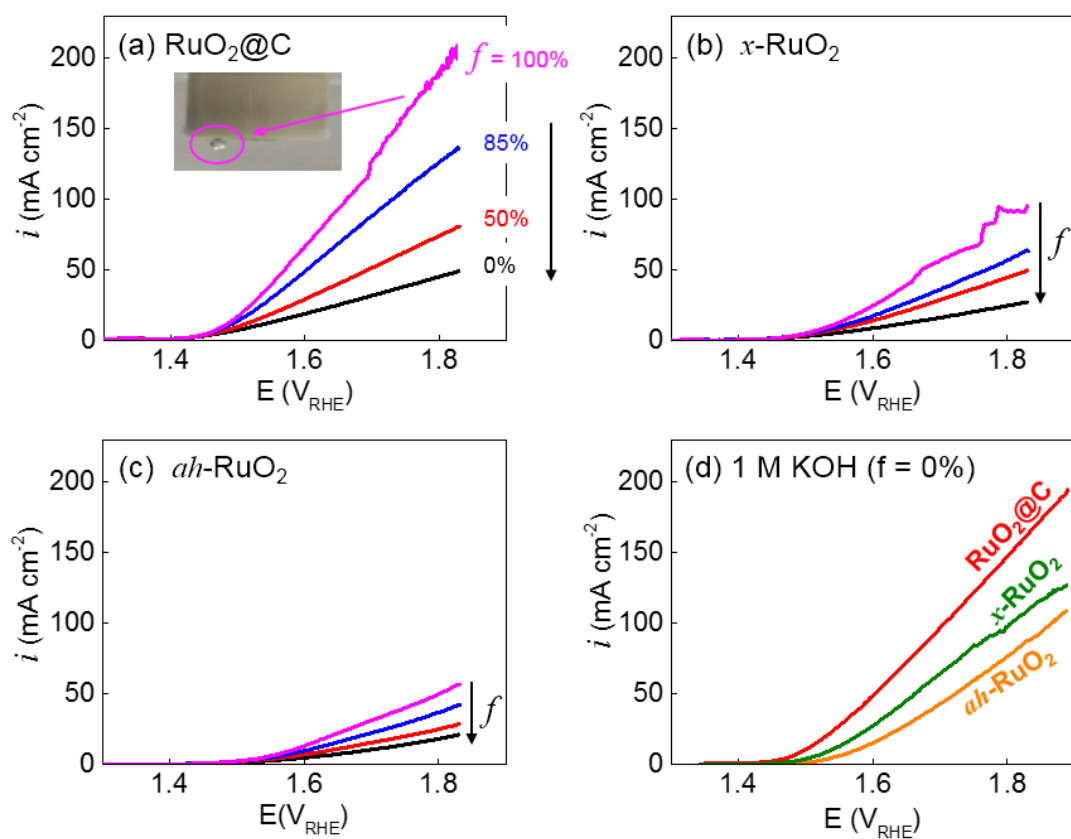


Figure S7. IR-compensated OER polarization at 10 mV s⁻¹ on 1600 rpm. (a to c) 0.1 M KOH with various percentages of IR compensation f . (d) 1 M KOH at $f = 0\%$. The potential shift corrected by the IR compensation factor f affected the current values at a fixed potential and the onset potential seriously. Therefore, we should use the IR compensation function carefully and indicate the value of f .

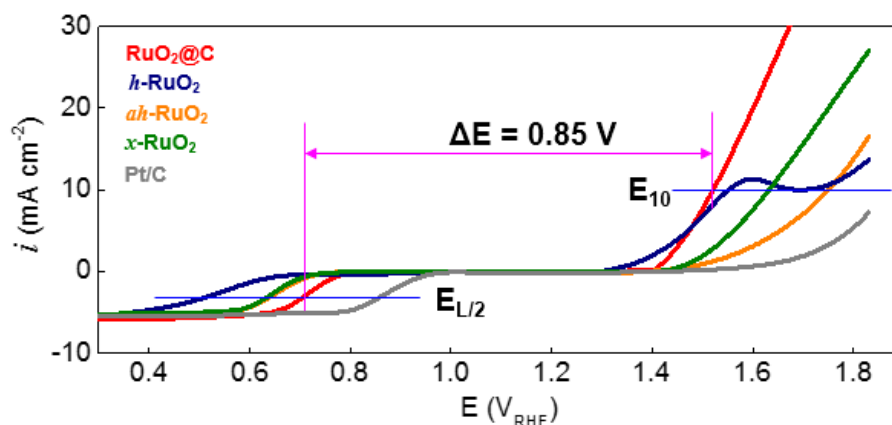


Figure S8. ORR and OER in 0.1 M KOH. The overall polarization curves of ORR and OER.

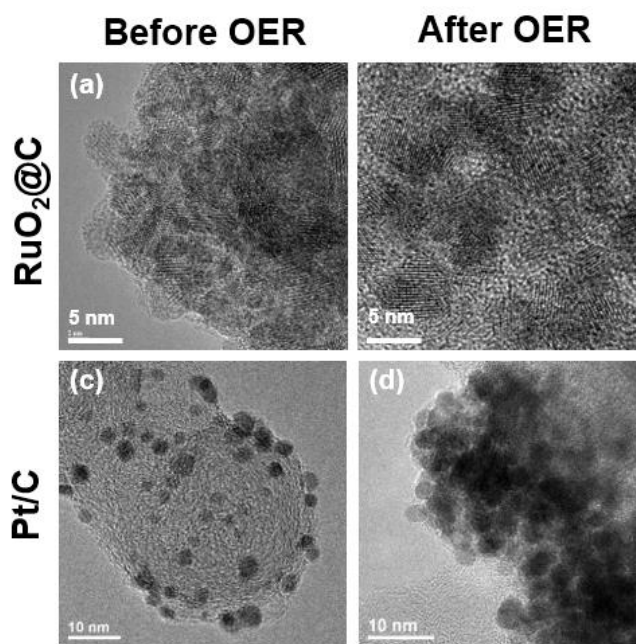


Figure S9. OER stability. (a to d) TEM images showing morphological changes of catalysts between before and after OER at 1.73 V_{RHE} for 1 h in 0.1 M KOH (aq).

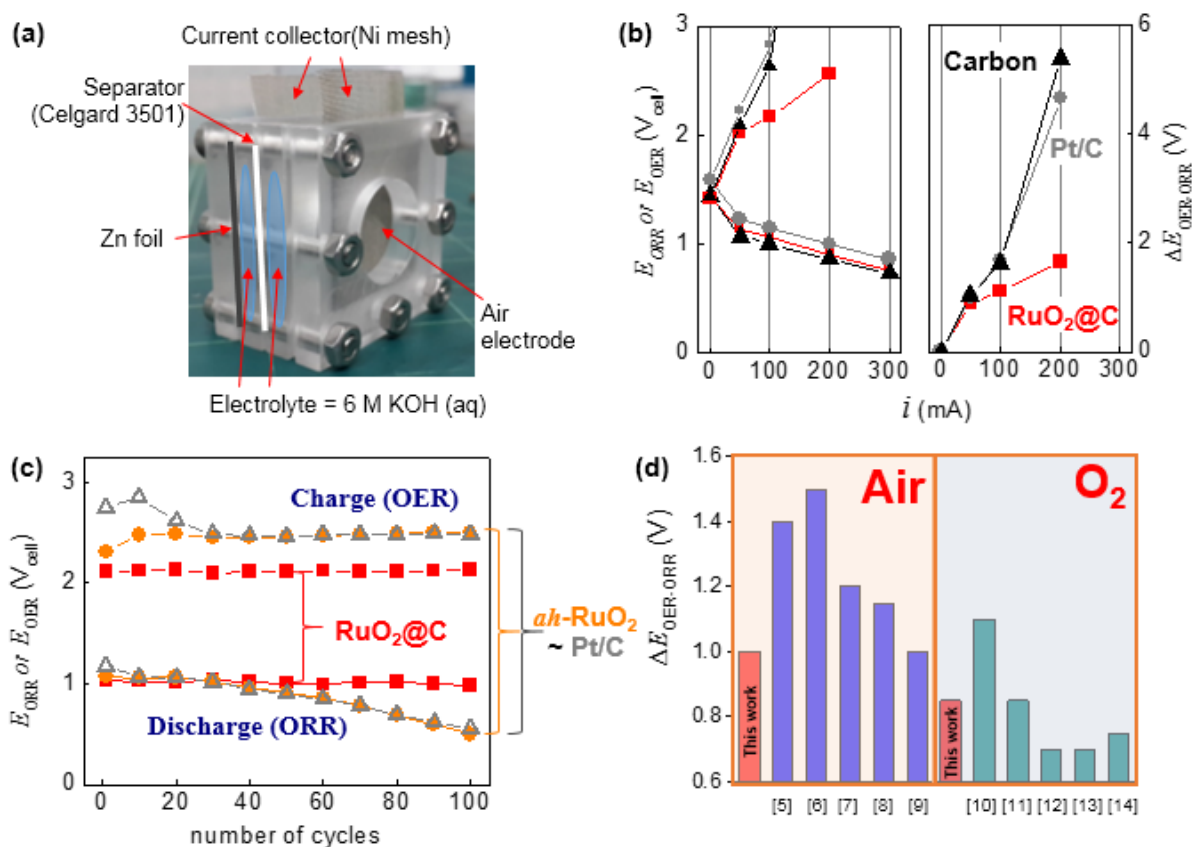


Figure S10. Zn-air battery cells. (a) The home-made Zn-air cell. Geometric area of air electrode = 2.2 cm^2 . (b) The ORR and OER potentials (E_{ORR} or E_{OER} in the left panel) and the potential gaps between ORR and OER ($\Delta E_{\text{OER-ORR}}$) calculated from E_{ORR} and E_{OER} as a function of current. Data were taken from Figure 4a and b. (c) Cell potentials during discharge and charge. Refer to Figure 4c and d for its full potential profiles. (d) Comparison of $\Delta E_{\text{OER-ORR}}$ between $\text{RuO}_2\text{@C}$ in this work and other electrocatalysts in other works [5-14]. The details were given in Table S2. The cells were categorized to groups in terms of fuels. 20 % and 100 % of molecular oxygen were used for Zn-air cells and Zn- O_2 cells, respectively.

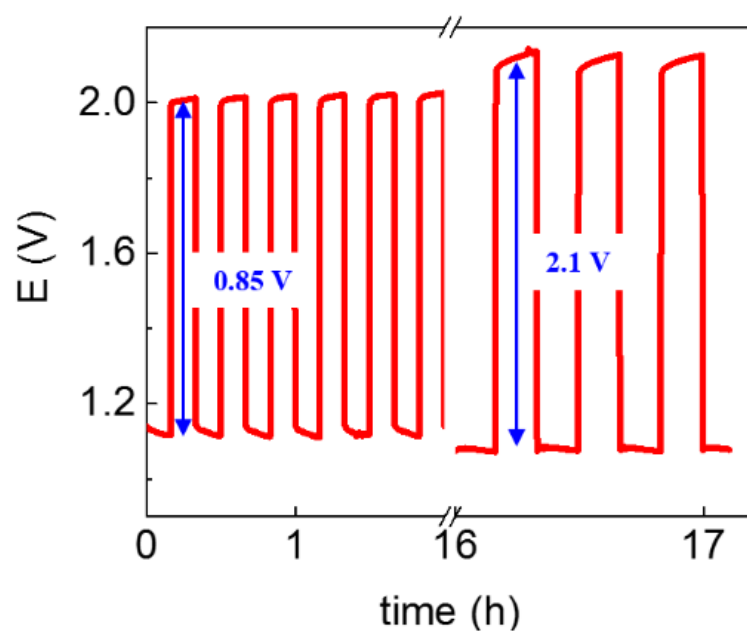


Figure S11. Galvanostatic charge/discharge cycles at 20 mA cm^{-2} in O_2 atmosphere at 1 atm.

Table S1. OER and ORR polarization.

Catalysts	ORR ^a			OER ^b		ΔE (V) ^c	Reference
	$E_{L/2}$ (V _{RHE})	$i_{L/2}$ (mA cm ⁻²)	n	E_{10} (V _{RHE})			
Pt/C	0.90	-3.0	~4	-	-	-	This work
RuO ₂ @C	0.70	-3.0	3.8~3.9	1.55 1.48, 1.47*	0.85		This work
ah-RuO ₂	0.65	-2.7	3.6~3.9	1.75 1.60, 1.58*	1.10		This work
RuO ₂	0.56	-1.2	~2	1.76	1.20		[1]
RuO ₂	0.40	-2.5	-	1.64	1.24		[2]
RuO ₂	0.42	-1.5	-	1.60*	1.18		[3]
RuO ₂	-	-	-	1.80	-		[4]

^a $E_{L/2}$ = Half wave potential at the half of limiting current ($i_{L/2}$). ^b E_{10} = Potential obtained at +10 mA cm⁻². ^c $\Delta E = |E_{L/2} - E_{10}|$. * Uncompensated IR was corrected in potentials. 85 % and 100 % compensation ($f = 85$ and 100 %) were used for the values with the asterisks in our work while the value of f was not reported in reference 3.

Table S2. Performance of rechargeable zinc-air batteries of various electrocatalysts published in the literature.

Catalyst	Charge (V) @ 20 mAcm ⁻²	Discharge (V) @ 20 mAcm ⁻²	Gap (V)	Cycle test condition	Atmosphere	Reference
RuO ₂ nanoclusters embedded in carbon matrix	2.05	1.05	1.0	20min per cycle, 150 cycles, @ 20 mA/cm ²	Air	This work
LaNiO ₃ microspheres / N-CNT N-CNT = nitrogen-doped carbon nanotube	2.4	1.0	1.4	10 min per cycle, 75 cycles @ 17.6 mA/cm ²	Air	[5]
MnO ₂ nanotube / N-CNT	2.6	1.1	1.5	10 min per cycle, 50 cycles, @ 20 mA	Air	[6]
Co ₃ O ₄ nanocrystals / N-CNT	2.2	1.0	1.2	10min per cycle, 240 cycles, @ 20 mA/cm ²	Air	[7]
Co ₃ O ₄ nanoparticle / modified MnO ₂ nanotubes	2.25	1.1	1.15	14 min per cycle, 60 cycles @ 15 mA/cm ²	Air	[8]
Co-doped TiO ₂	2.1	1.1	1.0	20 h per cycle, 37 cycles @ 20 mA/cm ²	Not specified	[9]
RuO ₂ nanoclusters embedded in carbon matrix	2.0	1.15	0.85	20min per cycle, 51 cycles, @ 20 mA/cm ²	O ₂ atmosphere	This work
cobalt and nitrogen embedded carbon nanotubes	2.2	1.1	1.1	10 min per cycle, 16 cycles @ 15 mA/cm ²	O ₂ atmosphere	[10]
CoO / N-CNT + NiFe LDH LDH = layered double hydroxide	2.05	1.2	0.85	240 min (4 hr) per cycle, 10 cycles @ 50.0 mA/cm ²	O ₂ purged	[11]
CoMn ₂ O ₄ nanoparticles anchored on N-doped rGO nanosheets	1.8	1.1	0.7	10 min per cycle, 100 cycles @ 20 mA/cm ²	O ₂ flow	[12]
1D-NiCo ₂ O ₄ nanostructures	1.8	1.1	0.7	40 min per cycle, 50 cycles @ 20.0 mA/cm ²	O ₂ flow	[13]
Co(II) _{1-x} Co(0) _{x/3} Mn(III) _{2x/3} S Nanoparticles / B/N-co-doped Mesoporous Nanocarbon	2.0	1.25	0.75	4 hr per cycle, 5 cycles @ 20 mA/cm ²	O ₂ purged	[14]

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