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Supporting Information

Structure-dependent electronic modulation of Pt on perovskite surfaces: bifunctional oxygen catalysts for rechargeable Zn–air batteries

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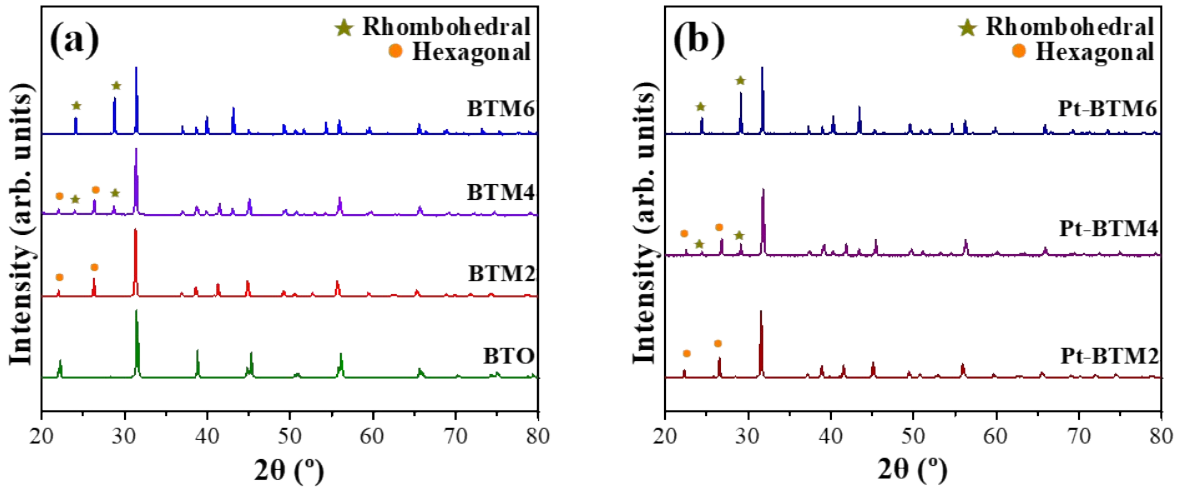

Fig. S1 XRD patterns of (a) BTMx and (b) Pt-BTMx.

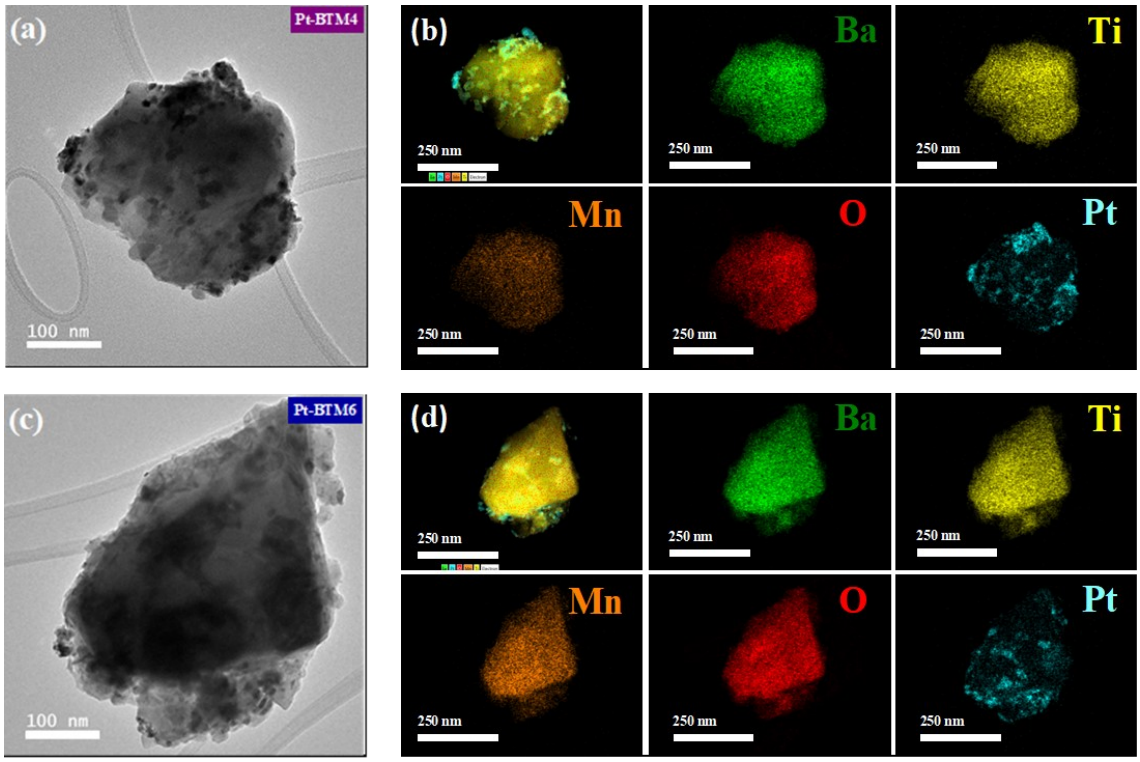

Fig. S2 TEM and EDS chemical mapping images of (a-b) Pt-BTM4 and (c-d) Pt-BTM6.

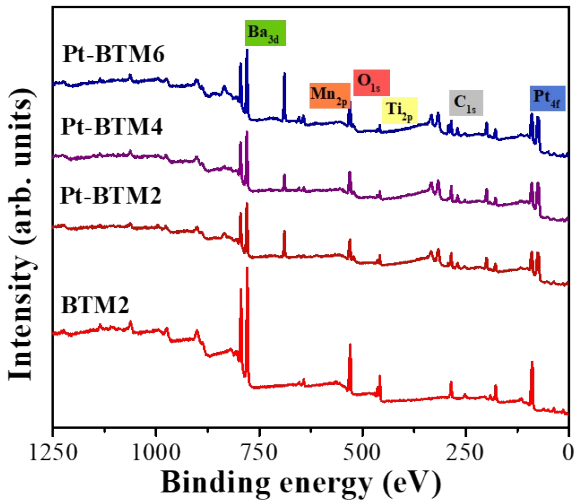

Fig. S3 Whole range XPS spectra of BTM2 and Pt-BTMx.

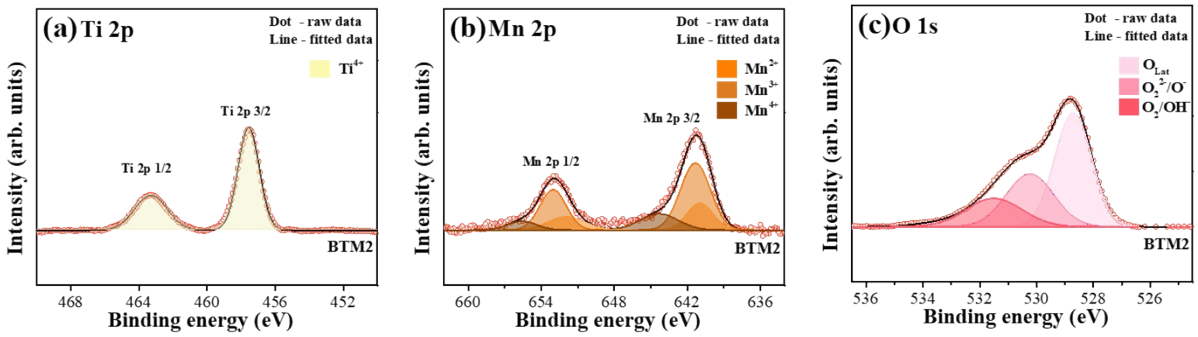

Fig. S4 High-resolution XPS spectra of BTM2, (a) Ti 2p, (b) Mn 2p and (c) O 1s.

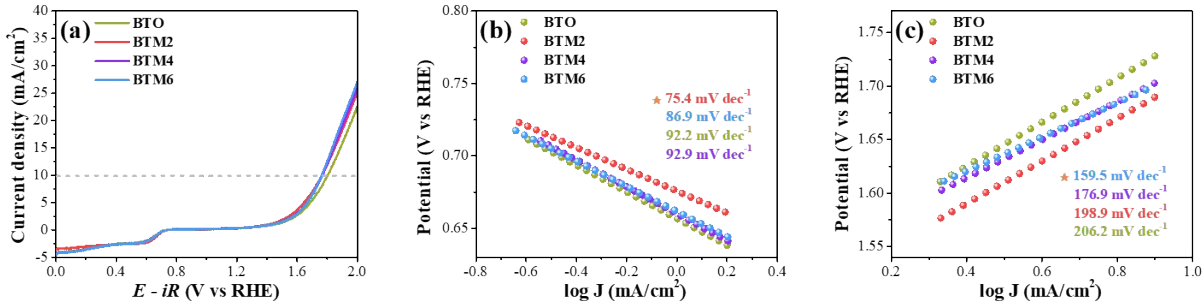

Fig. S5 (a) ORR and OER LSV plots of BTMx, (b) ORR and (c) OER Tafel plots obtained from (a).

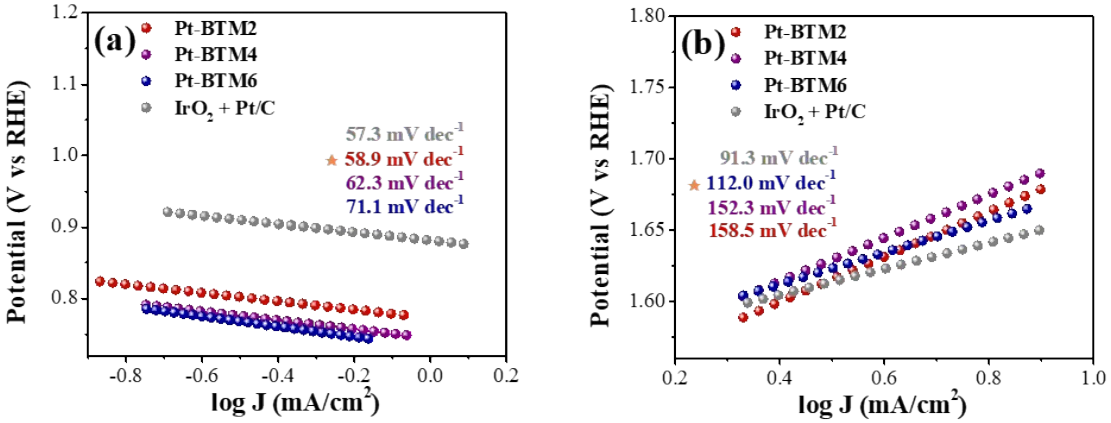

Fig. S6 (a) ORR and (b) OER Tafel plots of Pt-BTMx and commercial catalyst obtained from LSV plots.

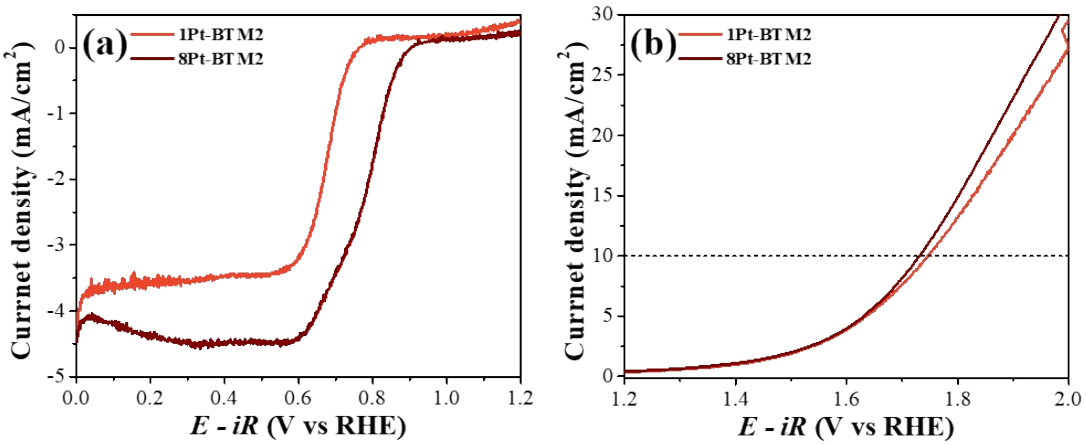

Fig. S7 LSV plots of 1wt% Pt and 8wt% Pt loaded BTM2, (a) ORR and (b) OER using RDE

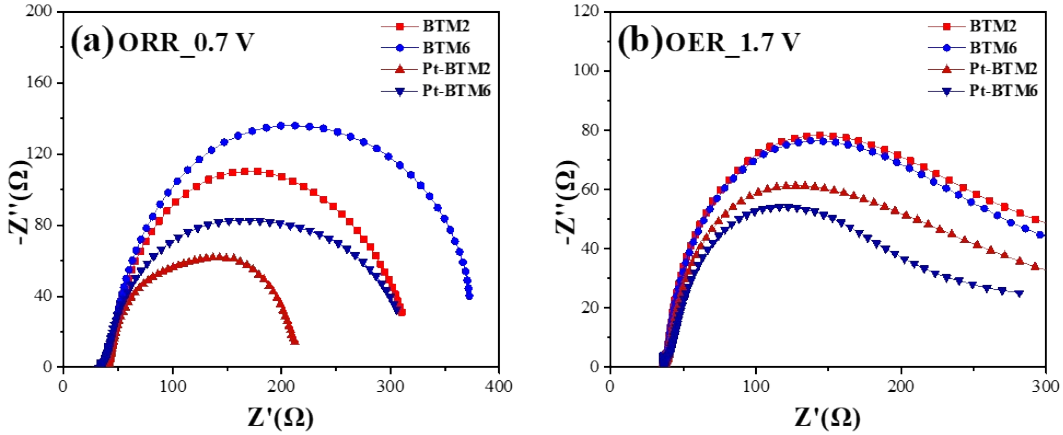

Fig. S8 EIS spectra of BTM2, BTM6, Pt-BTM2 and Pt-BTM6 potential at (a) 0.7 V and (b) 1.7 V, tested by RDE system.

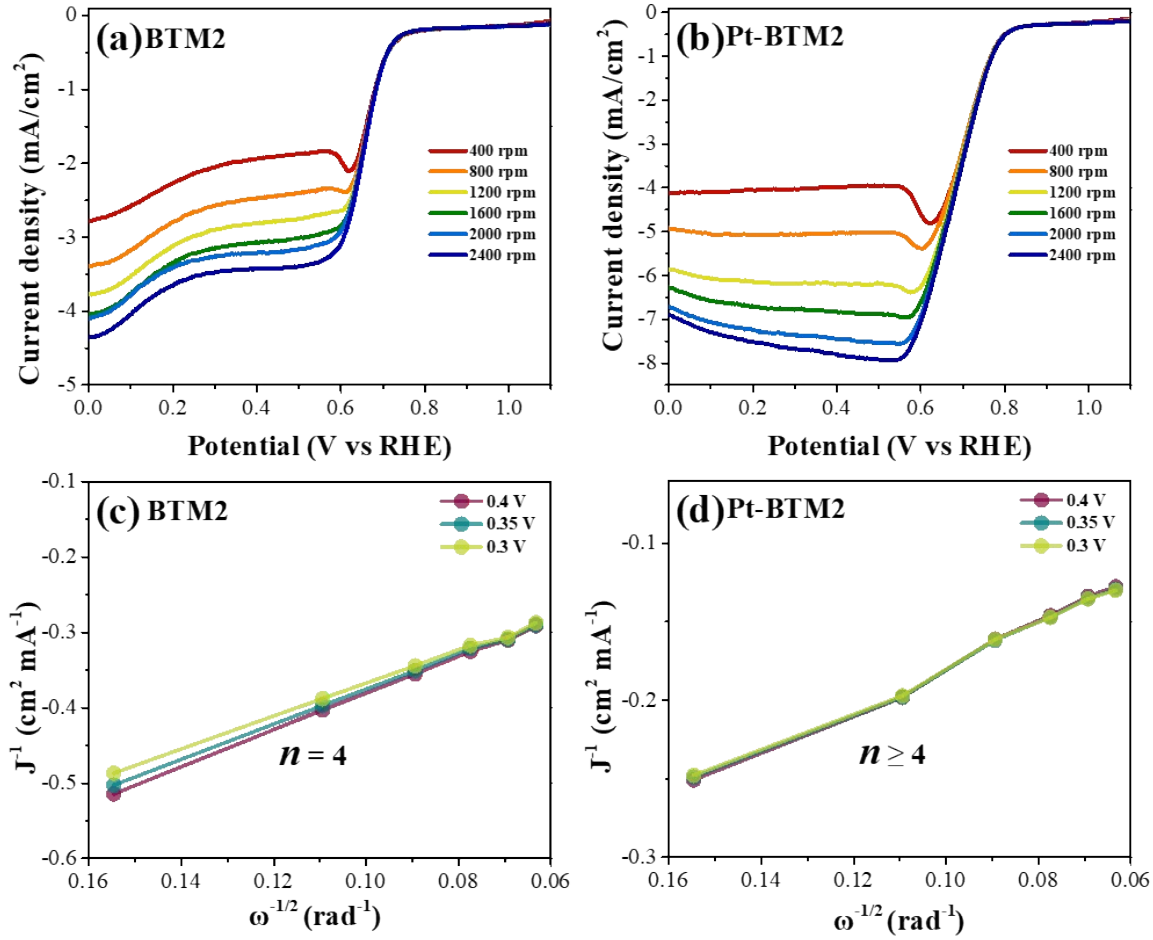

Fig. S9 LSV curves of the (a) BTM2 and (b) Pt-BTM2 at each rotation speeds (400-2400 rpm), respectively. Corresponded K-L plots of (c) BTM2 and (d) Pt-BTM2.

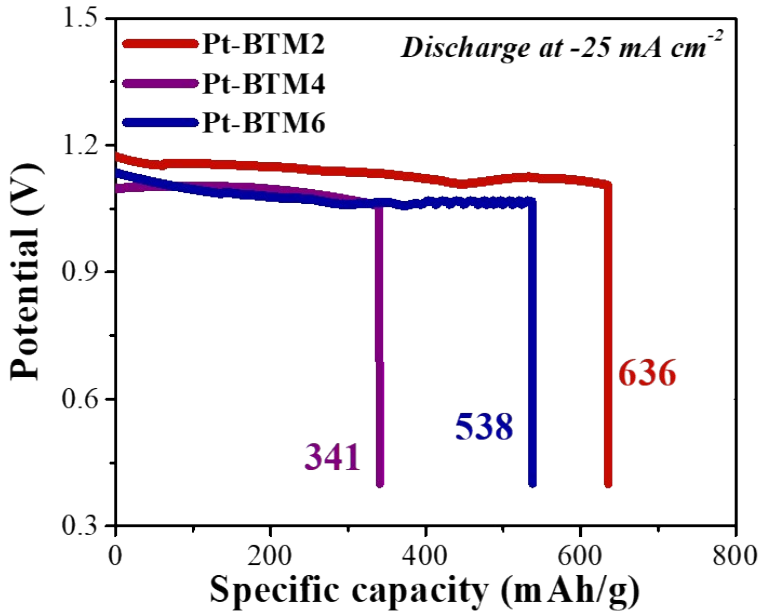

Fig. S10 Specific capacity of Pt-BTMx at a discharge current density of -25 mA cm^{-2}.

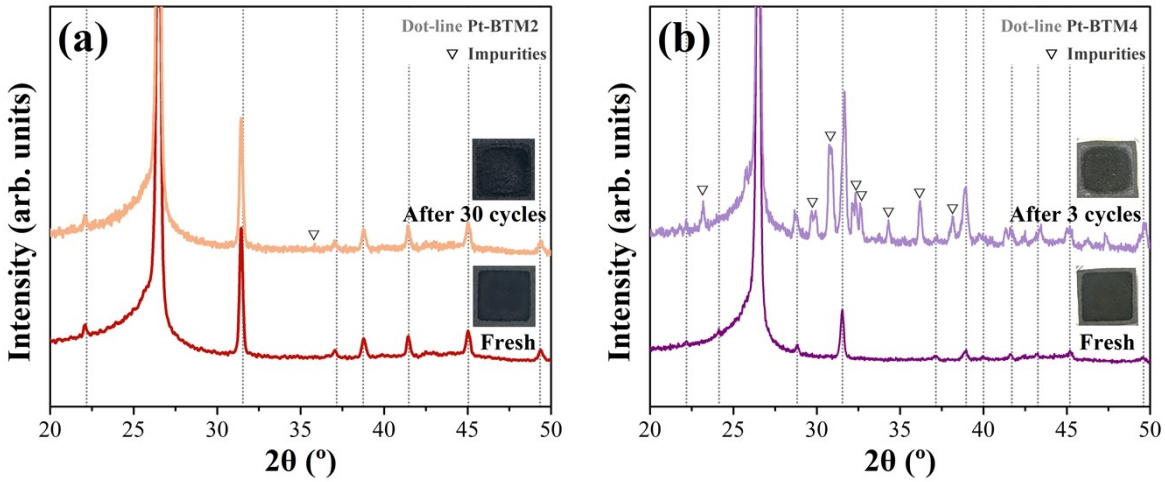

Fig. S11 XRD patterns of the fresh and long-term cycled cell bifunctional oxygen catalysts for ZAB cells, (a) Pt-BTM2 and (b) Pt-BTM4.

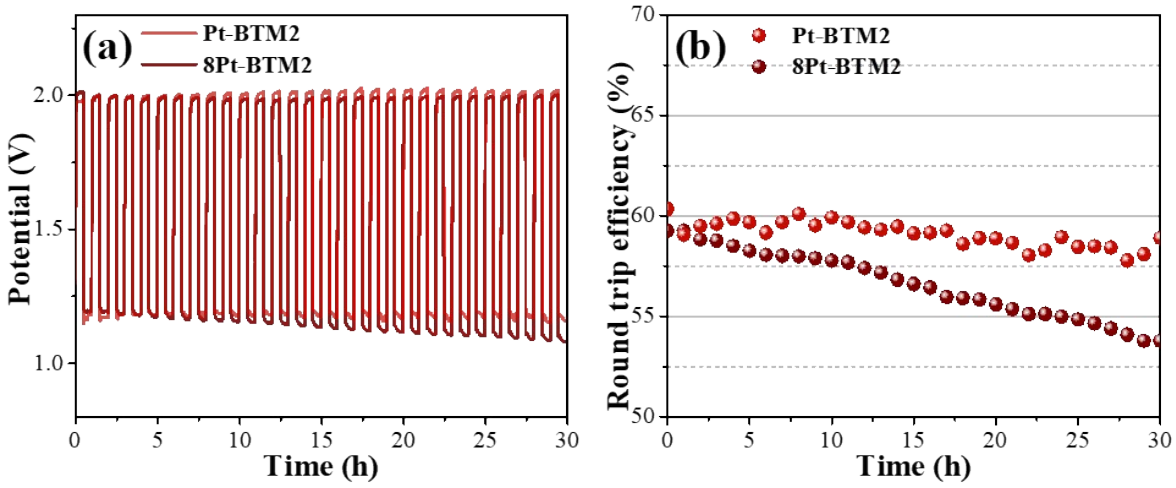

Fig. S12 (a) Galvanostatic charge-discharge cycling long-term stability of 8wt% Pt loaded BTM2 (8Pt-BTM2) comparing with Pt-BTM2 (5Pt-BTM2), (b) RTE efficiency obtained from (a).

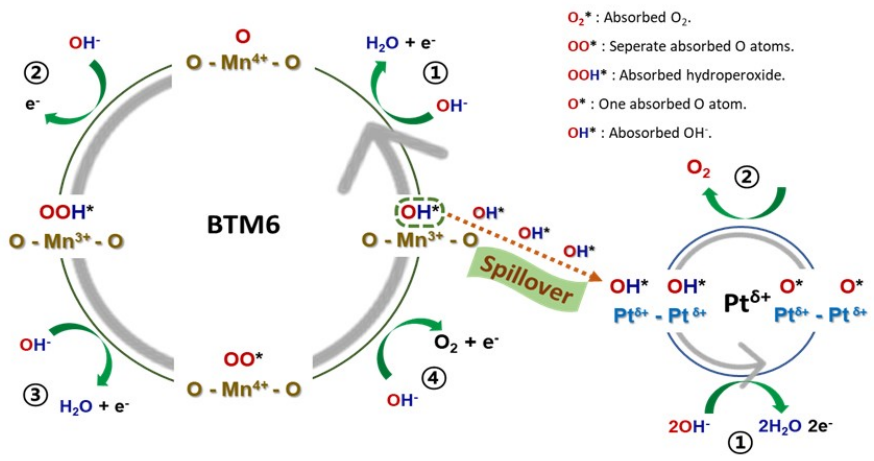

Fig. S13 OH* spill-over mechanism on Pt-BTM6 during OER.

Table S1. Summary of structural refined data of BTMx.

Catalyst	Tetragonal [Å] (P4mm) (a = b ≠ c) (α = β = γ = 90 °)	Hexagonal [Å] ($P6_3/mmc$) (a = b ≠ c) (α = β = 90 °, γ =120 °)	Rhombohedral [Å] (R3m-H) (a = b ≠ c) (α = β = 90 °, γ = 120 °)	Refined parameters R_{wp} [%] R_p [%] χ^2 (GOF)
BTO	a = 3.9937 c = 4.0347	-	-	6.45 5.12 1.587
BTM2	-	a = 5.6996 c = 13.9180	-	5.39 4.12 1.712
BTM4	-	a = 5.6805 c = 13.8730 (70.8%)	a = 5.6880 c = 27.9089 (29.2%)	6.21 4.85 1.639
BTM6	-	-	a = 5.6778 c = 27.8528	6.01 4.63 1.685

Table S2. Comparison of Pt-BTMx elemental composition by weight ratio, obtained by EDS map sum spectrum and calculated.

Catalyst	Pt-BTM2		Pt-BTM4		Pt-BTM6	
	EDS [wt%]	**Cal. [wt%]**	**EDS [wt%]**	**Cal. [wt%]**	**EDS [wt%]**	**Cal. [wt%]**
Ba	54.63	55.60	55.98	55.27	51.28	54.95
Ti	14.65	15.50	9.78	11.56	8.75	7.66
Mn	4.82	4.45	6.63	8.84	12.62	13.19
O	18.77	19.45	15.68	19.32	20.5	19.21
Pt	7.13	5.00	11.92	5.00	6.84	5.00
Total	100.0	100.0	100.0	100.0	100.0	100.0
Ti/Mn	3.04	3.48	1.48	1.31	0.69	0.58

Table S3. Relative concentration of components on each spectrum calculating by XPS.

Catalyst	Mn 2p (%)			O 1s (%)			Pt 4f (%)		
	Mn^{2+}	Mn^{3+}	Mn^{4+}	O_{Lat}	O_2^{2-}/O^-	O_2/OH^-	Pt^0	Pt^{2+}	Pt^{4+}
BTM2	23.98	59.49	16.53	50.53	30.31	19.16	-	-	-
Pt-BTM2	24.03	44.60	31.37	31.64	49.71	18.65	33.89	41.52	24.58
Pt-BTM4	-	71.82	28.18	29.32	52.75	17.93	26.37	48.95	24.68
Pt-BTM6	-	69.47	30.53	40.88	38.99	20.13	22.75	58.10	19.15

Table S4. The tested performances of ZABs compared with commercial catalyst (IrO_2 + Pt/C).

Electrocatalyst	Resistance			Specific capacity	ΔE_{CD} (long-term)		RTE (long-term)	
	R_s (Ω)	R_{int} (Ω)	R_{ct} (Ω)	(mAh g^{-1})	Initial (V)	Final (V)	Initial (%)	Final (%)
Pt-BTM2	1.5	0.36	1.01	636[a)]	0.82	0.84	60.34	58.09
Pt-BTM4	1.49	0.57	1.18	341[a)]	0.91	-	49.64	-
Pt-BTM6	1.5	0.49	1.21	538[a)]	0.82	1.14	58.03	43.02
IrO_2 + Pt/C	1.5	0.33	0.98	301[a)]	0.76	1.22	62.67	38.39

[a)] Discharged at current density of -25 mA cm^{-2}

Table S5. Recent performance of rechargeable ZABs with perovskite-based electrocatalyst.

Electrocatalyst	Specific capacity (mAh g^{-1})	PPD (mW cm^{-2})	ΔE_{CD} Initial (V)	ΔE_{CD} Final (V)	Current density (mA cm^{-2})	Cyclic stability (Cycle / h)	Electrolyte	Ref
Pt-BTM2	763[a)]	105.1	0.75	0.86	10	1500 / 250	6 M KOH	This work
$LaNi_{0.85}Mg_{0.15}O_3$	810	45	0.92	1.3	10	110 / 110	6 M KOH + 0.2 M $Zn(Ac)_2$	[1]
$La_{0.85}Ba_{0.15}CoO_3$	-	116.2	0.95	0.95	10	1200 / 200	6 M KOH + 0.2 M $Zn(Ac)_2$	[2]
$Pr_{0.6}Sr_{0.4}Fe_{0.8}Mn_{0.2}O_{3-\delta}$	-	56.3	0.9	1.03	10	135 / 135	6 M KOH + 0.2 M $Zn(Ac)_2$	[3]
$Pr_{0.5}Ba_{0.4}Ca_{0.1}Co_{0.6}Fe_{0.4}O_{3-\delta}$	-	74.76	0.83	0.86	10	220 / 220	6 M KOH + 0.2 M $Zn(Ac)_2$	[4]
$BaCo_{0.5}Fe_{0.5}O_{3-\delta}$	820	132	0.8	0.98	10	450 / 150	6 M KOH + 0.2 M $Zn(Ac)_2$	[5]
$LaCo_{0.8}Ru_{0.2}O_{3-\delta}$	433	136	0.78	-	5	1440 / 240	6 M KOH (Refill)	[6]
$La_{0.9}Ag_{0.1}Co_{0.7}Mn_{0.3}O_3$	698	137.2	1.0 (after 300 h)		5	2400 / 400	6 M KOH + 0.2 M $Zn(Ac)_2$	[7]
Pt-$Sr(Co_{0.8}Fe_{0.2})_{0.95}P_{0.05}O_{3-\delta}$-C	790	122	0.77	0.86	5	240 / 80	6 M KOH + 0.2 M $ZnCl_2$	[8]
$La_{0.5}Sr_{0.5}Co_{0.8}Ni_{0.2}O_3$	-	71.9	0.8	0.9	2	500 / 166	6 M KOH + 0.2 M $Zn(Ac)_2$	[9]
$La_{0.8}Sr_{0.2}Mn_{0.5}Co_{0.5}O_3/RuO_x$	-	159	0.58	0.81	2	300 / 100	6 M KOH + 0.2 M $Zn(Ac)_2$	[10]

[a)] Discharged at current density of -10 mA cm^{-2}

Supplementary references

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