

Supplementary information (ESI)

Unraveling e_g -band modulation as an alternate strategy to enhance lattice oxygen participation and entice oxygen electrocatalytic bifunctionality via switching of active site

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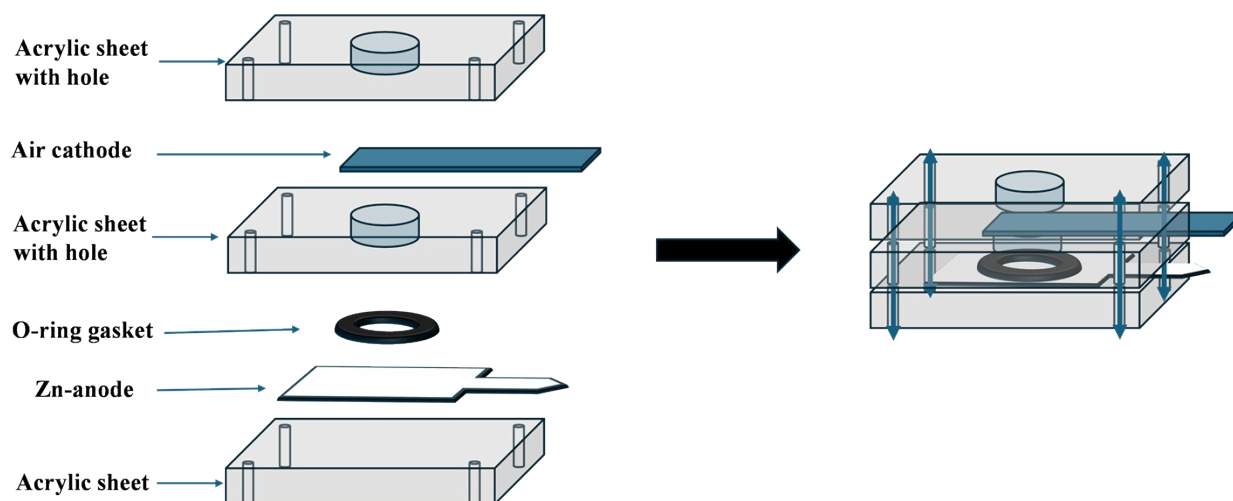
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Scheme S1. Schematic representation of Lab-made aqueous Zn-air battery setup.

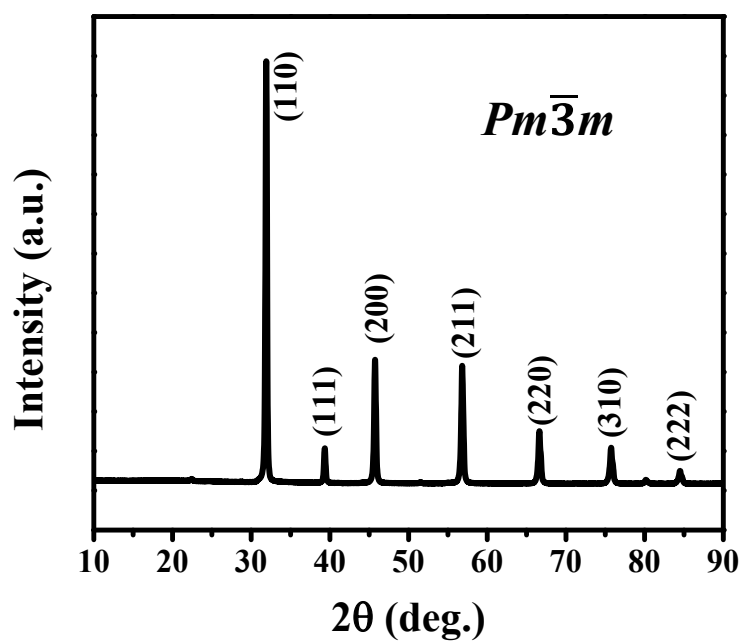


Fig. S1. P-XRD pattern of BSCMTS.

Table S1. Atomic position, Wyckoff site, occupancy, thermal parameter and reliability factors of $\text{Ba}_{0.33}\text{Sr}_{0.67}\text{Co}_{0.165}\text{Mn}_{0.165}\text{Ti}_{0.33}\text{Sb}_{0.33}\text{O}_3$.

Atom	Wyckoff site	X	Y	Z	f_{occ}	B_{iso} ($\text{\AA}$)
Ba/Sr	1b	0.5	0.5	0.5	0.33/0.67	0.58(2)
Co/Mn/Ti/Sb	1a	0	0	0	0.165/0.165/0.33/0.33	0.77(6)
O	3d	0.5	0	0	1.0	0.93(5)

Space group: $Pm\bar{3}m$; $a = 3.9691(5)$ $\text{\AA}$; Bond distances: Ba/Sr-O = $2.8066(4)$ $\text{\AA}$, Co/Mn/Ti/Sb-O = $1.946(3)$ $\text{\AA}$; Bond angle: Mn/Ti/Sb-O-Mn/Ti/Sb = 180° ; Reliability factors: $R_p = 1.36$ %, $R_{wp} = 1.89$ %, and $\chi^2 = 5.19$.

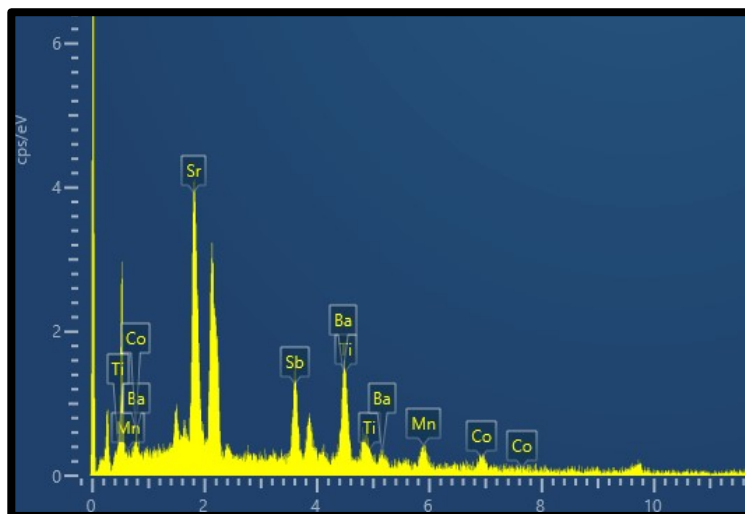


Fig. S2. EDS spectra of BSCMTS.

Table S2. Average observed and calculated atomic percentage of different elements.

Element	Obs. At. %	Calc. At. %
Ba	16.83	16.67
Sr	33.90	33.33
Co	8.52	8.33
Mn	8.50	8.33
Ti	15.53	16.67
Sb	16.72	16.67

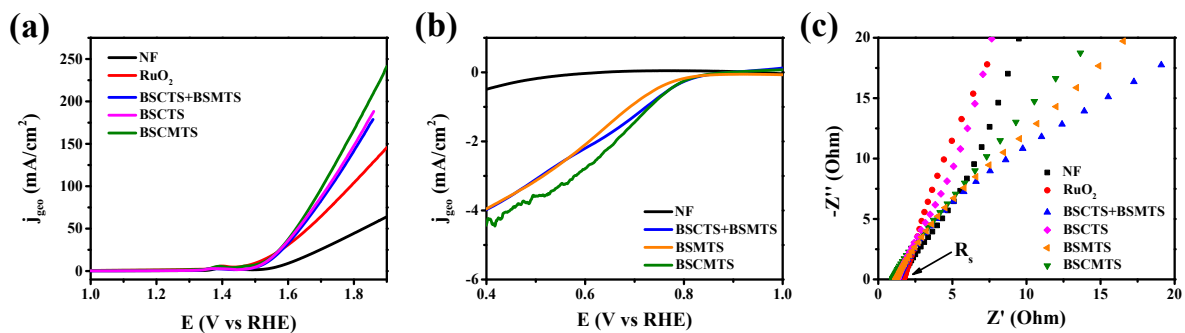


Fig. S3. iR-uncorrected (a) OER and (b) ORR LSV curves. (c) Magnified EIS Nyquist plot at OCP.

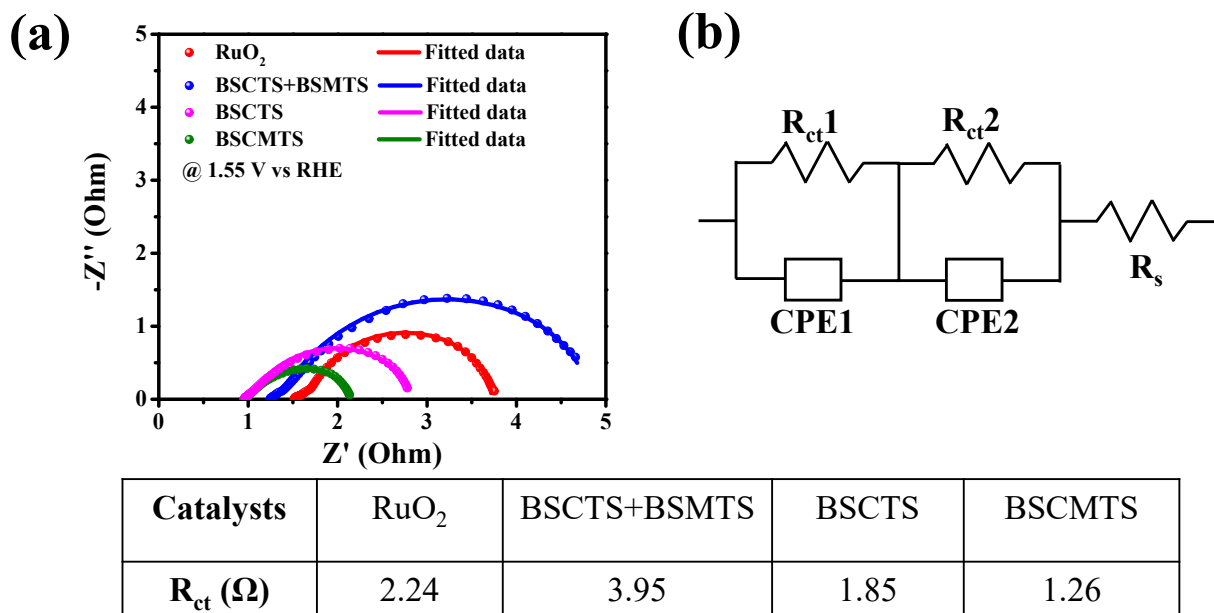


Fig. S4. (a) EIS Nyquist plot and fitted data at 1.55 V vs RHE, (b) fitted equivalent circuit. The lower panel shows the charge transfer resistance (R_{ct}) value obtained from the circuit fitting.

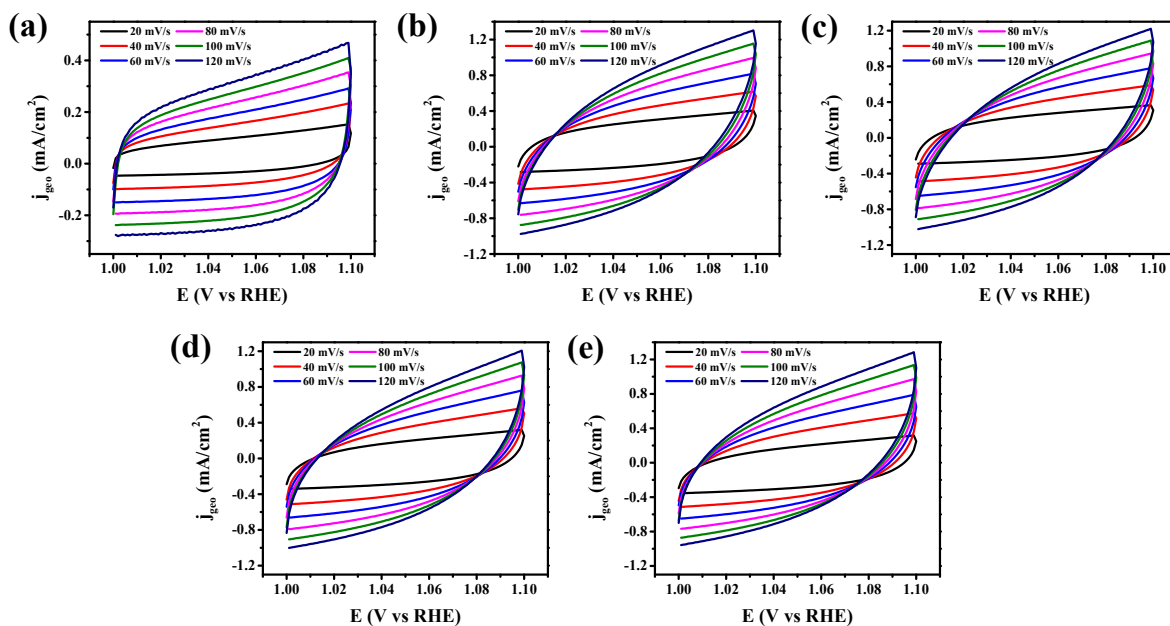


Fig. S5. Cyclic voltammograms in the region of 1.0 V to 1.1 V vs RHE of (a) NF, (b) RuO₂, (c) BSCTS + BSMTS, (d) BSCTS, and (e) BSCMTS.

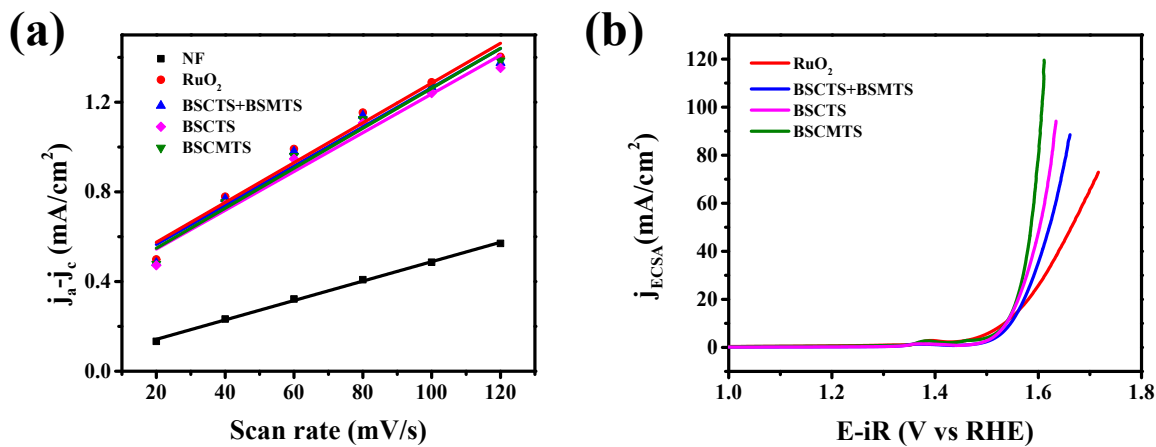


Fig. S6. (a) Plot of current density difference at 1.05 V (vs RHE) against scan rate. (b) ECSA normalized LSV curves of RuO₂, BSCTS + BSMTS, BSCTS and BSCMTS.

Table S3. Electrical double layer capacitance (C_{dl}) and ECSA.

sample	slope (mF/cm ²)	C_{dl} (mF/cm ²)	ECSA (cm ²)
NF	4.3	2.15	--
RuO ₂	8.9	4.45	2.07
BSCTS+BSMTS	8.7	4.35	2.02
BSCTS	8.6	4.30	2
BSCMTS	8.9	4.45	2.07

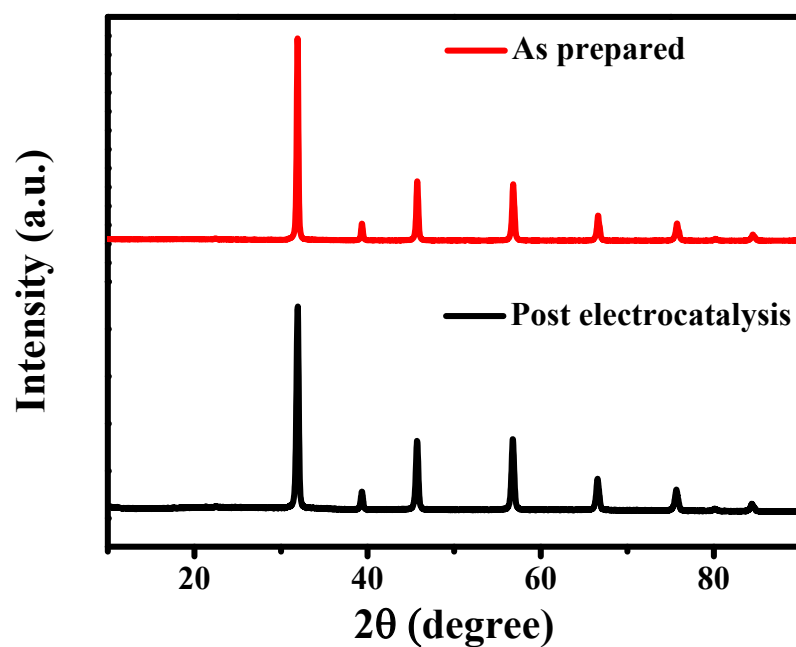


Fig. S7. Post-catalytic and as-synthesized P-XRD patterns of BSCMTS.

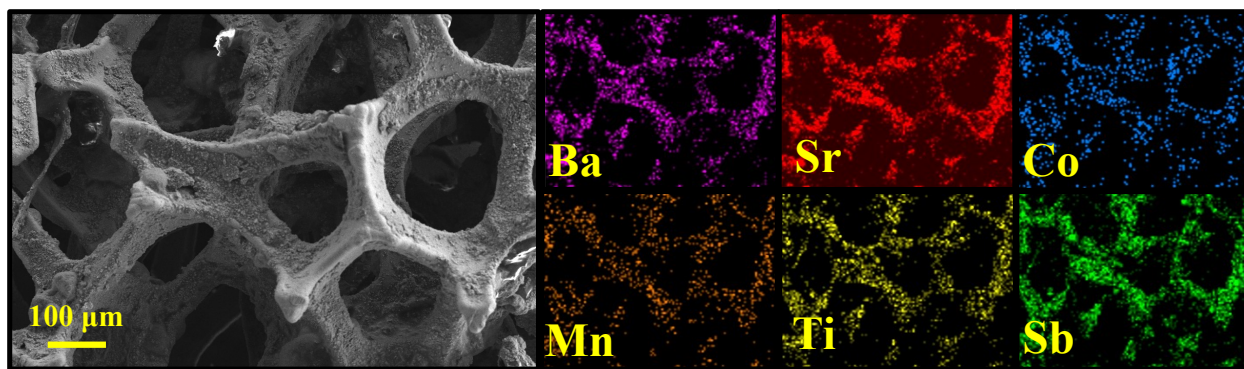


Fig. S8. Post catalytic FE-SEM image and elemental mapping of BSCMTS.

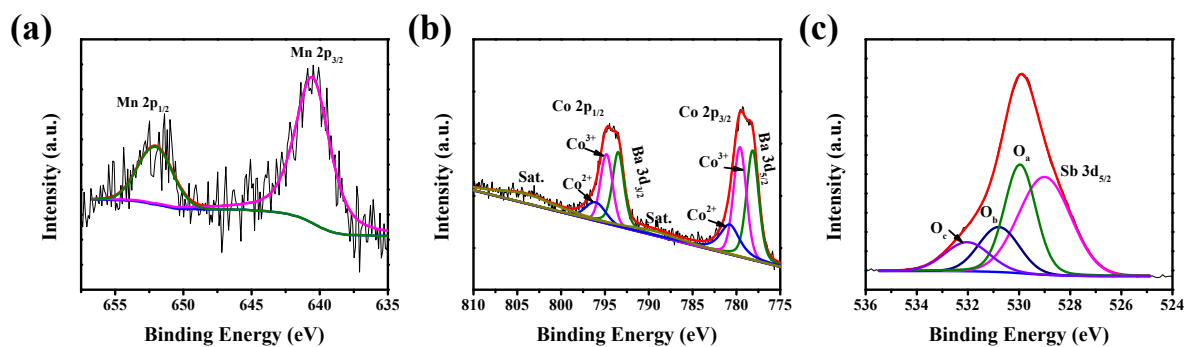


Fig. S9. Post catalytic deconvoluted (a) Mn 2p, (b) Co 2p and (b) O 1s XPS spectra of BSCMTS.

Table S4. Post-catalytic bulk elemental distribution of BSCMTS determined by MP-AES.

elements	elemental ratio
Ba	1.01
Sr	1.89
Co	0.47
Mn	0.49
Ti	1.03
Sb	0.98

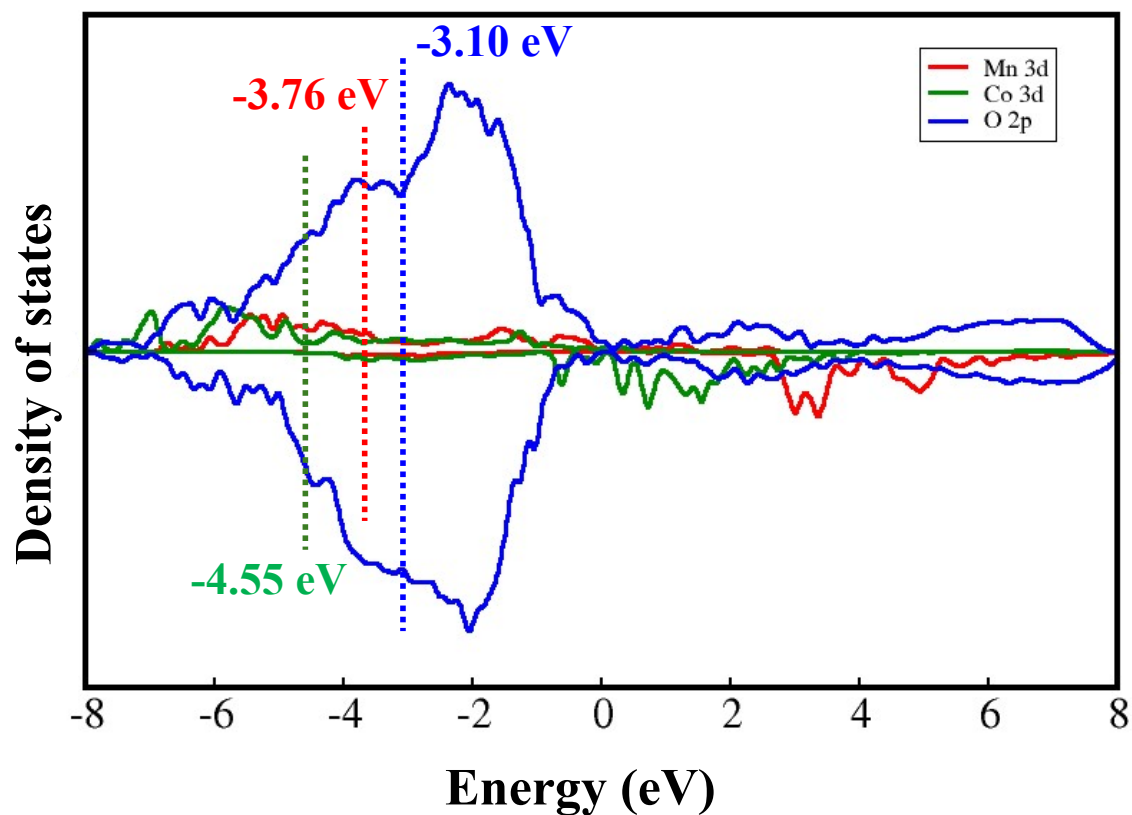


Fig. S10. Partial density of states (PDOS) of Co, Mn and O of BSCMTS. The blue, green and red dashed lines represent the band center of O 2p, Co 3d and Mn 3d, respectively.

Table S5. ICOHP values of different B–O bonds.

atom pair	ICOHP spin 1 (eV)	ICOHP Spin 2 (eV)	Δ ICOHP (Spin 2 - Spin 1) (eV)
Mn–O	-2.85	-3.24	-0.39
Co–O	-2.51	-3.23	-0.72
Ti–O	-2.44	-2.48	-0.04
Sb–O	-3.56	-3.62	-0.06