Enhanced Electrocatalysis of Bismuth Doped Zinc Stannate Towards OER and HER Through Oxygen Vacancies: p-block Metal Ion Doping Empowering d-block

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Figure S1: Schematic diagram for the solid state synthesis of Zn₂SnO₄: Bi

1.Experimental

S1. Catalyst slurry preparation

To make the catalyst slurry, the catalyst was well-ground in a mortar and pestle. The slurry was formed by adding 5 μ L of 5% Nafion solution to a combination of isopropyl alcohol (IPA, 50 μ L) and deionized water (950 μ L, 12 MΩ) to dissolve the 4.0 mg of the homogenously powdered catalyst. The mixture was then sonicated for one hour.

S2. Electrochemical investigation

Using a Biologic (VSP 300) potentiostat/galvanostat with a FRA7M module and EC-Lab V11.12 software, the electrochemical studies were conducted in a three-electrode setup. The working electrode (WE) was 0.5 * 0.5 cm catalyst-coated carbon paper, with a Hg/HgO/1 M NaOH as reference electrode (RE) and graphite rod as counter electrode (CE). We tested the electrocatalytic activity of the fabricated electrodes towards the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in a single-compartment electrochemical cell using linear sweep voltammetry (LSV) in 1 M KOH as alkaline electrolyte at 300 rpm constant stirring. For OER, the potential range was chosen to be 1.2 to 2.0 V *vs*. RHE, and for HER, it was 0.0 V to -0.75 V *vs*. RHE. The chronopotentiometry investigation was carried out to determine the electrode's long-term endurance. Cyclic voltammetry was used to calculate the electrochemical surface area (ECSA), specific surface area (SSA) and roughness of the electrodes in the non-faradic potential zone. To assure uniformity in the measurements, the current was defined in terms of current density, which was computed by dividing the recorded current by the geometric area of the working electrode (0.25 cm²), and the potentials were stated in terms of reversible hydrogen electrode (RHE) as follows:

 $E_{RHE} = E_{Ag/AgCl} + E^{\circ}_{Ag/AgCl} + 0.059 \text{ pH}$

S3. Quantification of gases

The eudiometric technique was used to determine the amount of O_2 and H_2 generated during water electrolysis. The catalyst coated carbon electrode was put within a burette filled with 1 M KOH, which was then inverted into the bulk 1 M KOH electrolyte. Next, chronoamperometry measurements were taken at various periods (10 – 60 minutes), and the O_2 and H_2 gases formed during the measurements were collected in the burette. The quantity of gas was determined by measuring the volume of gas collected after the electrolyte was displaced in the burette. Finally, the Faradaic efficiency (F.E.) was calculated by dividing the measured O_2 and H_2 volumes by their theoretical values.



Figure S2: (a) Rietveld refinement pattern (b) FTIR spectrum of Zn₂SnO₄:2%Bi



Figure S3: (a) SEM image (b) magnified SEM image $Zn_2SnO_4:2\%Bi$ (c) EDS of $Zn_2SnO_4:2\%Bi$



Figure S4: Diffuse reflectance spectra of (a) $Zn_2SnO_4:2\%Mn$ (b) $Zn_2SnO_4:2\%Bi$ (c) $Zn_2SnO_4:2\%Co$ and $Zn_2SnO_4:2\%Fe$



Zn₂SnO₄:2%Co and Zn₂SnO₄:2%Fe



Figure S6: XPS Core level spectra of (a) Zn-2p (b) Sn-3d (c) Mn-2p of Zn₂SnO₄:2%Mn



Figure S7: XPS core level spectra of (a) Zn-2p (b) Sn-3d (c) Bi-4f of Zn₂SnO₄:2%Bi



Figure S8: XPS core level spectra of (a) Zn-2p (b) Sn-3d (c) Co-2p of Zn₂SnO₄:2%Co



Figure S9: XPS core level spectra of (a) Zn-2p (b) Sn-3d (c) Fe-2p and Sn-3p of $Zn_2SnO_4:2\%Fe$



Figure S10: EPR spectra of Zn₂SnO₄:2%Mn, Zn₂SnO₄:2%Bi, Zn₂SnO₄:2%Co and Zn₂SnO₄:2%Fe

Full cell studies

To determine the total water splitting, full cell investigations were carried out in a two compartment H-type cell partitioned by a Nafion N-117 membrane. The membrane was cleansed in boiling deionized water before being fitted into the H-type cell. It was then treated with 0.05M H₂SO₄ for 30 minutes, rinsed three or four times with deionized water, and then exposed to an aqueous H₂O₂ (5%) solution at 80 °C for 15 minutes each. In a two electrode cell setup with an alkaline electrolyte of 1 M KOH, Zn_2SnO_4 (Bi³⁺) was used as both the anode and the cathode for an electrochemical water splitting investigation. Further, LSV and chronopotentiometry were recorded for overall water splitting employing Zn₂SnO₄ (Bi³⁺) as both anode and cathode.



Figure S11: Stability of LSV curves upto 200 cycles of Zn₂SnO₄ (Bi³⁺) samples for HER.

Table S1: Comparison of potential and current densities of all the Zn ₂ SnO ₄ samples for HER.			
Catalyst	E (V vs. RHE) @ 40 mA cm ⁻²	j (mA cm ⁻²) @ -0.7V vs. RHE	
ZSO-Bi	-0.54	183	
ZSO-Fe	-0.57	101	
ZSO-Co	-0.57	85	
ZSO-Mn	-0.59	109	



Figure S12: (a), (c), (e), (g) Cyclic voltammograms for all the Zn₂SnO₄ samples in the non-faradaic region for HER at different scan rates (25 mV s⁻¹ to 300 mV s⁻¹) and (b), (d), (f), (h) corresponding current density *vs.* scan rate curves for the measurement of C_{dl} , ECSA, SSA and roughness factor.

Table S2: C [*] _{dl} , ECSA and SSA of all the Zn ₂ SnO ₄ samples for HER.				
Catalyst	C* _{dl} (μF) at 0.125V vs. RHE	ECSA (mm ²)	SSA (m ² /g)	
ZSO-Bi	21.8	54.5	0.135	
ZSO-Fe	11.72	29.5	0.073	
ZSO-Co	9.86	24.6	0.0615	
ZSO-Mn	9.05	22	0.055	



Figure S13: (a) Nyquist plot of all variants at -0.5 V *vs*. RHE, (b) Nyquist plots obtained at different HER potentials ranging from -0.1 V to -0.8 V *vs*. RHE with a potential interval of 100 mV and (c) their corresponding bode plots for ZSO-Bi.

Table S3: Comparison of charge transfer resistance (R_{ct}) for all the variants towards HER.			
Catalyst	<i>R</i> _s (Solution resistance)	<i>R</i> _p (Polarization resistance)	$R_{\rm ct} = R_{\rm p} - R_{\rm s}$ (Charge transfer resistance)
Bi ³⁺	2.71	9.29	6.58
Mn ²⁺	2.81	10.0	7.19
C0 ³⁺	3.15	10.4	7.25
Fe ³⁺	3.0	11.4	8.4



Figure S14: Stability of LSV curves upto 200 cycles of Zn₂SnO₄ (Bi³⁺) samples for OER.

Table S4: Comparison of potential and current densities of all the Zn ₂ SnO ₄ samples for OER.			
Catalyst	E (V vs. RHE) @ 10 mA cm ⁻²	j (mA cm ⁻²) @ 2.0 V vs. RHE	
ZSO-Bi	1.76	91.7	
ZSO-Fe	1.78	39.2	
ZSO-Co	1.93	13.86	
ZSO-Mn	1.88	19.08	



Figure S15: (a), (c), (e), (g) Cyclic voltammograms for all the Zn₂SnO₄ samples in the non-faradaic region for OER at different scan rates (25 mV s⁻¹ to 300 mV s⁻¹) and (b), (d), (f), (h) corresponding current density *vs.* scan rate curves for the measurement of C_{dl} , ECSA, SSA and roughness factor.

Table S5: C [*] _{dl} , ECSA and SSA of all the Zn ₂ SnO ₄ samples for OER.				
Catalyst	С*а (µF) at 1.325vs. RHE	ECSA (mm ²)	SSA (m²/g)	
ZSO-Bi	13.64	14	0.046	
ZSO-Mn	4.8	12	0.035	
ZSO-Co	2.32	5.8	0.0145	
ZSO-Fe	2.36	5.9	0.01475	



Figure S16: (a) Post XP survey spectra of ZSO-Bi after long-term OER measurement, deconvoluted spectra of (b) O 1s, (c) Zn 2p, (d) Sn 3d and (e) Bi 4f_{7/2}.



Figure S17: (a)Linear sweep voltammetry (LSV) curve recorded for a full cell assembled with Zn_2SnO_4 (Bi³⁺) at both anode and cathode and (b) chronopotentiometry curves at 8 mA cm⁻² in 1 M KOH for 24 hours.



Figure S18: H₂ evolution rate utilizing ZSO-Bi at different time intervals up to 1 h at a cell potential of 2.5 V.