Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Improved Catalytic Activity on Transitioning from Inverse to Normal Spinel in $Zn_{2-x}Ga_{2x}Sn_{1-x}O_4$: A Robust Bifunctional OER and HER Electrocatalyst

Reshmi T. Parayil[a,b#], Santosh K. Gupta[a,b*], Kalpana Garg,[c#] Shivangi Mehta,[c] K. Sudarshan[a,b], M. Mohapatra[a,b], Tharamani C. Nagaiah[c*]

[a]*Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai – 400085, India*
[b]*Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094, India*
[c]*Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar 140001, Punjab, India*

Corresponding Author Email: *santoshg@barc.gov.in, *tharamani@iitrpr.ac.in

Experimental section

Table S1 Stoichiometric weight of precursors.			
	ZnO (mg)	**Ga_2O_3 (mg)**	**SnO_2 (mg)**
$ZnGa_2O_4$	162.8	374.9	0
$Zn_{1.2}Ga_{1.6}Sn_{0.2}O_4$	195.3	299.9	60.28
$Zn_{1.4}Ga_{1.2}Sn_{0.4}O_4$	227.9	224.9	120.6
$Zn_{1.6}Ga_{0.8}Sn_{0.6}O_4$	260.4	150	180.9
$Zn_{1.8}Ga_{0.4}Sn_{0.8}O_4$	293	74.98	241.1
Zn_2SnO_4	325.5	0	301.4

Catalyst slurry preparation

The catalyst was thoroughly ground in a mortar and pestle before preparing the catalyst slurry. The slurry was made by dissolving the 3.0 mg of the homogenously ground catalyst in a mixture of isopropyl alcohol (IPA, 60 µL) and deionized water (440 µL, 12 MΩ) with 5 µL of 5% Nafion solution and sonicated it for 1 hr.

Electrochemical investigation

The electrochemical studies were carried out in a three-electrode set up using Biologic (VSP 300) potentiostat / galvanostat with an FRA7M module, controlled by EC-Lab V11.12 software, with 0.5 * 0.5 cm catalyst-coated carbon paper serving as a working electrode (WE) with Hg/HgO/1 M NaOH reference electrode (RE) and Pt-wire counter electrode (CE). The electrocatalytic activity of the fabricated electrodes towards oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) was tested in a single-compartment electrochemical cell by performing linear sweep voltammetry (LSV) in the potential range of 1.2 to 1.95 V *vs.* RHE (for OER) and 0.0 V to -0.6 V *vs.* RHE (for HER) in 1 M KOH alkaline electrolyte at 400 rpm constant stirring. The chronopotentiometry study was carried out to access the long-term durability of the electrode. The electrochemical impedance spectroscopy (EIS) was employed to measure the charge transfer resistance (*R*ct) and rate constant (k). The electrochemical surface area (ECSA) of the electrodes was determined using cyclic voltammetric measurements in the non-faradic potential region. To ensure consistency in the measurements the current is described in terms of current density which was calculated by dividing the measured current

with the geometric area of the working electrode (0.25 cm^2) and the potentials were expressed in terms of reversible hydrogen electrode (RHE) as:

$$E_{RHE} = E_{Ag/AgCl} + E°_{Ag/AgCl} + 0.059\ pH$$

Further, we have computed the Specific activity and turnover frequency for both HER and OER by using following formulae:
Specific activity = current obtained/loading of the catalyst
Turnover frequency (TOF) = Turnover number (TON)/ loading of the catalyst

Full cell studies

Full cell studies were performed in a two compartment H-type cell separated by the Nafion N-117 membrane to determine the total water splitting. Prior to fitting in the H-type cell the membrane was cleaned in boiling deionized water, followed by aqueous H_2O_2 (5%) solution at 80 °C for 15 min each and then treated with 0.05M H_2SO_4 for 60 mins, finally rinsed with deionized water for 3-4 times. The $ZnGa_2O_4$ was applied as both anode and cathode in two electrode cell set up with 1 M KOH alkaline electrolyte for electrochemical water splitting study.

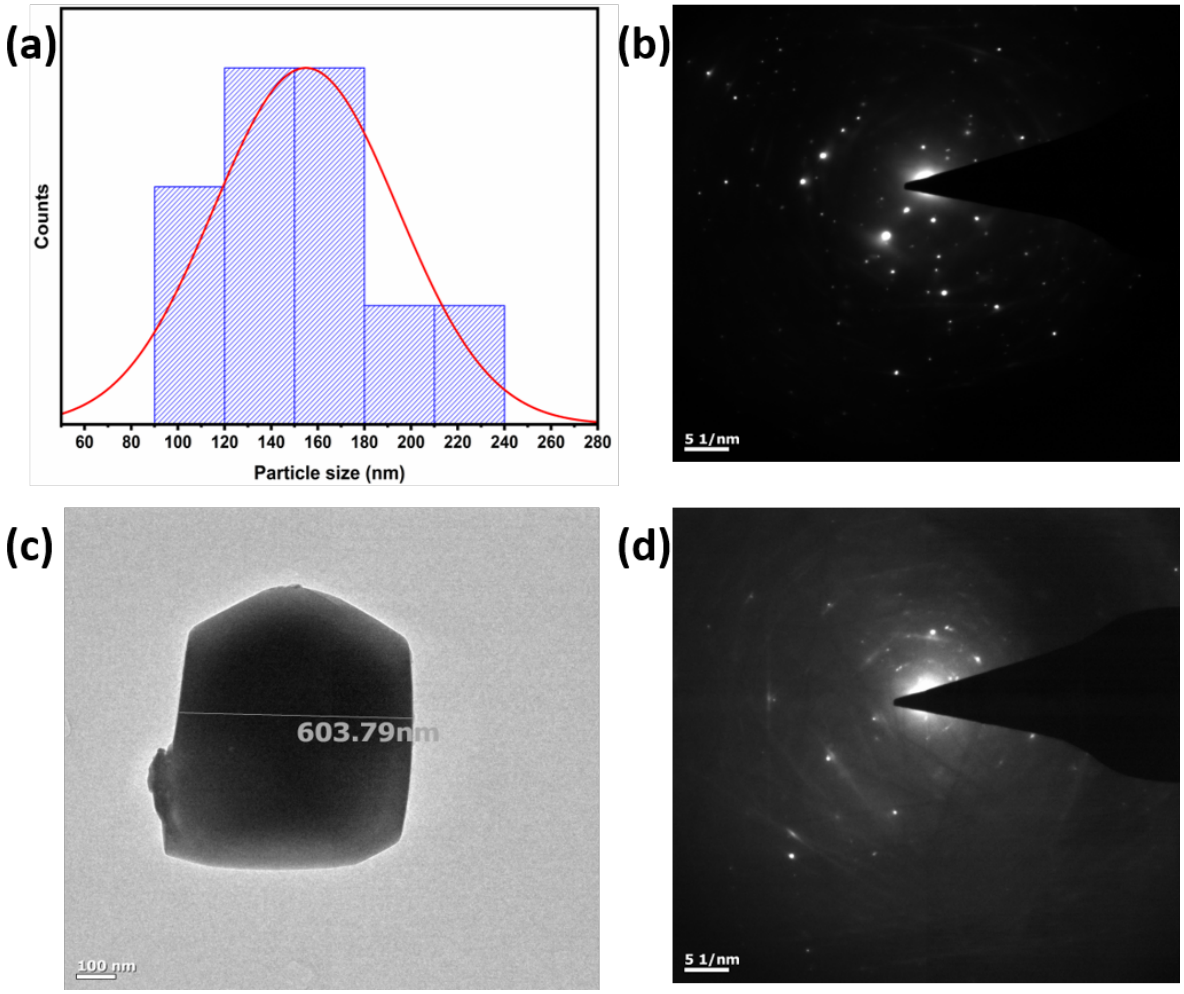


Fig. S1 (a) particle size distribution of $ZnGa_2O_4$ (b) SAED pattern of $ZnGa_2O_4$, (c) TEM image and (d) SAED pattern of Zn_2SnO_4.

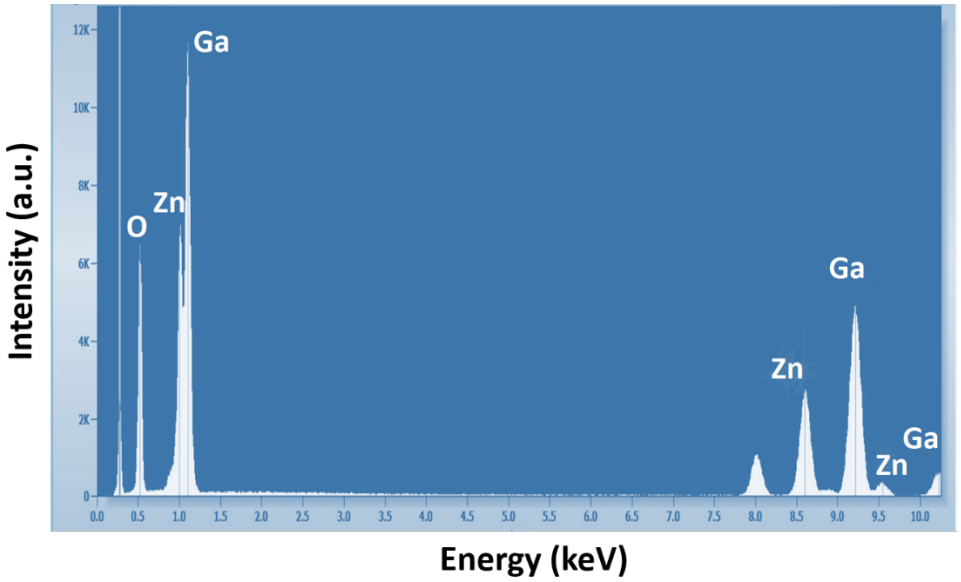


Fig. S2a EDX spectra of $ZnGa_2O_4$.

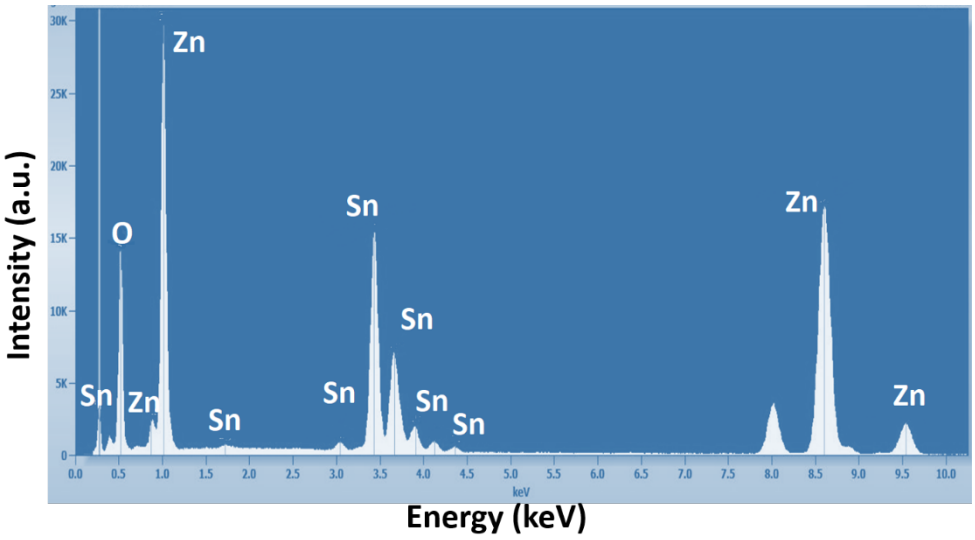


Fig. S2b EDX spectra of Zn_2SnO_4.

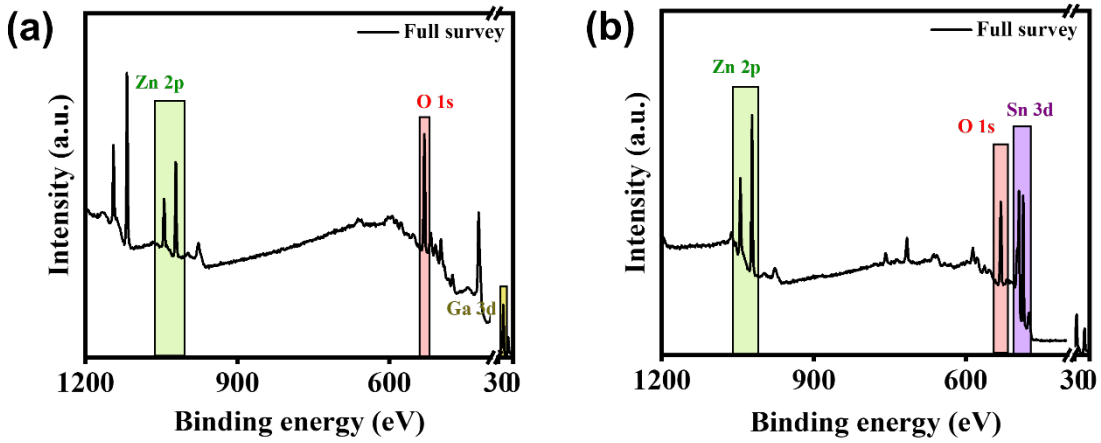


Fig. S3 XPS Survey scan of (a) $ZnGa_2O_4$ and (b) Zn_2SnO_4.

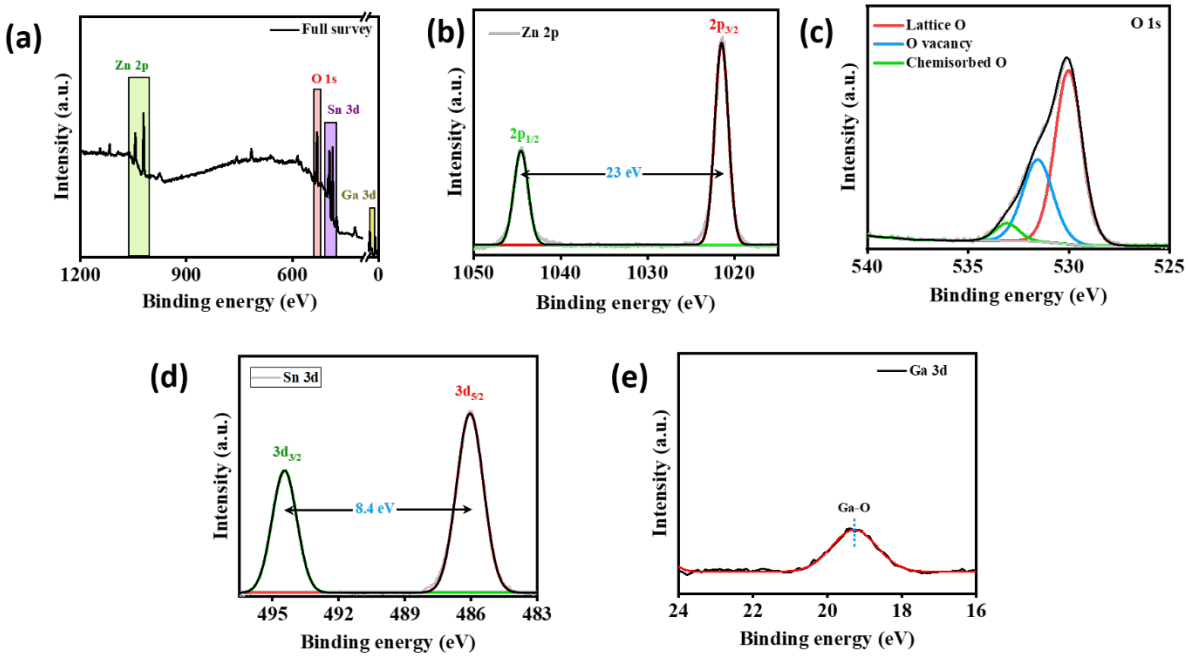


Fig. S4 (a) XPS Survey scan, core level spectra of (b) Zn 2p, (c) O 1s, (d) Sn 3d and (e) Ga 3d of $Zn_{1.8}Ga_{0.4}Sn_{0.8}O_4$.

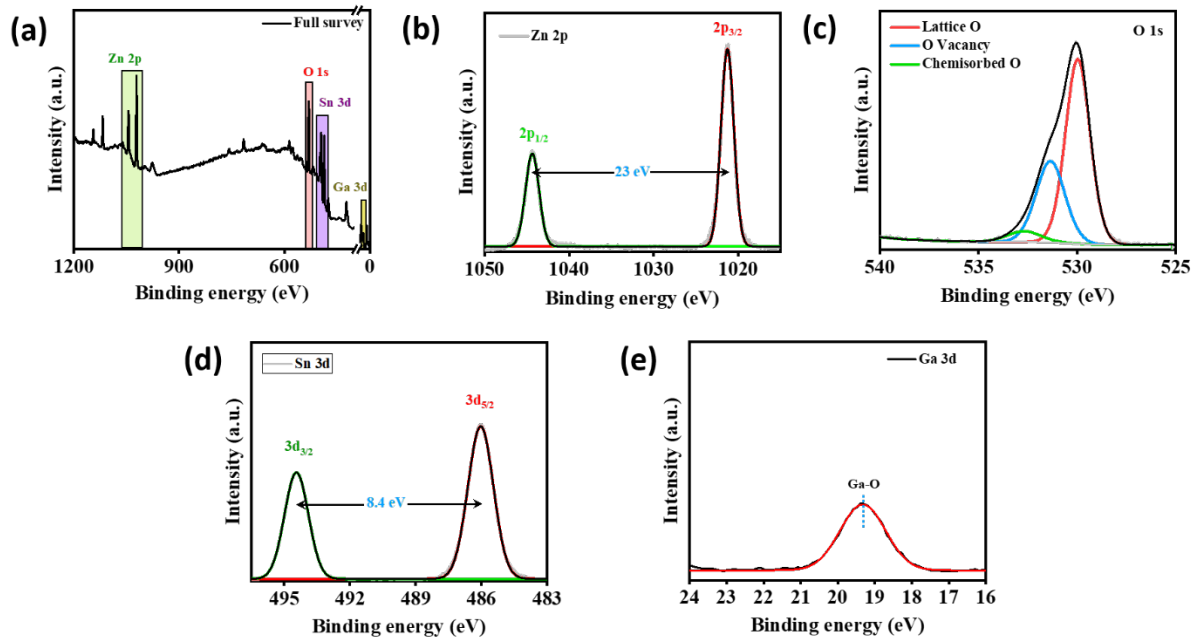


Fig. S5 (a) XPS Survey scan, core level spectra of (b) Zn 2p, (c) O 1s, (d) Sn 3d and (e) Ga 3d of $Zn_{1.6}Ga_{0.8}Sn_{0.6}O_4$.

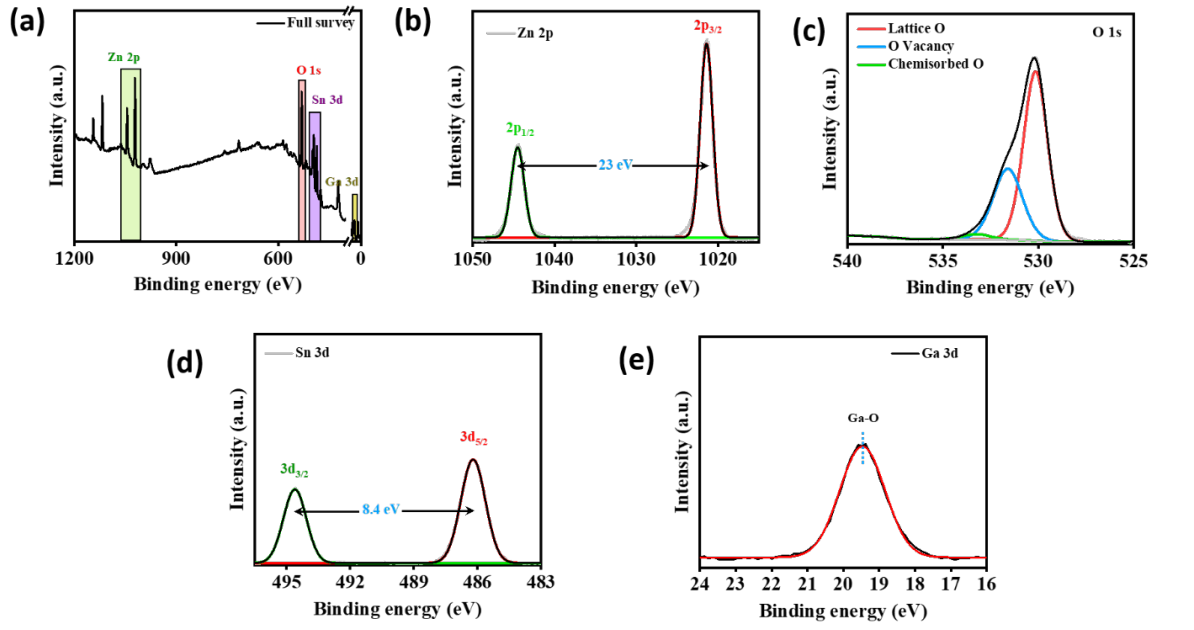


Fig. S6 (a) XPS Survey scan, core level spectra of (b) Zn 2p, (c) O 1s, (d) Sn 3d and (e) Ga 3d of $Zn_{1.4}Ga_{1.2}Sn_{0.4}O_4$.

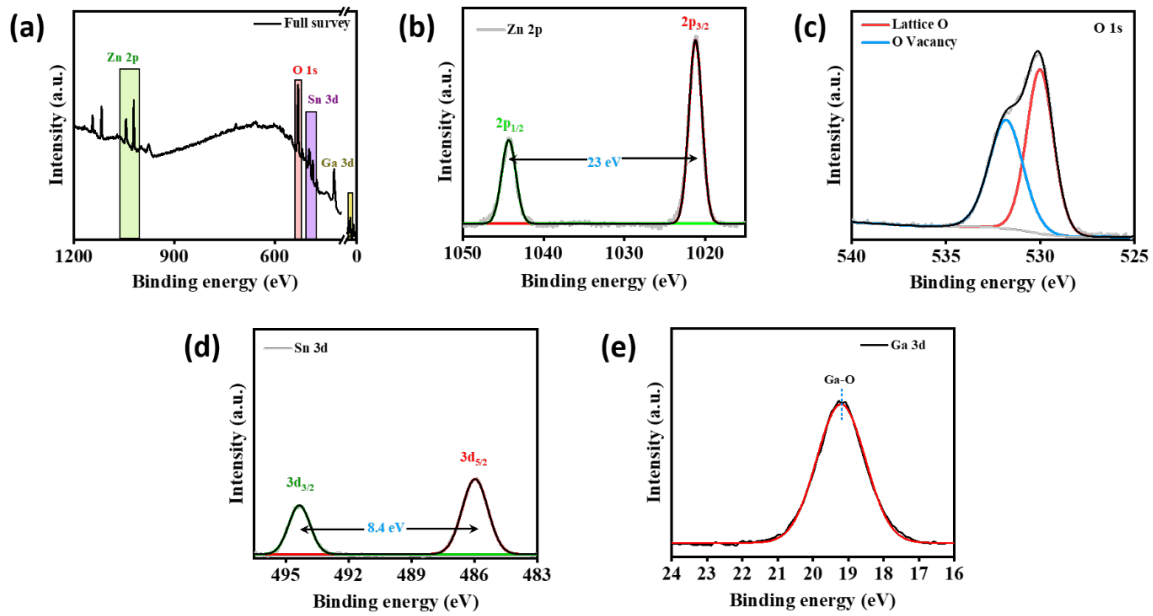


Fig. S7 (a) XPS Survey scan, core level spectra of (b) Zn 2p (c) O 1s (d) Sn 3d and (e) Ga 3d of $Zn_{1.2}Ga_{1.6}Sn_{0.2}O_4$.

Table S2 Atomic % of oxygen vacancy.

	Lattice O (~530 eV)	O-vacancy (~531 eV)	Chemisorbed O (~532 eV)
$ZnGa_2O_4$	45.28	54.72	-
$Zn_{1.2}Ga_{1.6}Sn_{0.2}O_4$	54.41	45.59	-
$Zn_{1.4}Ga_{1.2}Sn_{0.4}O_4$	64.75	33.01	2.24
$Zn_{1.6}Ga_{0.8}Sn_{0.6}O_4$	62.7	32.32	4.98
$Zn_{1.8}Ga_{0.4}Sn_{0.8}O_4$	62.63	29.94	7.43
Zn_2SnO_4	62.55	27.54	9.9

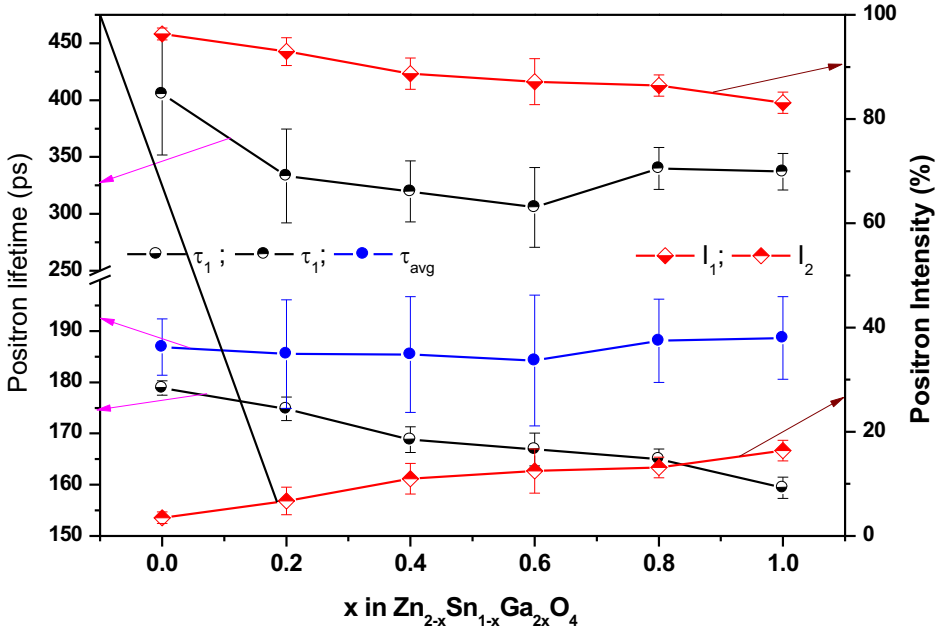


Fig. S8 Positron annihilation lifetimes and intensities in Zn_2SnO_4 with replacing Zn and Sn with Ga.

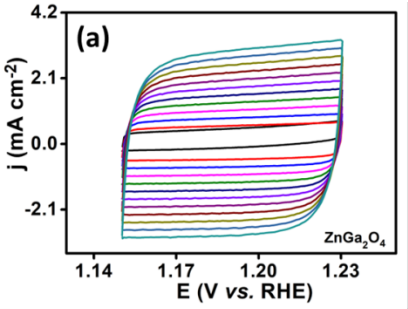
Quantification of gases

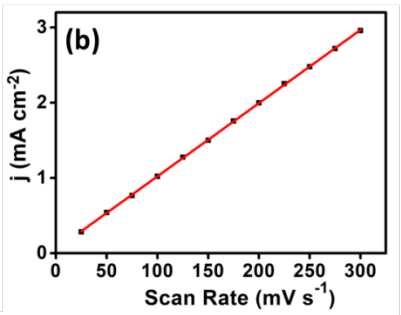
The eudiometric method was used to measure the amount of O_2 and H_2 produced during water electrolysis. The graphite counter electrode was placed inside a burette that was filled with 1 M KOH, and the burette was inverted inside the bulk 1 M KOH electrolyte. Next, chronoamperometry measurements were performed at different times and the O_2 and H_2 gases produced during measurement were collected in the burette. The volume of gas collected after displacement of the electrolyte in the burette was used to determine the quantity of gas. Finally, by dividing the observed volume of O_2 and H_2 by the theoretical value, the Faradaic efficiency (F.E.) was computed.

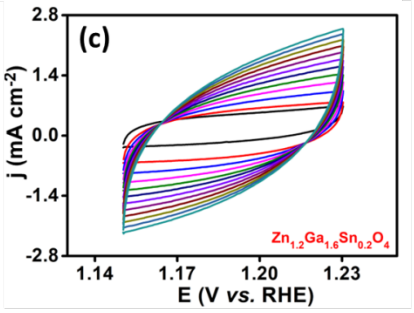
Table S3 Comparison of potential and current densities of all the $Zn_{2-x}Ga_{2x}Sn_{1-x}O_4$ samples for OER.		
Catalyst	**E(V *vs.* RHE) @ 10 mA cm^{-2}**	**j (mA cm^{-2}) @ -0.6 V *vs.* RHE**
$ZnGa_2O_4$	1.60	143
$Zn_{1.2}Ga_{1.6}Sn_{0.2}O_4$	1.64	109
$Zn_{1.4}Ga_{1.2}Sn_{0.4}O_4$	1.63	92
$Zn_{1.6}Ga_{0.8}Sn_{0.6}O_4$	1.62	71
$Zn_{1.8}Ga_{0.4}Sn_{0.8}O_4$	1.65	63
Zn_2SnO_4	1.66	50

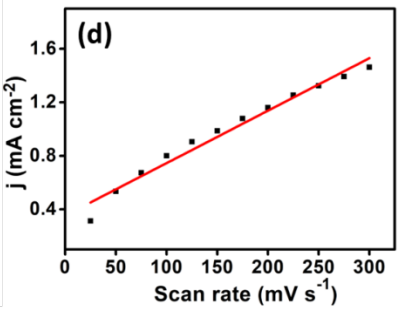
Table S4 EIS analysis (R_{ct} and rate constants) of all the $Zn_{2-x}Ga_{2x}Sn_{1-x}O_4$ samples for OER.		
Catalyst	**R_{ct} (Ω, Charge transfer resistance)**	**Rate constant, k (x 10^{-6}cm s^{-1})**
$ZnGa_2O_4$	36.1	1.84
$Zn_{1.2}Ga_{1.6}Sn_{0.2}O_4$	39.64	1.67
$Zn_{1.4}Ga_{1.2}Sn_{0.4}O_4$	43.06	1.54
$Zn_{1.6}Ga_{0.8}Sn_{0.6}O_4$	45.7	1.45
$Zn_{1.8}Ga_{0.4}Sn_{0.8}O_4$	46.2	1.44

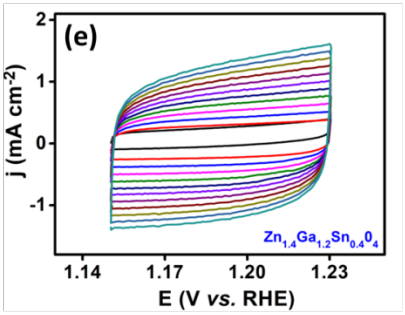
Zn_2SnO_4	59.94	1.11

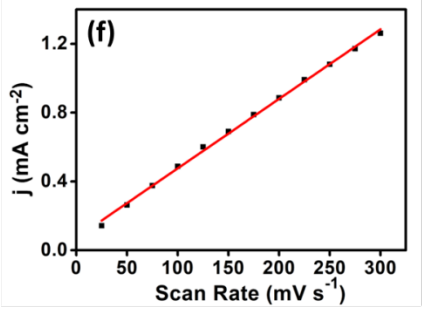

(a)
j (mA cm-2)
4.2
2.1
0.0
-2.1
ZnGa2O4
1.14
1.17
1.20
1.23
E (V vs. RHE)

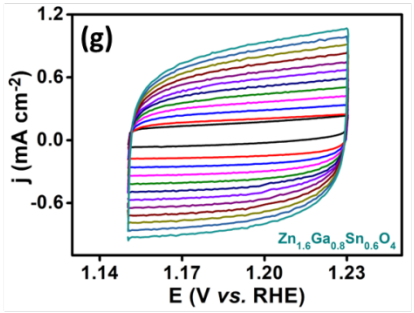

(b)
j (mA cm-2)
3
2
1
0
0
50
100
150
200
250
300
Scan Rate (mV s-1)

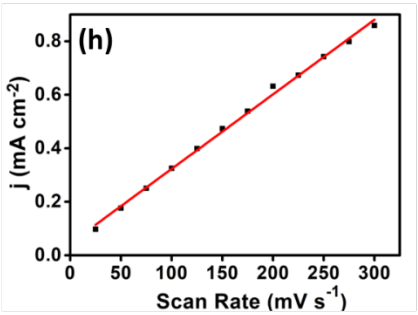

(c)
j (mA cm-2)
2.8
1.4
0.0
-1.4
-2.8
Zn1.2Ga1.6Sn0.2O4
1.14
1.17
1.20
1.23
E (V vs. RHE)

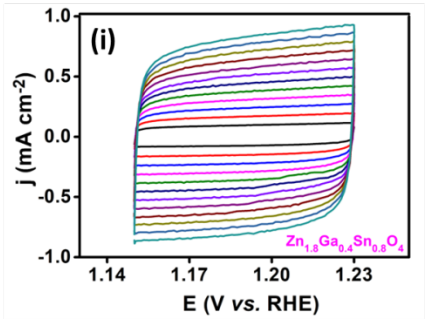

(d)
j (mA cm-2)
1.6
1.2
0.8
0.4
0
50
100
150
200
250
300
Scan rate (mV s-1)

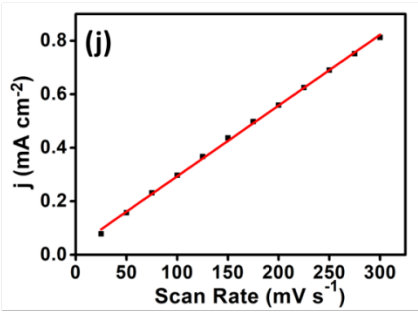

(e)
j (mA cm-2)
2
1
0
-1
Zn1.4Ga1.2Sn0.40.4
1.14
1.17
1.20
1.23
E (V vs. RHE)

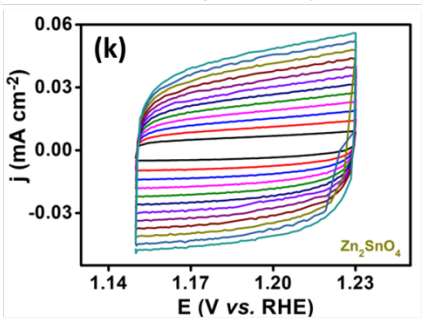

(f)
j (mA cm-2)
1.2
0.8
0.4
0.0
0
50
100
150
200
250
300
Scan Rate (mV s-1)


(g)
j (mA cm-2)
1.2
0.6
0.0
-0.6
Zn1.6Ga0.8Sn0.6O4
1.14
1.17
1.20
1.23
E (V vs. RHE)


(h)
j (mA cm-2)
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
Scan Rate (mV s-1)


(i)
j (mA cm-2)
1.0
0.5
0.0
-0.5
-1.0
Zn1.8Ga0.4Sn0.8O4
1.14
1.17
1.20
1.23
E (V vs. RHE)


(j)
j (mA cm-2)
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
Scan Rate (mV s-1)


(k)
j (mA cm-2)
0.06
0.03
0.00
-0.03
Zn2SnO4
1.14
1.17
1.20
1.23
E (V vs. RHE)

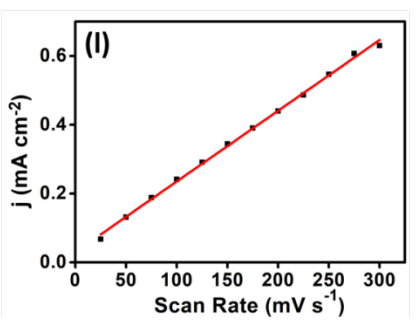

(l)
j (mA cm-2)
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
Scan Rate (mV s-1)

Fig. S9 (a), (c), (e), (g), (i), (k) Cyclic voltammograms for all the $Zn_{2-x}Ga_{2x}Sn_{1-x}O_4$ 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), (j), (l), corresponding current density *vs.* scan rate curves for the measurement of C_{dl}, ECSA and SSA.

Table S5 C^*_{dl}, ECSA and SSA of all the $Zn_{2-x}Ga_{2x}Sn_{1-x}O_4$ samples for OER.			
Catalyst	**C^*_{dl} (µF) at 1.18V *vs.* RHE**	**ECSA (mm^2)**	**SSA (mm^2/mg)**
$ZnGa_2O_4$	0.6811	1.7028	9.46
$Zn_{1.2}Ga_{1.6}Sn_{0.2}O_4$	0.2745	0.68	3.77
$Zn_{1.4}Ga_{1.2}Sn_{0.4}O_4$	0.2829	0.7073	3.92
$Zn_{1.6}Ga_{0.8}Sn_{0.6}O_4$	0.1950	0.4876	2.70
$Zn_{1.8}Ga_{0.4}Sn_{0.8}O_4$	0.1851	0.46	2.55
Zn_2SnO_4	0.1439	0.3598	1.9

Table S6 Comparison of potential and current densities of all the $Zn_{2-x}Ga_{2x}Sn_{1-x}O_4$ samples for HER.		
Catalyst	**E (V *vs.* RHE) @ 20 mA cm^{-2}**	**j (mA cm^{-2}) @ -0.6 V *vs.* RHE**
$ZnGa_2O_4$	-0.36	-124
$Zn_{1.2}Ga_{1.6}Sn_{0.2}O_4$	-0.40	-91
$Zn_{1.4}Ga_{1.2}Sn_{0.4}O_4$	-0.41	-71
$Zn_{1.6}Ga_{0.8}Sn_{0.6}O_4$	-0.43	-66
$Zn_{1.8}Ga_{0.4}Sn_{0.8}O_4$	-0.48	-48
Zn_2SnO_4	-0.50	-40

Table S7 EIS analysis (R_{ct} and rate constants) of all the $Zn_{2-x}Ga_{2x}Sn_{1-x}O_4$ samples for HER.		
Catalyst	**R_{ct}(Ω, Charge transfer resistance)**	**Rate constant, k (x 10^{-5}cm s^{-1})**
$ZnGa_2O_4$	5.73	4.64
$Zn_{1.2}Ga_{1.6}Sn_{0.2}O_4$	6.12	4.34
$Zn_{1.4}Ga_{1.2}Sn_{0.4}O_4$	6.24	4.26
$Zn_{1.6}Ga_{0.8}Sn_{0.6}O_4$	7.05	3.77
$Zn_{1.8}Ga_{0.4}Sn_{0.8}O_4$	8.29	3.21
Zn_2SnO_4	9.21	2.88

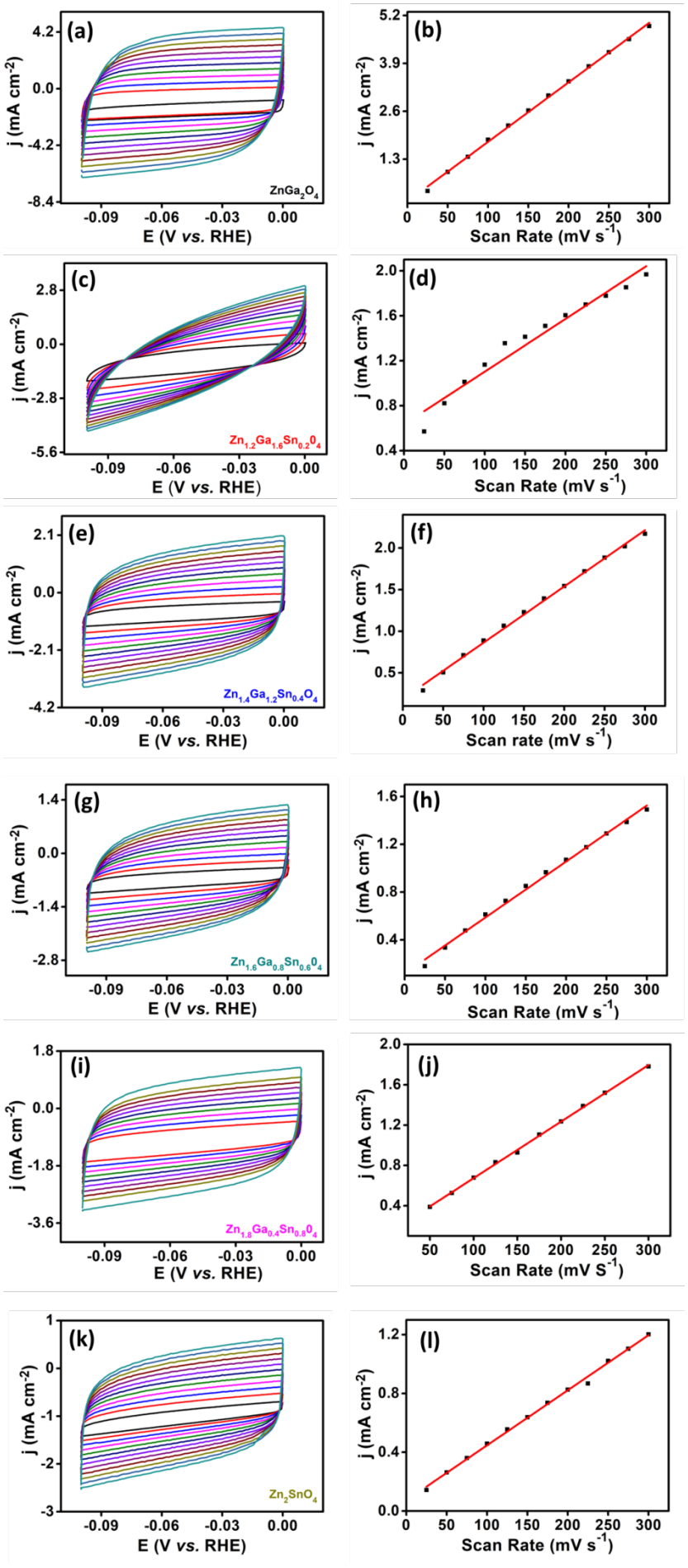

(a)
j (mA cm-2)
E (V vs. RHE)
ZnGa2O4
(b)
j (mA cm-2)
Scan Rate (mV s-1)
(c)
j (mA cm-2)
E (V vs. RHE)
Zn1.2Ga1.6Sn0.204
(d)
j (mA cm-2)
Scan Rate (mV s-1)
(e)
j (mA cm-2)
E (V vs. RHE)
Zn1.4Ga1.2Sn0.4O4
(f)
j (mA cm-2)
Scan rate (mV s-1)
(g)
j (mA cm-2)
E (V vs. RHE)
Zn1.6Ga0.8Sn0.604
(h)
j (mA cm-2)
Scan Rate (mV s-1)
(i)
j (mA cm-2)
E (V vs. RHE)
Zn1.8Ga0.4Sn0.804
(j)
j (mA cm-2)
Scan Rate (mV S-1)
(k)
j (mA cm-2)
E (V vs. RHE)
Zn2SnO4
(l)
j (mA cm-2)
Scan Rate (mV s-1)

Fig. S10 (a), (c), (e), (g), (i), (k) Cyclic voltammograms for all the $Zn_{2-x}Ga_{2x}Sn_{1-x}O_4$ 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), (j), (l), corresponding current density *vs.* scan rate curves for the measurement of C_{dl}, ECSA and SSA.

Table S8 C^*_{dl}, ECSA and SSA of all the $Zn_{2-x}Ga_{2x}Sn_{1-x}O_4$ samples for HER.			
Catalyst	**C^*_{dl} (µF) at -0.05V *vs.* RHE**	**ECSA (mm^2)**	**SSA(mm^2/mg)**
$ZnGa_2O_4$	1.13	2.825	15.6
$Zn_{1.2}Ga_{1.6}Sn_{0.2}O_4$	0.3282	0.820	4.5
$Zn_{1.4}Ga_{1.2}Sn_{0.4}O_4$	0.4733	1.183	6.5
$Zn_{1.6}Ga_{0.8}Sn_{0.6}O_4$	0.3283	0.8209	4.5
$Zn_{1.8}Ga_{0.4}Sn_{0.8}O_4$	0.3928	0.982	5.4
Zn_2SnO_4	0.2623	0.655	3.6

Table S9 Color coordinate values of $ZnGa_{2-x}Sn_xO_4$ (x=0, 0.2, 0.4,0.6, 0.8, 1).		
	X	**Y**
$ZnGa_2O_4$	0.19082	0.19455
$Zn_{1.2}Ga_{1.6}Sn_{0.2}O_4$	0.24881	0.32652
$Zn_{1.4}Ga_{1.2}Sn_{0.4}O_4$	0.33554	0.42393
$Zn_{1.6}Ga_{0.8}Sn_{0.6}O_4$	0.40560	0.44084
$Zn_{1.8}Ga_{0.4}Sn_{0.8}O_4$	0.41694	0.38824
Zn_2SnO_4	0.40657	0.36015

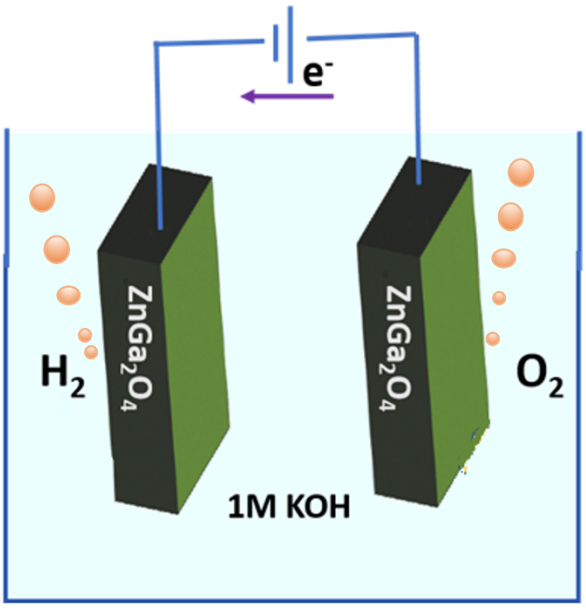


Fig. S11 Schematic representation of the full cell water splitting.

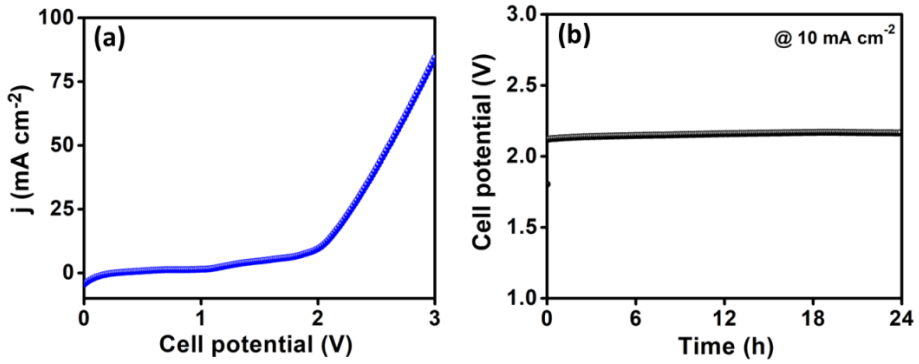


Fig. S12 (a) Linear sweep voltammetry (LSV) curve recorded for a full cell assembled with $ZnGa_2O_4$ at both anode and cathode and (b) chronopotentiometry curves at 10 mA cm^{-2} in 1 M KOH for 24 hours.