Supplementary information:

Competing double-exchange / super-exchange ordering for enhanced water oxidation kinetics

Materials and reagents used:

Chemical reagents were of analytical quality and used directly without further purification. Lanthanum oxide, Manganese (IV) oxide, Strontium Carbonate, Nafion, Ruthenium (IV) oxide, and Fluorine doped Tin Oxide coated glass substrate with a sheet resistance of $12-14 \Omega/cm^2$ were purchased from Sigma Aldrich.

Synthesis of Strontium doped Lanthanum manganite (LMO):

The conventional solid-state synthesis was followed for the synthesis of Lanthanum manganite. Lanthanum oxide, Manganese (IV) oxide were taken in stochiometric amounts and was ground using mortar and pestle for 45 minutes. The obtained powder was put under calcination at 1050°C for 12h in the air. The obtained samples were again ground for better homogeneity. For the synthesis of 0.3mol% Strontium doped lanthanum manganite, stoichiometric SrCO₃ was taken with lanthanum and manganese precursor, and the same procedure was followed as above.

Synthesis of Strontium and Ruthenium doped Lanthanum manganite:

The conventional solid-state synthesis was followed here also for the synthesis of 30 at. % Strontium and Ruthenium doped Lanthanum manganite. Lanthanum oxide, Manganese (IV) oxide, Strontium Carbonate, and Ruthenium (IV) oxide (0.1mol%,0.2mol%,0.3mol%,0.4mol%) were taken in stochiometric amounts. The same steps were followed as that of lanthanum manganite synthesis. The different mol% doped samples are abbreviated as LSMR0.1, LSMR0.2, LSMR0.3, and LSMR0.4 respectively.

Fabrication of working electrodes

The FTO substrates used for fabrication were cleaned using soap solution, ethanol, acetone, and isopropanol one after the other. A requisite amount of the synthesized catalyst was taken and dispersed in ethanol. Then it was ground well in an agate mortar with terpineol and ethyl cellulose (5 wt% solution in ethanol) to obtain a smooth paste. Then the paste was applied on the FTO substrate, using the doctor blade technique. Then it was dried at 100 °C for 2h followed by calcination at 500 °C at a rate of 5 °C/min for 1.5h and the edges are covered with resin for further analysis.

Material characterization

Powder diffraction was used to analyse the produced catalysts for identification of phase and its purity. A 9 kW Rigaku Smart lab X-ray diffractometer with copper (Cu K_a=1.54 Å) as the source was used for X-ray diffraction. The XRD data were recorded over a range of 20 (10°-80°) while maintaining a fixed scan rate of 10° min⁻¹. Field emission scanning electron microscopy (FESEM) analysis was performed using a Zeiss (Model: Gemini and Sigma300) apparatus operated at an accelerating voltage of 5kV to ascertain the morphological characteristics of the samples. Energy dispersive X-ray Spectra of LSMO and Ruthenium-doped LSMO samples were obtained using a FESEM instrument at a voltage of 20 kV. A JEOL (JEM-2100F) transmission electron microscope with an operating voltage of 200 kV was used for field emission transmission electron microscopy (FETEM) analysis of the samples. GAMRY Instruments (Interface 1010E) tested the electrochemical properties of synthesized samples.

Electrochemical measurements

All the electrochemical measurements were performed in 1M NaOH solution using a potentiostat, wherein Hg/HgO electrode was used as the reference electrode, graphite as the counter electrode, and fabricated catalyst as the working electrode. To convert all the potentials to RHE, the following formula was used:

$$\mathbf{E}_{RHE} = \mathbf{E}_{(Hg/HgO)} + 0.0591 * \mathbf{pH} + 0.098$$
(1)

The electrocatalytic activity was examined by linear sweep voltammetry (LSV) from -0.2 V to 1.2 V vs Hg/HgO at 5 mV s⁻¹ scan rate. The electrochemical active surface area (ECSA) was investigated by cyclic voltammetry (CV) measurements carried out from 0.3 V to 0.4 V vs Hg/HgO at scan rates ranging from 2 to 10 mV s⁻¹ in the non-faradaic region. EIS spectra were obtained at a potential of 0.7 V vs Hg/HgO and the frequency ranges between 0.1 Hz to 100 Hz.

Calculation of turnover frequency (TOF)

The TOF value is calculated using the following equation,

$$\mathbf{TOF} = \frac{J * A}{4 * F * N^s}$$
(2)

where J, A, F and N_S are, respectively, current density at a certain overpotential (A/cm²), surface area of the working electrode (cm²), Faraday constant (96458 C/mol), and concentration of electrochemically active sites in the catalysts (mol/cm²). N_S for oxygen evolution reaction (OER) was determined by CV measurements at different scan rates in the voltage range where redox reaction occurs. The peak current is plotted against scan rate where the slope has the linear relationship,

$$Slope = n^{2}F^{2}AN_{\rm S}/4RT \tag{3}$$

in which n, R, and T are, respectively, the number of electrons transferred, ideal gas constant and absolute temperature.



FigureS1: FESEM image of La_{0.7}Sr_{0.3}Mn_{1-x}Ru_xO₃ (a) x=0.1 (b) x=0.2 (c) x=0.3 (d) x=0.4

Figure S1 displays FESEM images of LSMR with varying Ru doping concentrations. Interestingly, there is no discernible alteration in the morphology of the material with changes in Ru concentration.



FigureS2: Survey spectra of LSMR0.2



Figure S3: XPS spectra of (a) the La 3d core-level of LMO, LSMO and LSMR0.2 and (b) the Sr 3d core-level of LSMO and LSMR0.2

The XPS spectra of La 3d (FigureS3a) have been de-convoluted into $3d_{5/2}$ and $3d_{3/2}$. The peaks at 834.3 and 838.1 eV are due to La³⁺ and satellite, respectively.^{S1} In FigureS3b the XPS spectra for Sr 3d have been de-convoluted into respective $3d_{5/2}$ and $3d_{3/2}$. The peaks at 132.6 and 133.8 eV are assigned to Sr²⁺ in the bulk and surface of the material, respectively.^{S2}



Figure S4 (a) Linear sweep voltammetry and (b)Nyquist curve of LSMO with different wt% Ru doping in 1M NaOH solution

To reveal the effects of Ru doping on OER catalytic activities, the relevant catalytic activities of different Ru contents were first explored, as shown in (Figure S4a). From the test results, the optimal amounts of Ru introduction were determined. On this basis, the main analysis was carried out. Figure S4b shows the Nyquist plot of LSMO with different Ru mol% doping at an overpotential of 1.53V vs RHE where LSMR0.2 showed a better charge transfer resistance and maintained a similar trend with the results of the LSV.

To assess the electrochemical surface area (ECSA), an indicator of the number of electrochemically active sites in an electrocatalyst, cyclic voltammetry measurements were conducted on LMO, LSMO, and LSMR0.2 electrodes (depicted in Figure S5a, b, c). The measurements were carried out within the range of 1.18-1.28 V vs RHE (non-faradic range) at varying scan rates from 1 to 5 mV/sec. The double-layer capacitance (C_{dl}), providing a direct estimation of the ECSA value, was determined by plotting the difference in current density ($j_{anode} - j_{cathode}$ at 1.23 V vs RHE) for the electrodes against the scan rate, where C_{dl} is equal to half of the slope value derived from this plot.



Figure S5 Cyclic voltammetry of (a)LaMnO₃, (b) $La_{0.7}Sr_{0.3}MnO_3$ (c) $La_{0.7}Sr_{0.3}Mn_{0.8}Ru_{0.2}O_3$ taken in non-faradic region in 1M NaOH solution at different scan rate (1-5mV /sec).

The CV was taken in the non-faradic region and current density cathodic was taken at 1.23V vs RHE for the calculation of C_{dl} value. Here we can see with an increase in scan rate the current density is also increasing which infers that the electroactive species is confined to the electrode surface.

Mass Activity:

The mass activity serves as a quantitative measure that characterizes the catalytic activity of a catalyst by determining the current generated at a specified overpotential, expressed as amperes per gram of the catalyst.

Mass activity
$$(A/mg) = j/m;$$
 (4)

Where, j = current density (A); m = loading catalyst amount (g)

Electrocatalysts	Mass loading (mg/cm ²)	Current density @ 470mv	Mass Activity (A/g)	
LSMR 0.2	1.1	0.068A	61.81	
LSMO	1.1	0.021A	19.09	
LMO	1.1	0.01A	9.09	

Table S1:

Having the same mass loading of 1.1 mg cm⁻², LSMR0.2 electrocatalyst has shown better catalytic OER activity than that of LSMO and LMO.

To ascertain whether the evolved gas in the process is exclusively a result of water oxidation and not influenced by potential side reactions or by-products, Faradaic yield measurements were conducted. These measurements were carried out through chronoamperometry in a 1 M NaOH solution at an applied potential of 1.53 V vs RHE over an hours. The evolved gas was continuously monitored using gas chromatography (GC). The Faradaic yield was determined by employing equation 5 in conjunction with the quantity of gas generated, as calculated using equation 6, during the electrocatalytic process.

The amount of gas evolved was calculated using the formula

Amount of gas evolved =
$$\frac{J * t}{n.F}$$
 (6)

Where J is the current density (A/cm²), t is the time (sec), n is the number of moles charge required to produced one mole of gas and F is the Faraday constant 96485(C (eN_A)).



Figure S6 (a) Experimental O_2 production on the LSMR 0.2 catalyst and theoretical O_2 quantities as function of time in the water electrocatalysis in 1 M NaOH at 10 mA cm⁻² (b) Experimental production of O_2 as a function of current density and applied potential.



Figure S7 (a)Linear sweep voltammetry of LSMR0.2 before and after stability test and (b)CV of LSMR0.2 measured at a scan rate of 100mV/sec

The plot (Figure S7a) shows a negligible reduction in the current density upon continuous run for 24hr. Thus, it can be inferred that the is LSMR0.2 stable in alkaline conditions and can be utilized as an electrocatalyst for the long run. The plot (Figure S7b) shows a negligible reduction in the current density upon continuous run up to 500 cycles with no shift in the peak positions.



Figure S8. (a)Powder-XRD and (b) FE-TEM image of LSMR0.2 after stability test.

Figure S8 shows the PXRD and FE-TEM image of LSMR0.2 after the stability test, which shows that the morphology of the prepared catalyst is retained after the stability test and there is no change in the XRD pattern.

Table S2:

Electrocatalyst	Electrolyte	Overpotential(mV)	Tafel slope(mV/d ec)	Reference
La _{0.7} Sr _{0.3} Mn _{0.8} Ru _{0.2} O	1M NaOH	300mV@10mA/m ²	110	This
3 LaMnOa		$450 @ 0.4 mA/cm^2$	382	S3
		450 @ 10 m A / am ²	07	S3
LaMn _{0.75} Co _{0.25} O ₃	0.1MKOH	450 @ 10 mA/cm ²	97	54
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$	0.1MKOH	$510 @ 10 \text{ mA/cm}^2$	100	S5
La ₂ NiMnO ₆	1М КОН	500mV@101.8mA/cm ²	58	S6
$Pr_{0.7}Sr_{0.3}Co_{1-}$	1M KOH	321mV @10mA/cm ²	118.1	S7
$_{x}Ru_{x}O_{3}(x=0.05)$				
$La_{0.3}(Ba_{0.5}Sr_{0.5})_{0.7}Co_{0.8}$	1M KOH	480 @ 10 mA/cm ²	-	S8
$Fe_{0.2}O_3$				
$La_{0.7}Sr_{0.3}Fe_{1-x}Ni_{x}O_{3-\delta}$	0.1MKOH	$320 \text{ mV} @ 10 \text{ mA cm}^{-2}$	35	S9
Ce-doped LaCoO ₃	1M KOH	380mV @10 mA/cm2	80	S10

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