# **Electronic Supplementary Material (ESI)**

# Electronic and Surface Engineering of Mn Active Sites by Femtosecond Lasers: Enhancing Catalytic Performance for Seawater Electrolysis Through Mn<sup>4+</sup>-OH<sup>-</sup> Layers

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## **Turnover Frequency (TOF) Calculation for P-LSMO and LT-LSMO**

To evaluate the intrinsic catalytic activity of P-LSMO and LT-LSMO, the turnover frequency (TOF) for the oxygen evolution reaction (OER) was calculated using the active site density derived from the XRD refinement data. The TOF was determined based on the total number of Mn active sites per unit volume, following the equation:

$$TOF = \frac{I(A) \times 6.022 \times 10^{23} atoms}{1cm^2 \times 96485C \times 4 \times x \text{ atoms}}$$

Where:

- I (A) is the measured current during OER,
- 6.022×1023 is Avogadro's number (atoms per mole),
- 96485 C/mol is the Faraday constant,
- x represents the number of atoms per unit volume, obtained from the XRD refinement results,
- The denominator accounts for the four-electron transfer process in OER.

### **Electrochemical active surface area (ECSA)**

Electrochemically active surface area was calculated by double layer capacitance method as reported by **McCrory et al.**<sup>1</sup> In this regard, cyclic voltammograms were collected in the non-Faradic region with the potential sweep of 0.1 V, initially determined from static CV.

Equation 1  $i_c = vCdl$ 

$$ECSA = \frac{Cdl}{C_s}$$

**Equation 2** 

where Cs is the specific capacitance of a sample under the specific condition of electrolyte and CDL is the double layer capacitance in the non-faradic region of voltammogram. For Mn the reported value of *Cs* varies from 0.033 mF to 0.056 mF in alkaline conditions.<sup>1</sup> Hence, we chose an average value (0.040 mF) to get the average value of ECSA of our catalyst).

### **Exchange current density from EIS**

RT

Exchange current density (I <sub>ex</sub>) =  $\overline{nF\theta}$ 

R = Gas constant (8.314 j/ K. mol)

T = Reaction temperature

n = Number of electrons transfer (4)

 $\theta$  = Charge transfer resistance calculated from the EIS.



**Figure S1.** EDX spectrum of (a) P-LSMO and (b) LT-LSMO samples; XPS Survey (c) P-LSMO and (d) LT-LSMO samples.

The refined structural parameters (**ESI**, **Fig S2-b**, **Table S2**) confirm the orthorhombic perovskite structure (**SG: Pnma**) for both P-LSMO and LT-LSMO, with no secondary phases detected. Additionally, the Mn–O bond lengths were extracted from the refinement, allowing us to calculate the Jahn-Teller distortion index ( $\Delta$ JT).

 $\Delta_{JT} = \frac{1}{6} \sum_{i=1}^{6} \left( \frac{dl_i - dl_0}{d_0} \right)^2$ 

 $d_0$  = average Mn–O bond length.  $d_i$  = individual Mn–O bond lengths.

The results indicate a reduction in Jahn-Teller distortion in LT-LSMO compared to P-LSMO, demonstrating that FS laser treatment enhances structural symmetry by stabilizing MnO6

octahedra. These findings support the conclusions regarding the effect of laser treatment on structural modification and catalytic performance, aligning with previous studies where Rietveld refinement was effectively used to evaluate Jahn-Teller distortions in perovskite oxides.



Figure S2: (a) XRD Patterns of (104) Peak. (b)XRD Rietveld Refinement of P-LSMO and LT-LSMO: Effect of FS Laser Treatment on Structural Parameters



**Figure S3**. FTIR analysis for P-LSMO and LT-LSMO samples.



Figure S4. BET Surface Area



Figure S5. Mn3s line for P-LSMO and LT-LSMO samples



Figure S6: CV for different scan rates 20, 50, and 100 mV/s



Figure S7. Double-layer capacitance (Cdl) for P-LSMO and LT-LSMO samples



Figure S8. Electrochemical active surface area



Figure S9. ECSA normalized activity



Figure S10. Surface Hydrophilicity of P-LSMO and LT-LSMO samples



Figure S11. chronopotentiometry of LT-LSMO at 100mA/cm<sup>2</sup> for 24 hours



Figure S12. XPS of Mn2p line of LT-LSMO after catalysis



Figure S13. UV/Vis. spectrum of LT-LSMO after catalysis



**Figure S14.** High-resolution XPS spectra of (a) La 3d3/2 and (c) Sr 3d for the P-LSMO sample and (b) La 3d3/2 and (d) Sr 3d for the LT-LSMO sample.

The C 1s XPS spectra of P-LSMO and LT-LSMO (ESI Fig. S15) reveal the presence of surface carbon species, which can be attributed to both adventitious contamination and residual organic compounds from the sol-gel synthesis process. The deconvoluted spectra exhibit three distinct peaks: C–C/C–H (~284.80–284.81 eV), corresponding to adventitious carbon, C–O (~285.75–285.81 eV), which may originate from organic residuals or surface carbonates, and O–C=O (~288.75–288.76 eV), indicative of oxidized carbon species likely resulting from the incomplete combustion of citric acid and ethylene glycol during synthesis. After FS laser treatment, no significant shift in peak positions is observed, indicating that the chemical state of surface carbon remains unchanged. However, a slight reduction in peak intensity suggests a partial removal of surface carbon species, likely due to laser-induced localized heating, which facilitates further decomposition of residual organic matter. This modification may contribute to improved surface properties, potentially enhancing the catalyst's electrochemical performance. A detailed deconvolution of the C 1s spectra is provided in Figure S13 (ESI) for further clarification.



Figure S15. deconvoluted C 1s spectra for both samples

**Table S1:** Cell parameters, Bond lengths, bond angles, and distortion parameters indicated byRietveld structural refinements of P-LSMO and LT-LSMO samples.

Samples		P-LSMO (Orthorhombic structure SG: Pnma)	LT-LSMO (Orthorhombic structure SG: Pnma)	
	a (Å)	5.4503	5.4608	
Cell parameters	b (Å)	7.7162	7.7093	
	c(Å)	5.4688	5.4757	
	V(Å)	229.9899	230.5212	
Bond lengths	Mn–O1(×2) (Å)	2.06010	2.01118	
	Mn–O2(×2) (Å)	2.07209	2.08953	
	Mn–O2(×2) (Å)	1.81470	1.84244	
	<mn–o> (Å)</mn–o>	1.98229	1.98105	
	<la sr–o2=""> (×2) (Å)</la>	2.47727	2.33801	
	<la sr–o1=""> (Å)</la>	2.35954	2.35255	
	<la sr–o1=""> (Å)</la>	2.22682	2.44980	
Jahn-Teller distortion	$\delta_{ m JT}$	≈0.0598	≈ 0.0520	
bond angles	Mn–O1–Mn (×2) (°)	138.906	146.774	
	Mn–O2–Mn (×4) (°)	166.625	159.040	
	< Mn–O–Mn > (°)	157.38533	154.95133	
Average Mn-O-Mn bond angles	<ω>	22.614	25.048	

 Table S2: Fitting parameters Mn2p line

	Mn2p <sub>3/2</sub>		Mn2p <sub>3/2</sub>		Ratio Mn3+/Mn4+	
Sample Without FS laser	Mn <sup>3+</sup>	Mn <sup>4+</sup>	Mn <sup>3+</sup>	Mn <sup>4+</sup>		
	33%	27%	14%	13%	1 00	
	Peaks positions				1.22	
	641.04	642.67	652.49	653.70		
Sample with FS laser	Mn <sup>3+</sup>	Mn <sup>4+</sup>	Mn <sup>3+</sup>	Mn <sup>4+</sup>		
	<b>20</b> %	37%	14%	14%	0 6 4	
	Peaks positions				0.54	
	640.72	642.04	652.58	653.68		

Table S3: Surface area and pore size distribution of P-LSMO and -LTLSMO derived from the BET adsorption isotherm

	P-LSMO	LT-LSMO				
Average pore size	2.2650e+00 nm	1.9110e+00 nm				
BJH Pore Size Distribution Adsorption						
Surface Area	2.50236 m <sup>2</sup> /g 2.3072 m <sup>2</sup> /g					
Pore Volume	0.00422819 cc/g	00422819 cc/g 0.00406757 cc/g				
Pore radius Dv(r)	ius Dv(r) 1.94566 nm 1.92529 nm					
BJH Pore Size Distribution Desorption						
Surface Area	2.46113 m²/g	2.2928 m²/g				
Pore Volume	0.00359908 cc/g	g 0.00340444 cc/g				
Pore radius Dv(r)	1.71626 nm	1.71512 nm				
Surface area	3.940 m²/g					
Total Pore Volume						
Total Pore Volume	4.2499e-03 cc/g	4.4625e-03 cc/g				
for pores smaller than	21.27 nm (radius)	20.17 nm (radius)				
at relative pressure	0.95256	0.94985				