

Investigation of an Impedimetric LaSrMnO₃-Au/Y₂O₃-ZrO₂-Al₂O₃ Composite NO_x Sensor

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Section S1 Elemental Mapping (EDS) of LaSrMnO₃-Au Composite Electrode.

Figure S1 and Table S1 show the atomic percent and mole content of the LSM-Au sensing electrode elements. The EDS measurements confirmed the electrode elemental composition; however, the analysis of the elemental concentration deviated from the expected values. A likely reason is that these complex heterogenous oxides, such as LSM with non-stoichiometric phases with enriched Mn and depleted La, Sr elements have overlapping peaks involving oxygen that can interfere with accurate detection [1]. Such deviation in measurements can arise from the background signal resulting in low detection of elements and strong matrix effects from multiple electrons scattering in the thick LSM-Au sample. Such scattering may cause a reduction in the spatial resolution and chemical sensitivity of LSM-Au samples during EDS measurements. Since the LSM-Au electrode cross-section was non-homogenous and EDS captured only a portion of the cross-section, the measurements for Au were lower than the actual amount of Au within the entire bulk electrode.

Nonetheless, the EDS measurements enabled an analysis of the elemental composition and estimates of the proportion of such elements at different positions within the LSM-Au electrode. The elemental measurements consequently provided localized mapping of the bulk LSM-Au sample. The data for La signified ~0.4% of the lattice volume sites had La³⁺ cation deficiencies, which aided Mn³⁺ ion (3d³ electronic configuration) enhancement activity [2–5]. Though the stoichiometric ratio (A/B>1) for (La,Sr)MnO₃ may have possessed other small proportions of low conductive non-stoichiometric phases such as (La,Sr)₃Mn₂O₇, La₂O₃, and (La,Sr)₂Mn₂O₄ promoted by Sr doping, it did not contribute towards sluggishness during charge transfer [6]. Increased Sr doping may result in the distributed partial oxidation of Mn ions to form the formal (3+δ)⁺ oxidation state in LSM leads to shrinking Mn-O bonds, thus decreasing unit-cell volume [7–10]. The La_{0.8}Sr_{0.2}MnO₃ usually has monoclinic symmetry in the lattice structure but does possess hexagonal-rhombohedral distortions in the lattice structure for Sr doping range 0.1<x<0.5 [6]. The minor phases such as, (La, Sr)₂Mn₂O₄ are only stable and observable at lower temperatures ~ 1200°C for Sr doping level (x)> ~ 0.3 mole [4,6]. We assume (La, Sr)₂Mn₂O₄ phases would not be adversely affecting the LSM-Au surface response after exposure around 1400°C [4,6]. The (La, Sr)₃Mn₂O₇ minor phases (Ruddlesden-Popper phase) may be present at a temperature around 1400°C only for the higher Sr doping levels (x>0.3)[4]. The A-site nonstoichiometry of LSM at the electrode surface facilitated more cation vacancies via Schottky disorder, which promoted charge transfer reactions at the electrode-electrolyte interface [3].

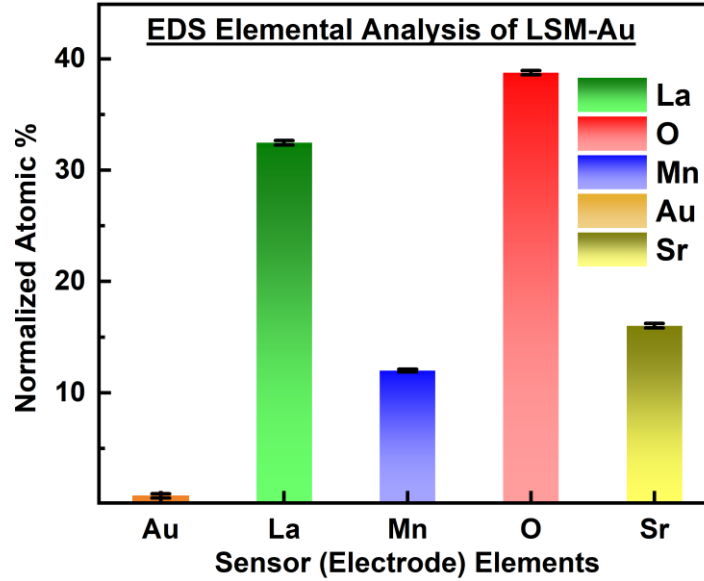


Figure S1. The Figure shows the atomic percentage of LSM-Au governing the phase behavior within the sensor.

Table S1 EDS analysis for LSM-Au

Elements	At%±Error	Mole±Error
Lanthanum (La)	32.5±1.5	0.44±0.02
Strontium (Sr)	16±1.6	0.22±0.02
Manganese (Mn)	12±0.4	0.16±0.00
Oxygen (O)	38.6±2.3	0.53±0.05
Gold (Au)	0.74±0.1	0.01±0.00

*All error measurements are approximated based on the number of measurements at four different electrode sample sites.

Section S2 Structural analysis via XRD of FSZ-PSZ-2wt%Al₂O₃/LaSrMnO₃-Au Sensor.

Further analysis of the composite electrolyte and electrode structure is provided by considering the associated space group, which describes the crystal orientation that influenced defects within material phases. The XRD data in Figure 3b indicated PSZ (4.7 mol% Y₂O₃-ZrO₂) contained a mixture of both tetragonal and monoclinic phases of ZrO₂ (monoclinic-ZrO₂, JCPDS: 37-1484)(tetragonal-ZrO₂, JCPDS: 42-1164), which related to the space group of P4₂/nmc & P2₁/c, respectively [11–14]. In addition, the average crystallite size obtained for PSZ was about 46 nm. Figure 3c shows FSZ (8 mol% Y₂O₃-ZrO₂) primarily consisted of distorted cubic zirconia phases (cubic-ZrO₂, JCPDS: 49-1642) due to having a space group of Fm $\bar{3}$ m. The average crystallite size of FSZ was approximately 3 nm, which has been seen in other studies [11,15–18]. The crystal planes and space groups were indicative of defects and arrangements that corresponded to the electrical and mechanical properties of the electrolyte.

The LSM diffraction peaks were indexed to the pseudo-cubic perovskite structure (space group Pm $\bar{3}$ m) with high crystallinity [19,20]. Moreover, splitting of the (220) diffraction peak into two peaks coupled with the (224) diffraction peak attributed to the tetragonal crystal structure (space group 14/mcm), resulting in the formation of tetragonal polymorph for LSM [21,22]. The XRD finding indicated that the nanoparticles in LSM and LSM-Au samples might be a mixture of cubic and tetragonal structures. The average crystallite size of LSM was about 10 nm. The Sr doping changed the valence state of Mn ions

($\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$) to keep both samples electrically neutral. The presence of tetragonal phases exerted less distortion or irregularities in both samples' crystal structure, which helped enlarge the conduction band. Such enlargement enhanced the double exchange phenomenon; thereby, enhancing the charge transfer properties at a lower frequency [23].

Section S3 XPS analysis for $\text{LaSrMnO}_3\text{-Au}$ / FSZ Composite NO_x Sensor in Table S2.

Table S 2											
FSZ composite electrolyte											
Spectra	Zr3d & Y3d								Al2s		
	Spin doublet Splits										
	Monoclinic phases of Zirconia		Tetragonal/cubic phases of Zirconia		Tetragonal phases of Yttria		Cubic phases of Yttria		α -Al ₂ O ₃		
	Zr3d _{5/2}	Zr3d _{3/2}	Zr3d _{5/2}	Zr3d _{3/2}	Y3d _{5/2}	Y3d _{3/2}	Y3d _{5/2}	Y3d _{3/2}	Al2s		
BE (eV)	181.2	183.5	182.0	184.5	156.6	158.7	157.2	159.3	119.3		
At%	13	13	29.4	29.4	3.2	3.2	4.4	4.4	100		
FWHM (eV)	1.82	2.14	1.35	1.42	1.70	1.70	1.25	1.35	2.76		
LSM-Au electrode											
Spectra	La3d						Sr3d				
	Spin doublet Splits						Satellite	Spin doublet Splits			
	Electron transfer from O ₂ ligand		From La ₂ O ₃ of the inner LSM-Au surface		Shake up features from outer LSM-Au surface		Mixing of 3d ⁹ 4f ² & 3d ⁹ 4f ³ states	Sr ²⁺ ions in the LSM lattice		SrO species on the LSM	
	La3d _{5/2}	La3d _{3/2}	La3d _{5/2}	La3d _{3/2}	La3d _{5/2}	La3d _{3/2}	La3d	Sr3d _{5/2}	Sr3d _{3/2}	Sr3d _{5/2}	Sr3d _{3/2}
BE (eV)	833.9	850.8	835.3	852	838.4	855.2	848	132.5	134.3	133.0	134.8
At%	10.6	10.6	18.4	18.3	21	20.9	0.2	31.6	31.6	18.4	18.4
FWHM (eV)	1.48	1.52	2.76	3.11	2.33	2.86	5.55	0.81	0.92	1.85	3.50
Spectra	Mn2p				Au4f		Mn3s				
	Spin doublet Splits				Doublet Split		Relative Mn ⁴⁺ content				
	LaMn ³⁺ O ₃ species of LSM-Au		SrMn ⁴⁺ O ₃ species of LSM-Au		Metallic Au ⁰ from LSM-Au surface		High Spin		Low Spin		
	Mn2p _{3/2}	Mn2p _{1/2}	Mn2p _{3/2}	Mn2p _{1/2}	Au4f _{7/2}	Au4f _{5/2}	Mn3s ₁		Mn3s ₂		
BE (eV)	641.5	653.2	644.1	655.3	84.3	87.9	82.4		90.6		
At%	42	42	8	8	5.5	5.5	53.2		35.8		
FWHM (eV)	2.92	3.23	2.59	2.47	2.67	2.44	2.07		2.73		

Section S4 Defect Model Influencing Ion Transport in FSZ Composite Electrolyte

According to the Kroeger-Vink defect model, the porous FSZ composite electrolyte results in oxygen vacancies for charge compensation that helps to achieve optimum conductivity (see Figure 5a) [24,25].



Here, the Y'_{Zr} is the Y^{3+} impurity in the site of Zr^{4+} in the lattice having a relative charge of -1, the V''_O represents the free oxygen vacancy with a relative charge of +2, and the O^\times_O denotes the quasi-stable lattice oxygen vacancy generated under reducing conditions. The O^\times_O undergoes through a Schottky defect pair formation reaction under equilibrium condition releasing oxygen from the FSZ-PSZ-2wt% Al_2O_3 lattice & V''_O .



During the electroneutrality condition (having a proportional relation or equilibrium between oxygen vacancies and holes) at nominal oxygen partial pressure, P_{O_2} , the overall oxygen vacancy V''_O is dominated by Y'_{Zr} , the Y^{3+} impurity and electron concentration are as follows [24].



The oxygen ion diffusion in FSZ composite electrolyte occurred via vacancy-ion interactions to the triple-phase-boundary (TPB). The ion diffusion was regulated by a vacancy hopping mechanism, mostly at cation-bounded lattice edges in the FSZ composite electrolyte [24,26,27].

Section S5 Electrochemical Reaction Pathways and Heterogeneous Diffusion During NO_x Sensing at Electrolyte-Electrode Interface of Composite NO_x Sensor.

The Bode Plot provides an additional means of analyzing the electrochemical behavior of the FSZ composite sensor, as it displays the frequencies associated with the electrical response with and without NO_x presence. Figure S2 shows the Bode plot of the FSZ composite sensor that featured Hockey-Stick (10 to 10^6 Hz) and Ski-slope (1 to 10^4 Hz) shapes, indicating the sophisticated nature of charge transfer occurring via multiple LSM-Au surface pathways [9,28]. The Hockey-Stick shape was symbolic of the low impedance of the FSZ composite electrolyte material, where the spectra almost flattened out at higher frequency. The constant phase element Q_{HF} represented the high-frequency dielectric dispersive capacitance. The Q_{HF} represents the coupling current leakage through the FSZ composite porous electrolyte. The electrolyte resistance was the following flat part of the dielectric at the high-frequency region modulated by the surface geometry of the electrolyte, including thickness and the effective impedance of the gas diffusion path offered by the FSZ composite electrolyte. The Q_{HF} and electrolyte resistance, R_{HF} do not differ with and without 100 ppm NO_x , suggesting no cross-reaction resulting in changed current leakage.

The n values associated with the Q_{HF} were around 0.75 for data collected with and without 100 ppm NO_x . The n values show the non-ideal capacitive nature of the dielectric coupling at the high frequency [23]. During 100 ppm NO_x exposure, the electrode or interface capacitance value decreased due to a lower impedance pathway for enhanced charge transfer. The Ski-slope shape indicated a parasitic leakage pathway, resulting in a sizeable actual impedance without 100 ppm NO_x . The lower frequency region (<10 Hz) indicated the parasitic leakage associated with the reaction pathways through the grain boundary and associated Au particles at the LSM surface. The decrease in the magnitude of the impedance, $|Z|$, at 1 Hz signified a leakage path due to shunt resistance R_{LF} . The parasitic pathway occurred at a high impedance region that offered significantly higher impedance without 100 ppm NO_x and enhanced charge transfer at the LSM surface in the presence of 100 ppm NO_x . During exposure to 100 ppm NO_x , the lower frequency curve flattens out more, signified the availability of a comparably lower impedance path, revealing a more

resistive nature [28,29]. The PSZ mostly had prevailing tetragonal phases with a mix of cubic phases and FSZ composed of cubic phases, both particle sizes ranging from 40-1000 nm [12]. The addition of PSZ combined with Al_2O_3 in FSZ provided better fracture toughness to the composite electrolyte but resulted in lower electrical conductivity at a higher temperature ($T > 550^\circ\text{C}$).

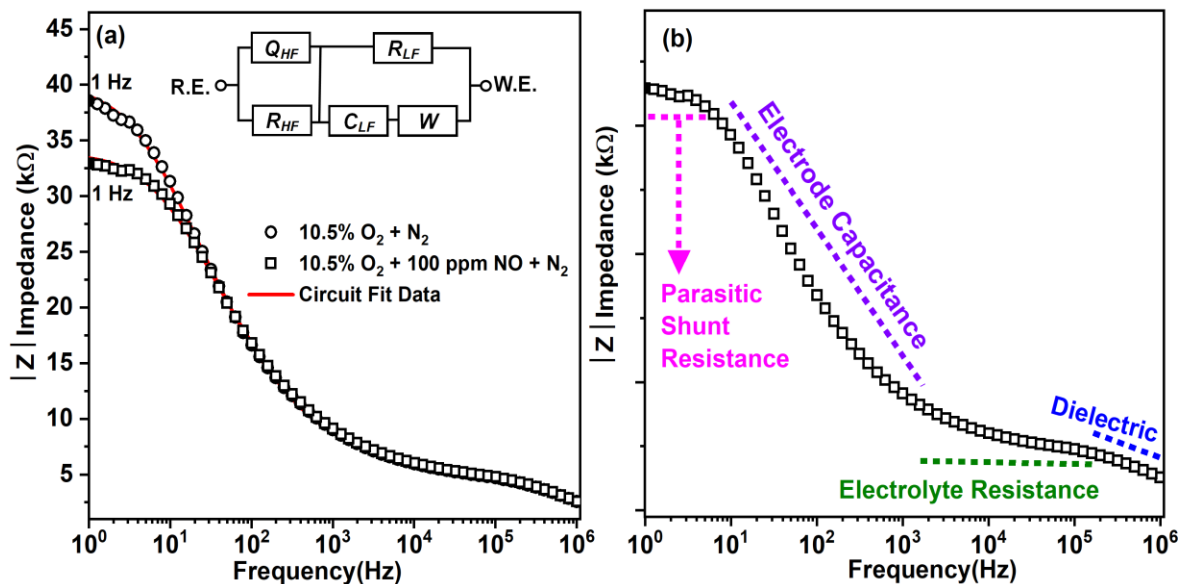


Figure S1. (a) The bode Impedance plot of the FSZ composite NO_x sensor at 575°C with and without 100 ppm NO present. The Bode plot comprises varied shapes like Hockey-Stick (10 to 10^6 Hz) and Ski-slope (1 to 10^4 Hz). Inset the equivalent represents both types of NO_x sensors. (b) The high-frequency region comprises the coupling of electrolyte resistance through a dielectric constant phase element (CPE). The lower frequency region is composed of electrode capacitance and parasitic shunt resistance.

Section S6 The Table S3 for R^2 Values Obtained for Linear Fitting Trends Obtained from Figure 8 For both Dry and Humidified Conditions in FSZ and FSZ Composite Sensor.

Table S3								
Range	FSZ Composite NO_x Sensor				FSZ NO_x Sensor			
	0-25 ppm		25-100 ppm		0-50 ppm		50-100 ppm	
Conditions	Dry	Humid	Dry	Humid	Dry	Humid	Dry	Humid
R^2	0.98534	0.97617	0.99595	0.99951	0.99952	0.99992	0.99936	0.99985

Note: Dry condition is without 10% H_2O ; the wet condition is with 10% H_2O . Besides, both conditions have 10.5 % O_2 , NO , N_2 present during measurement. The R^2 values confirm the linearity of the presented dataset in Figure 8. All Linear Fitting is performed in OriginPro Software 2021b.

Section S7 Water Cross Sensitivity for FSZ Composite NO_x Sensor at Various Temperatures.

The water cross-sensitivity diminished with increasing operating temperatures beyond ($T > 575^\circ\text{C}$) for the FSZ composite NO_x sensor. The water cross-sensitivity demonstrated a decreasing trend of ~7% as the operating temperature increases by 25°C from 575 to 600°C (Figure S3).

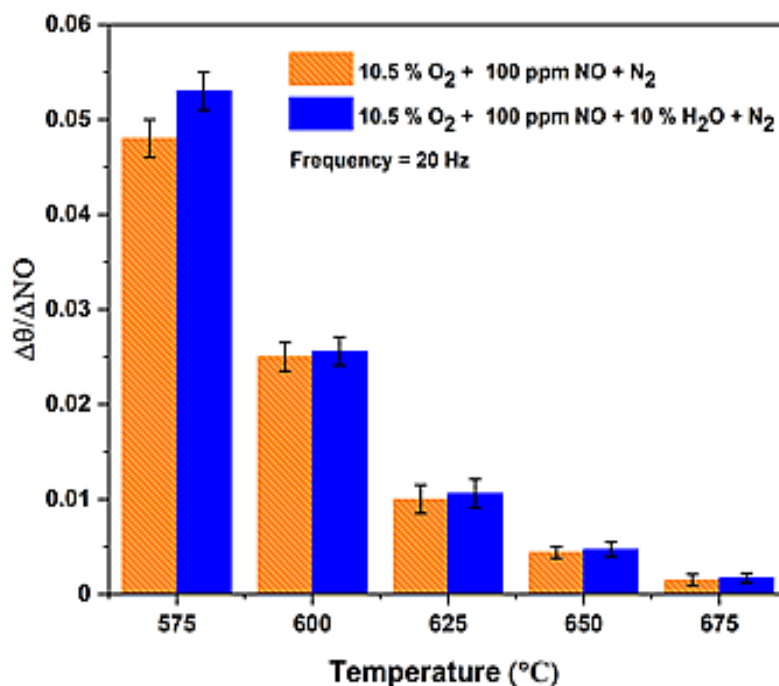


Figure S3. Change in water cross-sensitivity with increasing operating temperature for FSZ composite NO_x sensor.

Section S8 Rate Limiting Mechanism Associated with FSZ Composite NO_x Sensor.

The rate-limiting mechanisms associated with the FSZ composite sensors were evaluated using the power-law relationship $R_{LF} \propto P_{O_2}^m$ where R_{LF} was the charge transfer resistance determined from equivalent circuit analysis of the low-frequency arc, P_{O_2} described the oxygen partial pressure, and m indicated the rate-limiting mechanism. Figure S4 shows the value of the power-law exponent, m , for the FSZ composite sensors. The transport of partially reduced atomic oxygen to the TPB where charge transfer occurs has been associated with a slope value of $m = -0.25$ [30,31]. The P_{O_2} dependence for dry gas conditions resulted in data extremely near this value, thus suggesting atomic oxygen reduction was the rate-limiting mechanism for the FSZ composite sensors. The sensing LSM-Au electrode surface may act as an oxygen-deficient surface at low oxygen partial pressures [3,9,10]. Such a scenario likely affected the mechanism of surface oxygen vacancy formation in the FSZ composite electrolyte. The increase in the P_{O_2} dependence due to the addition of 10% water in the operating environment suggests that charge transfer became more rapid as partial reduction of atomic oxygen was enhanced.

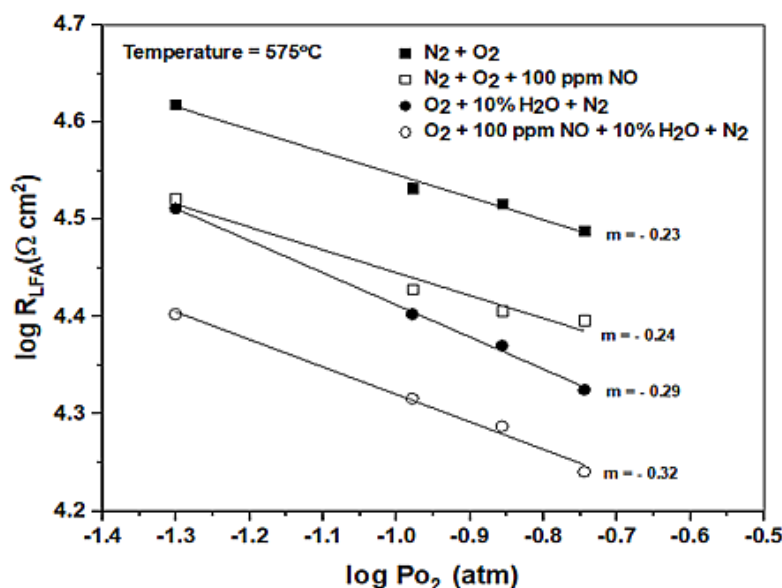


Figure S4. Power law exponent determination for FSZ composite sensors with various gas concentrations of NO and H₂O at 575°C.

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