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Supplemental Information

Increased Activity in the Oxygen Evolution Reaction by Fe^{4+}-Induced Hole States in Perovskite $La_{1-x}Sr_xFeO_3$

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Table S1. The actual metal concentrations in LSFO-x powders determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The molar ratios are calculated using metal atomic weight: $M_{\mathrm{Sr}} = 87.620\ \mathrm{g\ mol^{-1}}$, $M_{\mathrm{La}} = 138.905\ \mathrm{g\ mol^{-1}}$, $M_{\mathrm{Fe}} = 55.845\ \mathrm{g\ mol^{-1}}$.

LSFO-x	Sr (mg L^{-1})	La (mg L^{-1})	Fe (mg L^{-1})	Molar ratio Sr:La:Fe
LFO	0	14.845	5.866	0:1:1
LSFO-0.1	0.510	7.669	3.366	0.10:0.90:1
LSFO-0.33	2.525	7.982	4.838	0.33:0.66:1
LSFO-0.67	7.792	6.162	7.421	0.67:0.33:1
LSFO-0.8	8.373	3.235	6.639	0.80:0.20:1
SFO	13.21	0	8.452	1:0:1

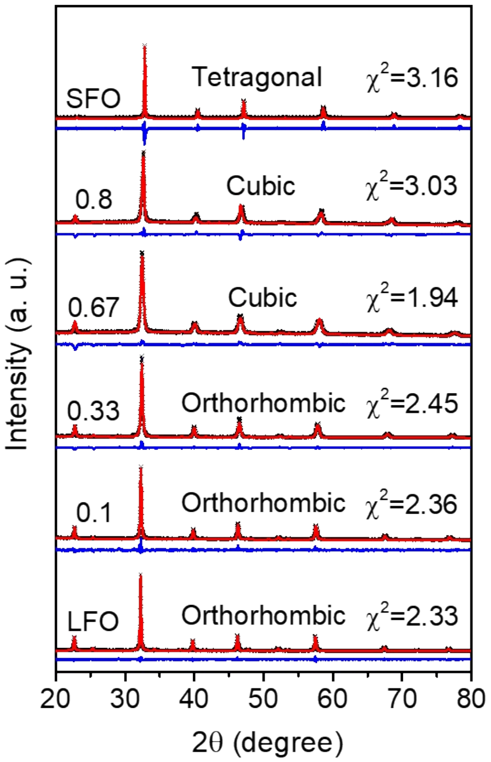


Fig. S1. XRD Rietveld refinement for LSFO polycrystalline powders, showing the crystal structure changing from orthorhombic to cubic at x=0.67 and tetragonal phase for SFO.

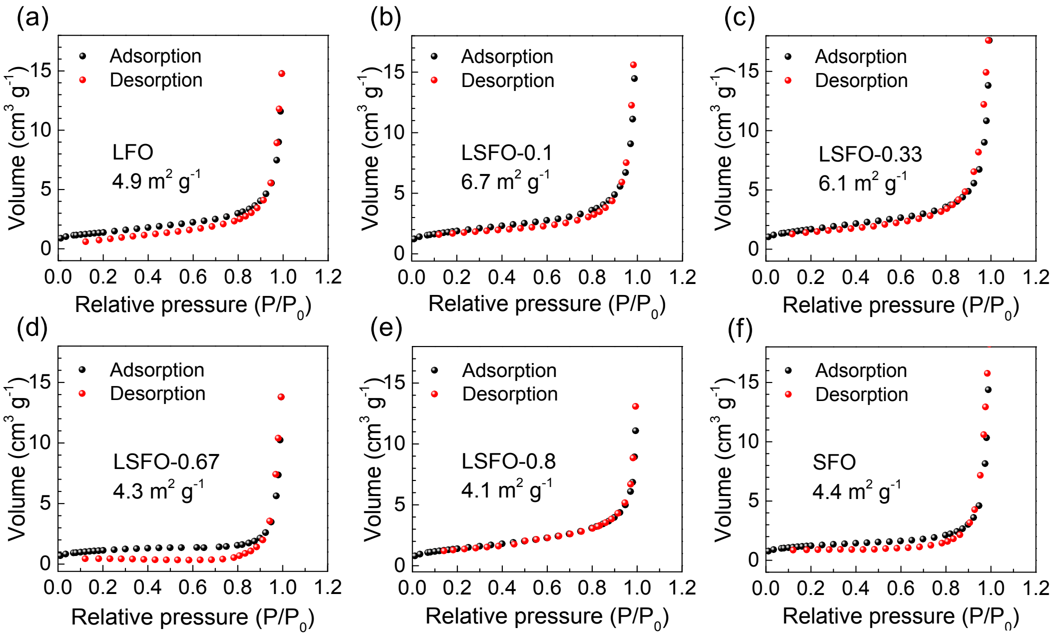


Fig. S2. Isothermal N_2 adsorption and desorption plots and specific surface areas determined by Brunauer-Emmett-Teller (BET) method for (a) LFO; (b) LSFO-0.1; (c) LSFO-0.33; (d) LSFO-0.67; (e) LSFO-0.8; (f) SFO.

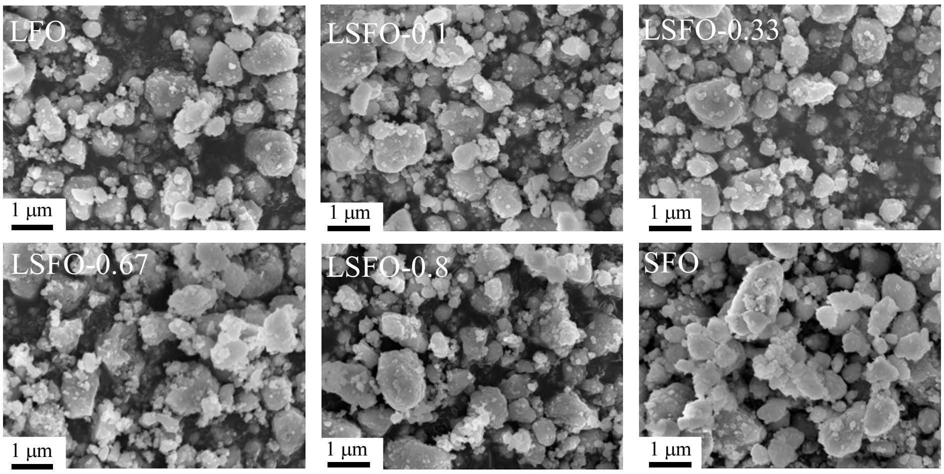


Fig. S3. Scanning electron microscope (SEM) images of LSFO-x powders.

Table S2. The fitted charge transfer resistance (*R_{ct}*) values of LSFO-x from electrochemical impedance spectroscopy (EIS).

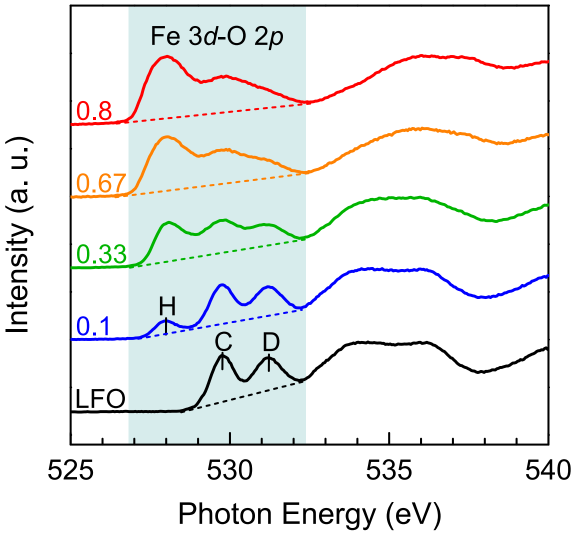
LSFO-*x*	LFO	LSFO-0.1	LSFO-0.33	LSFO-0.67	LSFO-0.8	SFO
$R_{\mathrm{ct}}(\Omega)$	4320	2820	1720	500	390	7610

Hybridization degree calculation:

The O *K*-edge XAS spectra probe the electronic transitions from the O 1*s* core-level to unoccupied states with partial O 2p character hybridized with empty Fe 3d states. The spectral intensity can be qualitatively related to the density of states, especially the unoccupied Fe 3d states[1]:

$$I = \text{Hybridization parameters} * h_{3d}$$

where I is the integrated areas of peaks H, C and D in O *K*-edge XAS (shown in the following figure), which is proportional to the unoccupied states in O 2*p* that hybridizes with Fe 3*d* states, h_{3d} is the nominal numbers of unoccupied orbitals of Fe



3*d*.

Fig. S4. O *K*-edge XAS. The area of peak H, peak C, peak D for unoccupied Fe 3*d*-O 2*p* states are integrated after the background subtraction.

Table S3. Integrated peak areas of O *K*-edge XAS for LSFO and nominal numbers of unoccupied orbitals of Fe 3*d*.

Sample	$I_{\text{Peak H}}$	$I_{\text{Peak C}}$	$I_{\text{Peak D}}$	I_{Total}	h_{3d}
LFO	0	1.298	1.572	2.870	5
LSFO-0.1	0.467	1.368	1.579	3.414	5.1
LSFO-0.33	1.327	1.397	1.410	4.134	5.33
LSFO-0.67	2.107	1.983	0.750	4.840	5.67
LSFO-0.8	2.445	1.938	0.689	5.072	5.8

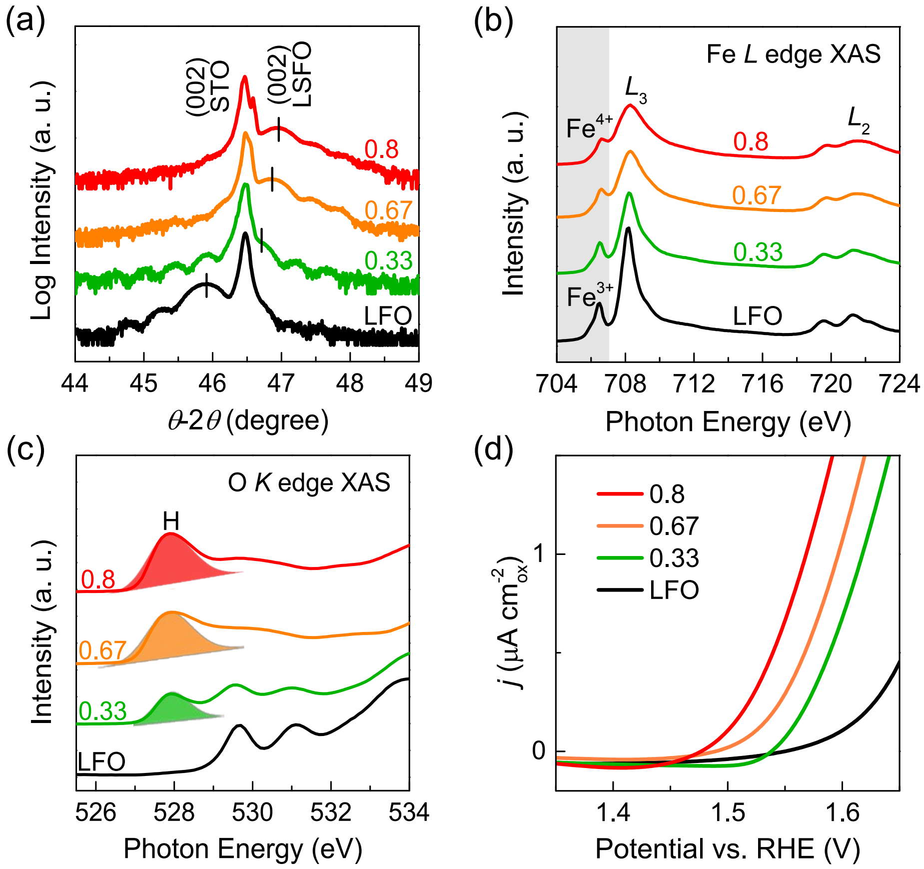


Fig. S5. (a) XRD *θ*-2*θ* scans near the (002) diffraction peak for the LSFO thin films, showing the epitaxial growth of LSFO thin films on Nb doped $SrTiO_3$(STO); (b) Fe $L_{2,3}$ edge XAS for the LSFO thin films; the systematic change of the pre-peak at ~706 eV photon energy suggests Fe^{4+} oxidization state. (c) O *K*-edge XAS for LSFO thin films, showing an increase of hole state (marked as "H"). (d) Linear sweep voltammetry polarization curves after three cycles of cyclic voltammetry for LSFO thin films. All the characterizations for the LSFO thin films suggest that the epitaxial thin films exhibit similar electronic structures and trend of OER activities as those of LSFO polycrystalline powders.

Reference

1. J. Suntivich, W. T. Hong, Y.-L. Lee, J. M. Rondinelli, W. Yang, J. B. Goodenough, B. Dabrowski, J. W. Freeland and Y. Shao-Horn, *J. Phys. Chem. C*, 2014, **118**, 1856-1863.