Supporting Information

Tuning Spin State in LaCoO₃ Thin Films for Enhanced High Temperature Oxygen Electrocatalysis

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THIN FILM GROWTH

Synthesis of the pulsed laser deposition (PLD) targets. LaCoO₃ (LCO) powder for the PLD target was synthesized using solid-state reaction from stoichiometric mixtures of La₂O₃ and Co₃O₄ (Alfa Aesar, USA), and sintered at 1,000 °C in air for 12 hours. The 20 mol% Gd₂O₃:CeO₂ (GDC) powder was synthesized via Pechini method using Gd(NO₃)₃ and Ce(NO₃)₃, which were dissolved in a mixture of ethylene glycol and citric acid (Sigma-Aldrich, USA) in de-ionized water. After esterification at ~100 °C, the resin was charred at 400 °C and then calcined at 800 °C in air for 1 hour. Phase purity was confirmed using X-ray powder diffraction (XRD, PANalytical). Subsequently, PLD targets of 25 mm in diameter were formed by uniaxial pressing at ~50 MPa and sintered at 1350 °C in air for 20 hours.

Synthesis of the polycrystalline ceramic pellet sample for Raman spectroscopy. The LCO pellet for Raman spectroscopy measurements was synthesized via solid-state reaction from stoichiometric mixtures of La_2O_3 and Co_3O_4 (Alfa Aeser, USA). Precursor oxides were dried at 770 °C before weighing. The precursors were ground and uniaxially cold-pressed into 25 mm diameter pellets at ~50 MPa before sintering at 1000 °C for 10 hours. The samples were then ground, pressed, and sintered again at 1100 °C for 12 hours. Phase purity was confirmed using X-ray diffraction (XRD, PANalytical).

Epitaxial thin film deposition. 10 mm x 5 mm x 0.5 mm, one-side polished (surface roughness < 1 nm), (001)-oriented single crystals of 9.5 mol% Y₂O₃-stabilized ZrO₂ (YSZ, Princeton Scientific, USA) were used as the substrates for pulsed laser deposition (PLD). Platinum ink (Pt, #6082, BASF, USA) counter electrodes were painted on the unpolished side of the YSZ and sintered at 800 °C in air for 1 hour. The 20 mol% GDC electrolytic buffer layer (which prevents decomposition reactions between YSZ and LCO¹), and the LCO thin films were deposited by PLD using a KrF excimer laser ($\lambda = 248$ nm) at a pulse frequency of 10 Hz and laser fluence of ~1.5 J/cm². Films were deposited under 50 mTorr of O₂ in the following manner: 500 pulses of GDC (~5 nm based on previous scanning transmission electron microscopy measurements performed on similarly prepared samples²) at 475 °C, followed by 5,000/10,000/15,000 pulses of LCO at ~550 °C. Reflection high-energy electron diffraction (RHEED) was used to provide *in situ* monitoring of film growth.

Film growth RHEED patterns. RHEED images were collected throughout the LCO deposition (**Figure S2**). The diffraction pattern contains information about both the crystallinity and morphology of the surface.³ The patterns indicate a Stranski-Krastanov mixed island/layer-by-layer growth, and the film undergoes a clear change after 1,000 pulses (~10 nm), which then remains constant up to 15,000 pulses. This change may indicate a change in the size or orientation of island facets during growth.

X-ray diffraction (XRD). In addition to the θ -2 θ scans shown in Figure 1a, off-normal measurements of the in-plane film orientation and pseudocubic lattice parameters using the $\{202\}_{pc}$ reflections were performed on all films (Figure S3 and S4). The phi scans show that the $(001)_{pc}$ LCO films are epitaxial with a well-defined in-plane orientation, 45° with respect to the GDC and YSZ (Figure S3). However, a peak splitting is present in the off-normal diffraction peaks that may result from film relaxation or formation of rhombohedral domains in the film (Figure S4). The pseudocubic lattice parameters presented in Figure 2 were determined using the more intense, low angle peak. A comprehensive table of the substrate-constrained pseudocubic lattice parameters, relaxed film lattice parameters, in-plane and out-of-plane strains, and volumetric strains is provided in Table S1. The relaxed film lattice parameters were determined as $\frac{c-\hat{e}}{\hat{e}} = -\frac{2\nu}{1-\nu}\frac{a-\hat{a}}{\hat{a}}$, where $\nu = 0.25$ was estimated as the Poisson ratio for typical thin film oxides.⁴

ELECTROCHEMICAL MEASUREMENTS

Microelectrode Fabrication. OCG positive photoresist (Arch Chemical Co., USA) was applied on the film surface and patterned using a Mask Aligner (Karl Süss, German, $\lambda = 365$ nm). The photoresist was developed using Developer 934 1:1 (Arch Chemical Co., USA), and the films were subsequently etched in hydrochloric acid (HCl) to form circular microelectrodes (diameters ~50 µm, ~100 µm, ~150 µm, and ~200 µm; exact diameter determined by optical microscopy). The photoresist was removed with acetone. AFM was used to measure sample thickness for each film after microelectrode patterning: LCO 15,000 pulses (107.6 ± 8.2 nm); 10,000 pulses (71.7 ± 5.3 nm), 5,000 pulses (44.2 ± 3.9 nm). *Electrochemical impedance spectroscopy (EIS).* EIS was collected using a microprobe station setup (Karl Süss, Germany) connected to a frequency response analyzer (Solartron 1260, USA) and a dielectric interface (Solartron 1296, USA). Pt-coated tungsten carbide probes were utilized to contact ~200 µm LSC electrodes and the porous Pt counter electrode. Temperature was controlled at 800 K with a heating stage (Linkam TS1500, UK) and measured with a second thermocouple on the sample surface. EIS data was collected between 1 MHz to 1 mHz using a voltage amplitude of 10 mV under Ar / O₂ mixtures from $p(O_2) = 10^{-3}$ to 1. Figure S5 details the equivalent circuit and representative Nyquist plots for this experimental system. *ZView* software (Scribner Associates, USA) was used to construct the equivalent circuit and perform complex least-square fitting to extract the fitting parameters describing the system.

The electrical oxygen surface exchange coefficient (k^{q}) was determined using Eq. S1:^{5, 6}

$$k^{\mathbf{q}} = \frac{RT}{4F^2 R_{LF} A_{\text{electrode}} c_0} \tag{S1}$$

R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), *T* is the absolute temperature, *F* is Faraday's constant (96,500 C mol⁻¹), R_{LF} is the low frequency real resistance, $A_{\text{electrode}}$ is the area of the microelectrode, and c_0 is the lattice oxygen concentration in LCO ($c_0 = (3-\delta)/V_m$, where δ is the oxygen non-stoichiometry and $V_m = 33.74$ cm³ mol⁻¹ is the molar volume of LCO at room temperature⁷. V_m was treated as constant for all experimental contributions, as the influence of molar volume scales linearly with k^q and chemical expansion of the lattice due to spin state and/or oxygen vacancies is expected to be no more than 5%).

The oxygen non-stoichiometry, δ , was determined from the volume specific capacitance (VSC). The VSC of the thin films was obtained from the EIS data using **Eq. S2**:⁸

VSC =
$$V_{\text{electrode}}^{-1} (Z^{(1-n)}Q)^{1/n}$$
 (S2)

where Z, Q, and n are fitting parameters from the Nyquist plot (real impedance, capacitance, and non-ideality respectively). The oxygen non-stoichiometry can then be determined as:

$$\delta = \frac{3}{2} - \frac{1}{2}\sqrt{9 - \frac{12RT}{\left[\left(\frac{4F^2}{VSC} \cdot V_m\right) - a(x)\right]}}$$
(S3)

a(x) is a factor that describes the materials' deviation from ideal solid solution (221 kJ/mol).⁹

MAGNETOMETRY

SQUID measurements. The magnetic properties of the LCO thin films were measured by SQUID magnetometry (Quantum Design MPMS 5S). The magnetizations as a function of temperature

with *H* applied along the in-plane direction are shown in **Figure S6**. Note that the magnetization is shown in units of $\mu_{\rm B}$ /mol, indicating very low magnetization on the order of the substrate and sample holder background levels even near the ground state (5 K), illustrating the LS Co³⁺ ground spin configuration. No ferromagnetic transition ($T_{\rm C} \sim 80$ K reported in literature for LCO on LSAT and STO¹⁰⁻¹²) is observed in any of the films and the slight increase in magnetization near 5 K can be attributed to the substrate and sample holder background, also supporting the LS ground state.

RAMAN SPECTROSCOPY AND ANALYSIS

Raman measurements. Raman spectroscopy was performed on a LabRAM HR800 microscope (Horiba Jobin Yvon) using an external 50 mW DPSS 532 nm laser (Horiba Jobin Yvon), focused with a 50× long working distance objective and a $10^{-0.3}$ neutral density filter. A silicon substrate was used to calibrate the Raman shift. The sampling time and range were identical for all acquisitions (150-800 cm⁻¹, 15×120 s) using a high resolution 1800 mm⁻¹ grating. A heating and freezing microscope stage (Linkam THMS600, Linkam T95 system controller, Linkam LNP95 cooling system) was used to study the samples at various temperatures from 175 K to 800 K. The sample was heated/cooled at a rate of 10 K/min and the beam was refocused and realigned to the same position at each temperature. A YSZ substrate with a ~10 nm GDC film was used as a reference to check for substrate contributions in the Raman spectra (Figure S7). Peak positions for the La Eg stretching mode and CoO₆ A_{2g} breathing mode were determined using the peak maximum after a 10-point fast Fourier Transform (FFT) filter smoothing. The instrumental resolution (0.5-1.0 cm⁻¹) is significantly smaller than the user error introduced when identifying peak position due to the low signal intensity and broad full-width-half-maximum. Error bars provided in Figure 4 were thus taken as a cautiously large constant of ± 5 cm⁻¹, and it is clear that even with these artificially large error bars, the trends between samples and as a function of temperature remain evident. A table of temperatures measured for each sample and their peak positions are tabulated in Table S2.

New peak evolution in polycrystalline LCO. Changes in the Raman selection rules (quenching of peaks and appearance of new ones) in the polycrystalline LCO sample occur at two primary transition temperatures (~375 K and ~675 K). These temperatures correspond well with the

insulator to semiconductor transition and semiconductor to metal transition previously reported for LCO.¹³ The itineracy of the valence electrons is expected to play an important role in the symmetry of the polarizability tensor (and thus the Raman selection rules). Consequently, these changes may reflect the temperature-dependent changes in electrical conductivity.

The vibrational energies of the new peaks (200 cm⁻¹ and 400 cm⁻¹) are similar to those predicted through lattice dynamics calculations for the A_{2u} (M+O)-La and A_{2u} M-O bending modes, which are IR active modes.¹⁴ In general, the rule of mutual exclusion for Raman and IR activity only holds if center of inversion symmetry is preserved, otherwise normal vibrations result in a mix of even and odd parity and the mutual exclusion principle breaks down. Thus, these peaks may be related to IR modes that become active due to a break in the unit cell inversion symmetry. Both changes in the itineracy of electrons and breaks in inversion symmetry may be accomplished by the mixing of spin states.^{13, 15} More detailed studies are necessary to explore this hypothesis.

Relation between bond stiffness and bond strength using a Lennard-Jones potential. A rough approximation for how bond strength changes with bond stiffness (vibrational energy) can be determined by assuming a Lennard-Jones potential:

$$V_{\rm LJ} = \varepsilon \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right]$$
(S4)

For small deviations from the equilibrium bond strength (ε) and bond length (r_0), the perturbation can be treated in the harmonic limit. The bond stiffness, k, is thus simply the curvature of the potential well, evaluated at equilibrium ($r = r_0$), which gives: $k \sim \varepsilon / r_0^2$.

The bond stiffness is experimentally obtained from the A_{2g} breathing mode energy (i.e. the Co-O stretching frequency), $k \sim \bar{\nu}^2$. Thus, using half the lattice constant (or relaxed film lattice constant for the thin films) as an estimate of the Co-O bond length r_0 , the ratio $k_{\text{film}}/k_{\text{bulk}}$ obtained from Raman measurements can be used to determine the ratio $\varepsilon_{\text{film}}/\varepsilon_{\text{bulk}}$ (Eq. S5). A range for the film:bulk equilibrium bond strength ratios (percent change in bond strength) is provided in **Table S3** using the CoO₆ breathing mode energies of bulk data (single crystal¹⁶ and polycrystalline) and thin film data (110 nm and 70 nm).

$$\frac{\varepsilon_{\rm film}}{\varepsilon_{\rm bulk}} = \left[\left(\frac{a_{\rm pc,bulk}}{\hat{a}_{\rm pc,film}} \right) \left(\frac{\overline{\nu}_{\rm film}}{\overline{\nu}_{\rm bulk}} \right) \right]^2 \tag{S5}$$

Spin transition model. The spin transition model is based on a two-state model (low spin-high spin, LS-HS) originally developed by Bari and Sivardière¹⁷ as an extension of the Chestnut model¹⁸ for spin transitions. A set of equations for a two-state system with spin-ordering was also developed in their work. Asai, et al.¹⁹ and Radaelli, et al.²⁰ later extended the model to describe a three-state system (low spin – intermediate spin – high spin, LS-IS-HS). For further details regarding these models, the reader is referred to the original papers.

Both models operate by solving a set of self-consistent equations. Two spin transition theories were considered: a LS-IS-HS system, and a LS-HS system with spin ordering. The self-consistent equations for these systems are given by Eq. S6: $^{17, 19}$

$$\langle x_s \rangle = \frac{\nu_s \mathrm{e}^{-\beta E_s}}{Z} \tag{S6}$$

where x_s is the fractional occupancy of spin state *s* (LS, IS, HS), v_s is the degeneracy of the spin state, β is thermodynamic beta (1/*k*_B*T*), and *Z* is the partition function of the canonical ensemble. E_s is the energy of the spin state and determines the nature of the spin transition. The definitions for E_s in the LS-IS-HS system and the spin ordered LS-HS system are provided in **Eq. S7** and **Eq. S8** respectively.

LS-IS-HS system:

$$E_{s} = \frac{1}{2}\xi(Q - Q_{s})^{2} + (\Delta_{s} - VQ)$$
(S7)

 ξ is the volumetric elastic energy for the CoO₆ distortion.

Q is the volumetric strain relative to the ground state at a given temperature.

Defined as $Q = x_{LS}Q_{LS} + x_{IS}Q_{IS} + x_{HS}Q_{HS}$.

Qs is the equilibrium volumetric strain for a given spin state.

V is defined as Δ_s/Q_s and represents weakening of the crystal field associated with increasing the Co-O bond length.

LS-HS spin ordered system:

$$\langle x_{\text{HS},i} \rangle = \frac{\nu_{\text{HS}}}{\nu_{\text{HS}+\exp\left(\beta(\Delta-2Kx_{\text{HS},i}+Lx_{\text{HS},j})\right)}}$$
(S8)

In this model, the unit cell is divided into two sub-lattices A and B, where the high spin fractional occupancy of a site *i* is described by the self-consistent equation S7 where $j \neq i$.

K is an attractive force between HS ions (as K increases, the energy penalty for occupying the HS state on site *i* decreases), while L is a repulsive force between

HS ions (as L increases, the energy penalty for occupying the HS state on site *i* increases).

The majority of the parameters in these equations can be treated as constants previously determined from literature.^{19, 20} The only free variables are the transition temperatures (Δ_{IS} and $\Delta_{\rm HS}$ in the three-state, $\Delta_{\rm order}$ in the two-state), and the interaction parameters K and L in the twostate system. Given these values, the fractional spin occupancies at a given temperature can be completely determined by solving the self-consistent equations using a fixed-point iterative algorithm. By iterating through a range of possible values for each of the free variables and using the fractional spin occupancies to calculate the CoO_6 breathing mode energy (using Eq. 1 in the main text), the best fit with the experimental data can be found using a least-squares regression method. <ELS> was determined by the 0 K limit from the experimental data, while <EHS> was determined by the T_{∞} limit (appropriately weighted by the spin degeneracies). $\langle E_{IS} \rangle$ was taken as an intermediate value. A table of the fitting parameters is provided in Table S4. It should be noted that in order to achieve good fits, the degeneracy of the IS state was taken to be 3 (spin degeneracy S = 3, orbital degeneracy $\eta = 1$, i.e. non-degenerate t_{2g} and non-degenerate e_g states), rather than 9 (spin degeneracy S = 3, orbital degeneracy η = 3, i.e. degenerate t_{2g} states and Jahn-Teller split e_g states). This has also been observed previously using different models for spin transitions in the Raman spectra in bulk single crystals¹⁶ and is expected from a Jahn-Teller distortion that breaks degeneracy of both the t_{2g} and e_g states (i.e. second order Jahn-Teller effect^{21, 22}).

Fits using the three-state model are presented in the main text (**Figure 5**), while fits for the twostate spin-ordered model are presented here (**Figure S8**). Figure S8b illustrates the site-specific HS fractional occupancies. Where the site A (solid lines) and site B (dashed lines) have equal occupancies, there is no preference for a given spin state on that particular site. However where the two lines deviate, there is a preference for the spin states to localize on a given site (i.e. spin ordering). It is evident that the spin-ordered model results in a poorer fit, particularly in bulk where $r^2 \sim 0.76$. The results are also fairly unphysical; the bulk data fitting shows a very narrow temperature range for spin ordering, yet the spin-ordered regime should extend from ~100 K (the first transition temperature observed by electrical conductivity) to ~500-600 K (the second transition)^{13, 19, 20}. The inaccuracy of this model is more likely a result of the assumptions in the model rather than a statement regarding the true nature of the system – due to oversimplification of the spin interactions, or the treatment of the breathing mode energy for spin-ordered ions as identical to spin-disordered ions.

DENSITY FUNCTIONAL THEORY (DFT) CALCULATIONS

DFT calculations were performed using Vienna Ab-initio Simulation Package (VASP)²³ with the generalized gradient approximation (GGA) (PW-91 version²⁴) and $U_{eff} = 3.3$ eV from Wang et al.²⁵, as well as the hybrid (HSE06) functional²⁶. Ionic cores were represented by PAW method. For the calculations with GGA+U, A 2×2×2 k-point mesh for a 2×2×2 (40-atom) cell was used with a 600 eV plane-wave energy cut-off. Different spin configurations (LS/IS/HS) were fixed by controlling the difference between total number of "up" and "down" spin electrons in the electronic configuration. Vacancy formation energy (E_{vac}) was calculated as:

 $E_{\rm vac} = E^{\rm defected} - E^{\rm perfect} + 0.5 \times E_{\rm O2}$

where $E_{defected}$ is the energy of a 2×2×2 supercell with 1 oxygen vacant site, and $E_{perfect}$ is the DFT energy of a stoichiometric 2×2×2 supercell of LaCoO₃. Energy E_{O2} is taken from Lee et al.²⁷

The bulk O *p*-band center was quantified as the energetic centroid of the O *p*-band density of states relative to the DFT computed Fermi level. Details for the robustness of the O *p*-band center to computational parameters such as U_{eff} can be found in our previous work.²⁸ The O *p*-band center for LCO in different spin configurations (LS, IS, HS) is shown in **Figure S9** and shows a monotonic increase in energy with increasing spin state, correlating linearly with the decrease in vacancy formation energy (**Figure 6a**). For the O *p*-band center value of the thin films shown in **Figure 6b**, we took the average value of the IS (-2.56 eV) and HS (-2.20 eV), and error bars in the *p*-band center ranging from -2.56 eV to -2.20 eV.



Figure S1. (a) Octahedral configuration of oxygen anions around the Co ion (CoO₆ octahedra). Due to the symmetry of the anions, the $d_{x^2-y^2}$ and $d_{z^2-r^2}$ Co orbitals (which point directly at the oxygen anions) are no longer degenerate with the remaining *d*-orbitals and are raised in energy, resulting in the so-called crystal field splitting. The d-orbitals are antibonding in character, where the higher energy states are σ -antibonding in character due to their overlap with the oxygen ligand orbitals.²⁹ (b) The crystal field splitting and electron pairing interactions result in different spin configurations. The spin states observed in LaCoO₃ from literature include low spin (LS), intermediate spin (IS), and high spin (HS).



Figure S2. RHEED images after various pulses during thin film deposition. Note the change in symmetry in the LCO surface as the number of pulses (p) increases, particularly the transition after 1000 pulses.



Figure S3. Off-normal XRD phi scan of $\{202\}_{pc}$ reflections from $(001)_{pc}$ 110 nm LCO thin film, representative of the relative in-plane orientations of the LCO, GDC, and YSZ. The $(001)_{pc}$ LCO grows at a 45° angle in-plane relative to the GDC and YSZ orientation, and four-fold cubic symmetry is observed from the $(001)_{pc}$ LCO film.



Figure S4. Off-normal XRD of the $\{202\}_{pc}$ reflections from $(001)_{pc}$ LCO thin films (110 nm, 70 nm, 45 nm). The splitting is present for all films, although the peak intensity ratio changes as a function of thickness.

Film Thickness (nm)	Constrained film in-plane lattice constant, $a_{ m pc}({ m \AA})$	Constrained film out-of-plane lattice constant, $c_{ m pc}({ m \AA})$	Relaxed film lattice constant, â _{pc} (Å)	In-plane strain, ɛ _{xx} (relative to bulk)	Out-of- plane strain, ε _{zz} (relative to bulk)	Volumetric strain, ε _ν (relative to bulk)
110 nm	3.856	3.830	3.845	0.287%	-0.383%	1.639%
70 nm	3.855	3.830	3.844	0.279%	-0.372%	1.611%
45 nm	3.858	3.828	3.845	0.333%	-0.445%	1.684%

Table S1. Constrained and relaxed lattice parameters determined for the thin films based on XRD measurements. In-plane and out-of-plane strains were determined relative to bulk lattice constants and used to determine the volumetric strain of the thin film pseudocubic unit cells relative to bulk LCO ($a_{pc} = 3.826$ Å)¹³, i.e. chemical and mechanical strain.



Figure S5. (a) Typical Nyquist plots of a LCO microelectrode with 200 μ m diameter. (b) Equivalent circuit (R₁ = YSZ electrolyte resistance, R₂ = electrode/electrolyte interfacial resistance³⁰, R₀₂ = oxygen surface exchange resistance, CPE = constant phase element) used to extract oxygen surface exchange coefficient.



Figure S6. Magnetization as a function of temperature for thin film LCO samples, with a magnetic field (1000 Oe) along the sample in-plane direction.



Figure S7. Raman spectra at various temperatures for a GDC/YSZ reference. Room temperature is given in black (300 K) and temperatures above room temperature in red/orange (325 K, 375 K, 475 K, 525 K, 575 K, 675 K, 800 K).

Sample	Temperature (K)	E _g La Stretching (cm ⁻¹)	A _{2g} Co-O Breathing (cm ⁻¹)
Single Crystal ⁹	5	171	676
	40	171	676
	50	170	675
	60	169	674
	70	168	674
	80	167	673
	90	166.5	673
	100	166	672
	150	164	673
	200	163	666
	300	160	663
Polycrystalline	225	157.2	654.2
	275	156.2	648.2
	300	155.2	643.8
	325	154.7	642.3
	370	152.2	641.3
	420	146.8	-
	440	148.3	-
	465	149.8	-
	490	150.7	-
	515	151.2	-
	560	146.3	-
	655	145.8	_
110 nm	175	157.2	642.3
	200	157.2	640.8
	225	156.2	636.8
	250	155.2	631.3
	275	155.2	629.8
	300	155.2	626.4
	325	154.7	625.9
	375	153.2	615.9
	425	151.2	595.5
	475	148.8	591.5
	525	148.3	588.1
	575	147.8	587.6
	625	146.8	583.6
	675	145.3	580.6
	750	143.8	581.1
	800	143.8	580.1
70 nm	300	153.7	610.9
	325	153.2	614.9
	375	151.2	606.0
	425	149.3	601.0
	475	145.8	593.0
	525	144.8	590.5
	575	146.3	589.6
	625	142.8	589.6
	675	139.8	586.6
	750	138.8	590.5
	800	136.3	585.6

Table S2. Raman peak positions and temperatures for the spectra collected.

	Thin Film A _{2g} CoO ₆ breathing mode energy (cm ⁻¹)	Bulk A _{2g} CoO ₆ breathing mode energy (cm ⁻¹)	Equilibrium Bond Strength Ratio (Eq. S5)
110 nm : Single Crystal	626.4	663	0.884
70 nm : Single Crystal	610.9	663	0.841
110 nm : Polycrystalline	626.4	643.8	0.937
70 nm : Polycrystalline	610.9	643.8	0.891
Average film : Average bulk	618.7	653.4	0.888

Table S3. Values used in **Eq. S5** for determining the relative change in Co-O bond strength from Raman vibrational energies under a harmonic approximation of the Lennard-Jones potential. Bond strength ratios are determined for various combinations of bulk data (single crystal and polycrystalline) and thin film data (110 nm and 70 nm) to estimate the range of strain-induced change in bond strength. For all ratios, the bulk pseudocubic lattice parameter used was $a_{pc} = 3.826$ Å and the relaxed film lattice parameter used was $\hat{a}_{pc} = 3.845$ Å.

	LS-IS-HS	Spin-Ordered
LS Degeneracy, $(2S+1)(\eta_{t2g})(\eta_{eg}) = v_{LS}$	(1)(1)(1) = 1	(1)(1)(1) = 1
IS Degeneracy, $(2S+1)(\eta_{t2g})(\eta_{eg}) = v_{IS}$	(3)(1)(1) = 3	-
HS Degeneracy, $(2S+1)(\eta_{t2g})(\eta_{eg}) = v_{HS}$	(5)(3)(1) = 15	(5)(3)(1) = 15
LS Equilibrium Co-O Bond Length, <i>Q</i> _{LS}	0	0
IS Equilibrium Co-O Bond Length, <i>Q</i> _{IS}	0.0077	-
HS Equilibrium Co-O Bond Length, <i>Q</i> _{HS}	0.032	0.032
Co-O Force Constant, ξ (eV)	50	50
Equilibrium LS A _{2g} Energy, <e<sub>LS></e<sub>	675	675
Equilibrium IS A _{2g} Energy, <e<sub>IS></e<sub>	610	-
Equilibrium HS A _{2g} Energy, <e<sub>HS></e<sub>	540	540
IS Transition Temperature, ΔIS (K)	439 (bulk), 177 (film)	-
HS Transition Temperature, ΔHS (K)	977 (bulk), 624 (film)	-
Ordering Temperature, Δ (K)	-	1024 (bulk), 674 (film)
Attractive Interaction Parameter, K	-	0.2
Repulsive Interaction Parameter, L	-	1.3 (bulk), 1.5 (film)

Table S4. Parameters used for modeling spin state transitions. Values given in italics were fitted using vibrational energies from Raman spectroscopy. The non-italicized values were taken as constant from literature. For degeneracy calculations of spin states, the total degeneracy is the product of the spin degeneracy (2S+1) where S is the total spin of the Co ion, the orbital degeneracy of the t_{2g} states, and the orbital degeneracy of the e_g states.



Figure S8. (a) Fittings of the disordered-ordered-disordered spin transition model, including the fitted transition temperatures (Δ) and r^2 values. (b) Site-specific HS fractional occupancies as a function of temperature obtained from the fit: n_B (dashed), n_A (solid). Spin occupancies for the bulk are given in gray and thin films in red.



Figure S9. Bulk O *p*-band center, a proposed *ab initio* descriptor for the SOFC cathode activity of perovskites, for different LCO spin configurations. O *p*-band center closer to zero suggests higher catalytic activity.

References for Supporting Information.

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