Electronic supplementary information

Temporal and Thermal Evolutions of Surface Sr-Segregation in Pristine and Atomic Layer Deposition Modified $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ Epitaxial Films

Yeting Wen[a], Tianrang Yang[a], Dongkyu Lee[a, b], Ho Nyung Lee[b], Ethan J. Crumlin[c] and Kevin Huang [a*]

[a] Department of Mechanical Engineering, University of South Carolina, Columbia, South Carolina 29201, United States

[b] Materials Sciences and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

[c] Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States.

*Corresponding author: huang46@cec.sc.edu

List of Contents

EIS cell setup

Figure S1 shows the cell configuration for EIS measurement. The LSCo thin films with and without ALD-ZrO_2 layer serve as the working electrode and silver paste serves as the counter electrode. Silver/silver mesh were also used as the current collector.

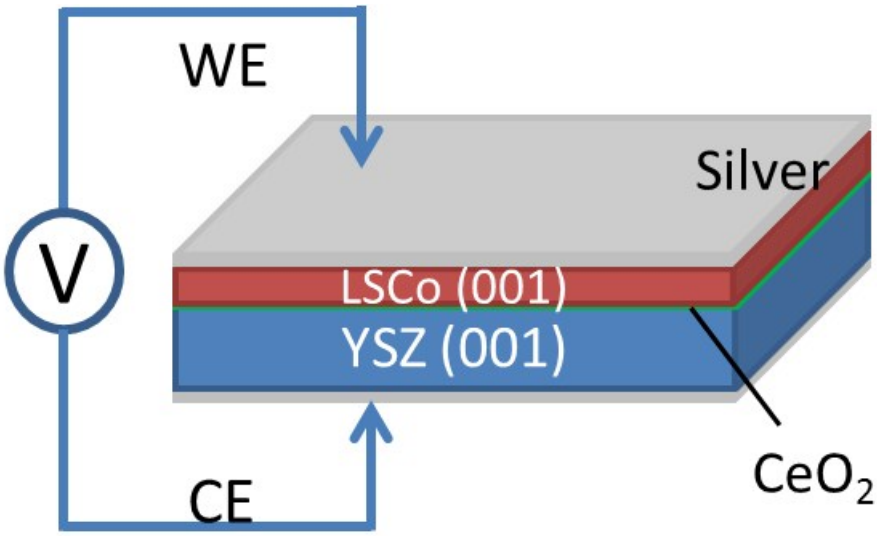

Figure S1. Schematic of EIS cell setup (WE = working electrode, CE = counter electrode)

XPS quantification analysis

The La 4d and Co 3p spectra of the pristine sample and La 4d, Co 3p and Zr 3d spectra of the coated sample are shown in Figure S2. The binding energies (E_b), full-width-half-maximum (fwhm), and peak area for each component of temperature-dependent high resolution scans are listed in Table S1 and S2.

Lanthanum: The La 4d spectra are composed of one doublet of La $4d_{5/2}$ and La $4d_{3/2}$ with the energy separation of 3.2 eV and other two sets of satellite peaks are associated with bonding and antibonding charge-transferred states [1]. The binding energy of La $4d_{5/2}$ peak was used to calibrate all other spectra at the same temperature.

Strontium: The Sr 3d spectra were treated to contain both lattice and surface components; lattice refers to the Sr^{2+} in the bulk lattice of LSCo and surface refers to Sr^{2+} in SrO or $Sr(OH)_2$. The Sr $3d_{5/2}$ and $3d_{3/2}$ doublets have an energy separation of 1.8 eV and area ratio of 1.5. The binding energy of lattice Sr was fixed by La 4d spectra.

Cobalt: The Co 3p spectra were deconvoluted as one doublet of Co $3p_{3/2}$ and Co $3p_{1/2}$ with the energy separation of 1.1 eV and one set of satellite peaks [2]. The large peak width and the low intensity of Co 3p spectra in the coated sample make it hard to obtain detailed information from Co. So only the peak areas were used for quantification analysis.

Zirconium: The Zr 3d spectra of the coated sample contain one doublet of Zr $3d_{5/2}$ and $3d_{3/2}$ with the energy gap of 2.3 eV corresponding to Zr^{4+}.[3] The Zr 3d spectra were quite reproducible during the whole heating process.

Quantification analysis: The peak area for each component was normalized by photoionized cross-section and inelastic mean free path (IMFP) using the following equation,

$$I_{nor} = I/\sigma\lambda \tag{S1}$$

where I_{nor} is the normalized peak area, I is the original peak area, σ is the photoionized cross-section obtained from the database [4, 5], and λ is the IMFP calculated based on the Gries inelastic scattering model [6]. The constants used and the calculated IMFPs are listed in Table S3[7]. For the pristine sample, only La and Co are considered as the lattice component in the bulk of perovskite LSCo; Sr and O are normalized separately as in LSCo and SrO based on the content obtained from Figure 4. For the coated sample, La, Sr and Co are normalized in the same way as the pristine sample, while Zr and O are considered as in ZrO_2. The atomic fraction of each component was calculated according to their normalized peak areas (denoted as I_{nor}^{A}, A = La, Sr_{tot}, Co, Zr or O). For the pristine sample, the atomic fraction of element A in LSCo can be determined using the following expression,

$$[A] = I_{nor}^{A}/(I_{nor}^{La} + I_{nor}^{Sr} + I_{nor}^{Co} + I_{nor}^{O}) \tag{S2}$$

where A = La, Sr_{tot}, Co or O. For the coated sample, the atomic fraction of element A can be determined using the following expression,

$$[A] = I_{nor}^{A}/(I_{nor}^{La} + I_{nor}^{Sr} + I_{nor}^{Co} + I_{nor}^{Zr} + I_{nor}^{O}) \tag{S3}$$

where A = La, Sr_{tot}, Co, Zr or O. For Sr in both samples, $[Sr]_{lat}$ and $[Sr]_{surf}$ were calculated separately based on the I_{nor} in LSCo and SrO; $[Sr]_{tot}$ is the sum of them.

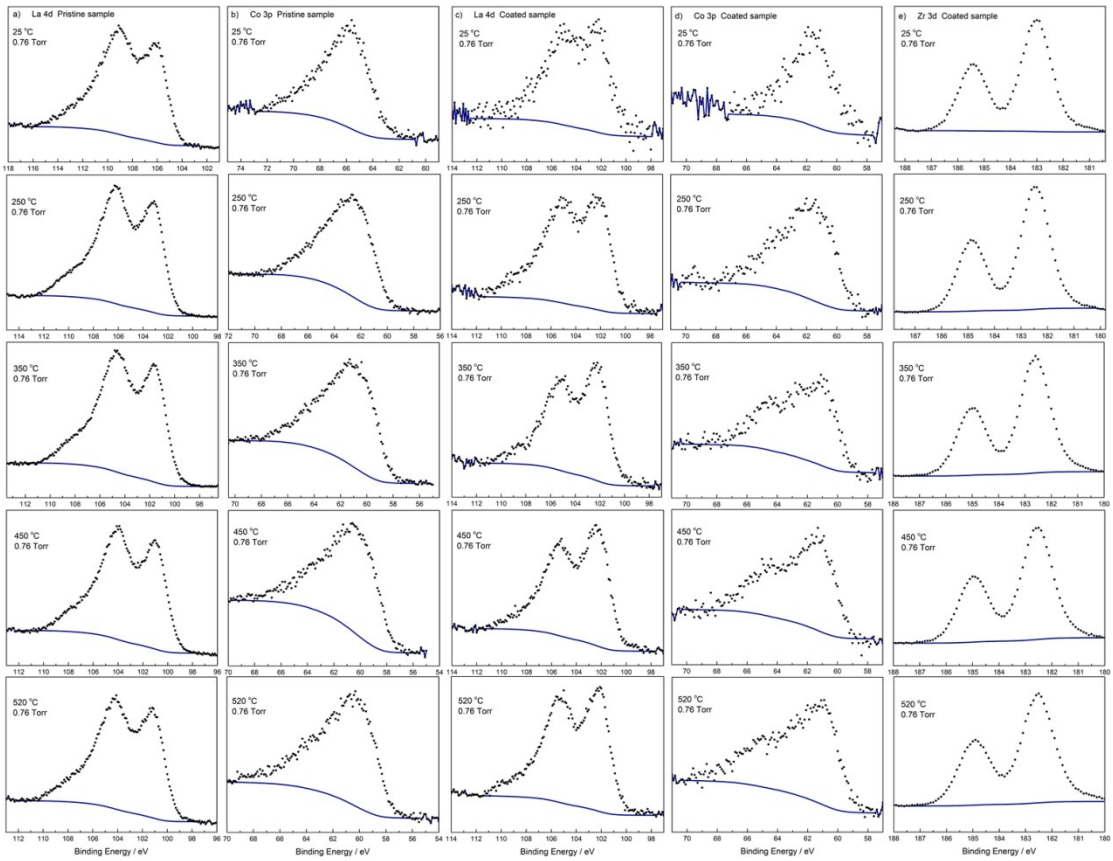

Figure S2. XPS spectra of the pristine and coated LSCo sample at different temperatures from 25 to 520 ^{o}C in an oxygen pressure of 0.76 Torr. a) La 4d and b) Co 3p spectra of the pristine sample, c) La 4d, d) Co 3p and e) Zr 3d spectra of the coated sample. The black dots represent the measured data, the dark blue lines represent the Shirley-type background. The Sr 3d and O 1s spectra for both samples are shown in Figure 4 and 5.

Table S1. The fitting parameters (binding energy, fwhm and peak area) of all elements (La 4d, Sr 3d, Co 3p and O1s) in pristine sample at different temperatures.

Sample	T/°C	Peak	Assignment	E_b / eV	fwhm / eV	Peak area
Pristine sample	25	La 4d	lattice (5/2, 3/2)	105.8, 109.0	1.6	112.9
		Sr 3d	lattice (5/2, 3/2)	136.9, 138.7	1.2	228.0
			surface (5/2, 3/2)	138.5, 140.3	1.6	347.2
		Co 3p	lattice (3/2, 1/2)	65.4, 66.5	3.0	72.1
		O 1s	lattice	534.3	1.2	29.4
			surface	535.6, 537.1	3.0, 1.8	229.9
	250	La 4d	lattice (5/2, 3/2)	102.9, 106.1	1.6	102.4
		Sr 3d	lattice (5/2, 3/2)	134.0, 135.8	1.4	216.3
			surface (5/2, 3/2)	135.3, 137.1	2.2	225.1
		Co 3p	lattice (3/2, 1/2)	62.2, 63.3	2.9	51.3
		O 1s	lattice	531.0	1.4	119.8
			surface	532.1, 535.5	1.2, 1.8	177.1
	350	La 4d	lattice (5/2, 3/2)	101.4, 104.6	1.7	90.6
		Sr 3d	lattice (5/2, 3/2)	132.4, 134.2	1.5	127.5
			surface (5/2, 3/2)	133.8, 135.6	2.3	249.
		Co 3p	lattice (3/2, 1/2)	60.6, 61.7	3.0	35.8
		O 1s	lattice	529.6	1.5	97.8
			surface	530.9, 532.7	1.4, 1.9	180.0
	450	La 4d	lattice (5/2, 3/2)	100.8, 104.0	1.8	89.8
		Sr 3d	lattice (5/2, 3/2)	132.0, 133.8	1.3	113.4
			surface (5/2, 3/2)	133.1, 134.9	2.2	309.6
		Co 3p	lattice (3/2, 1/2)	60.0, 61.1	3.0	33.3
		O 1s	lattice	528.8	1.4	61.9
			surface	530.1, 531.9	2.2, 2.5	210.7
	520	La 4d	lattice (5/2, 3/2)	101.0, 104.2	1.9	91.8
		Sr 3d	lattice (5/2, 3/2)	132.1, 133.9	1.3	125.6
			surface (5/2, 3/2)	133.1, 134.9	2.1	402.7
		Co 3p	lattice (3/2, 1/2)	60.0, 61.1	2.9	30.3
		O 1s	lattice	528.9	1.2	41.4
			surface	530.2, −	2.6, −	273.2

Table S2. The fitting parameters (binding energy, fwhm and peak area) of all elements (La 4d, Sr 3d, Co 3p, O 1s and Zr 3d) in coated sample at different temperatures.

Sample	T/°C	Peak	Assignment	E_b / eV	fwhm / eV	Peak area
Coated sample	25	La 4d	lattice (5/2, 3/2)	102.1, 105.3	1.8	5.4
		Sr 3d	lattice (5/2, 3/2)	133.0, 134.8	1.2	8.5
			surface (5/2, 3/2)	134.3, 136.1	1.6	19.3
		Co 3p	lattice (3/2, 1/2)	61.0, 62.1	2.6	8.6
		O 1s	lattice	530.5	0.8	4.6
			surface	531.8	0.5	2.0
			ZrO_2	531.2	0.9	32.7
		Zr 3d	5/2, 3/2	183.0, 185.4	1.4	105.7
	250	La 4d	lattice (5/2, 3/2)	102.0, 105.2	2.1	18.3
		Sr 3d	lattice (5/2, 3/2)	133.2, 135.0	1.9	33.1
			surface (5/2, 3/2)	134.2, 136.0	1.6	51.9
		Co 3p	lattice (3/2, 1/2)	61.1, 62.2	2.6	14.9
		O 1s	lattice	529.9	1.2	25.9
			surface	531.2	0.9	19.8
			ZrO_2	530.6	1.2	178.1
		Zr 3d	5/2, 3/2	182.5, 184.8	1.3	299.2
	350	La 4d	lattice (5/2, 3/2)	102.1, 105.3	1.9	23.8
		Sr 3d	lattice (5/2, 3/2)	133.2, 135.0	1.8	38.7
			surface (5/2, 3/2)	134.2, 136.0	1.7	76.0
		Co 3p	lattice (3/2, 1/2)	61.0, 62.1	2.4	17.4
		O 1s	lattice	530.0	1.4	35.4
			surface	531.3	0.9	19.9
			ZrO_2	530.7	1.3	210.6
		Zr 3d	5/2, 3/2	182.6, 185.0	1.4	336.8
	450	La 4d	lattice (5/2, 3/2)	102.2, 105.4	2.0	28.2
		Sr 3d	lattice (5/2, 3/2)	133.2, 135.0	1.8	35.4
			surface (5/2, 3/2)	134.3, 136.1	1.7	93.8
		Co 3p	lattice (3/2, 1/2)	61.0, 62.1	2.0	18.9
		O 1s	lattice	530.1	1.3	36.1
			surface	531.4	0.9	46.5
			ZrO_2	530.8	1.2	172.4
		Zr 3d	5/2, 3/2	182.6, 184.9	1.4	340.1
	520	La 4d	lattice (5/2, 3/2)	102.1, 105.3	1.9	33.7
		Sr 3d	lattice (5/2, 3/2)	133.1, 134.9	1.7	46.8
			surface (5/2, 3/2)	134.1, 135.9	1.8	140.3
		Co 3p	lattice (3/2, 1/2)	61.0, 62.1	2.3	22.9
		O 1s	lattice	530.1	1.2	27.9
			surface	531.4	0.9	35.2
			ZrO_2	530.7	1.2	168.2
		Zr 3d	5/2, 3/2	182.5, 184.9	1.4	316.8

Table S3. The atomic volume calculated from the density of each compound and the obtained IMFP for all elements.

Compounds	**Elements**	**Atomic volume (cm^3/mol)**	**IMFP (nm)**
$La_{0.4}Sr_{0.6}CoO_3$	La	57.9	2.38
	Sr	86.8	3.57
	Co	34.7	1.43
	O	11.6	0.48
SrO	Sr	22.0	2.08
	O	22.0	2.08
ZrO_2	Zr	21.7	0.77
	O	10.8	1.54

References

1. M. Sunding, K. Hadidi, S. Diplas, O. Løvvik, T. Norby and A. Gunnæs, *J. Electron. Spectrosc. Relat. Phenom.*, 2011, **184**, 399-409.
2. T. Ivanova, A. Naumkin, A. Sidorov, I. Eremenko and M. Kiskin, *J. Electron. Spectrosc. Relat. Phenom.*, 2007, **156**, 200-203.
3. H. Zhai, J. Kong, J. Yang, J. Xu, Q. Xu, H. Sun, A. Li and D. Wu, *J. Mater. Sci. Technol.*, 2016, **32**, 676-680.
4. J.-J. Yeh, *Atomic calculation of photoionization cross-sections and asymmetry parameters*, Gordon & Breach Science Publ.; AT&T Bell Laboratories, 1993.
5. J. Yeh and I. Lindau, *At. Data Nucl. Data Tables*, 1985, **32**, 1-155.
6. W. H. Gries, *Surf. Interface Anal.*, 1996, **24**, 38-50.
7. E. Bucher, W. Sitte, F. Klauser and E. Bertel, *Solid State Ion.*, 2012, **208**, 43-51.