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Supporting Information for:

Vertically Aligned Nanocomposite $La_{0.8}Sr_{0.2}CoO_3/(La_{0.5}Sr_{0.5})_2CoO_4$ Cathodes - Electronic Structure, Surface Chemistry and Oxygen Reduction Kinetics

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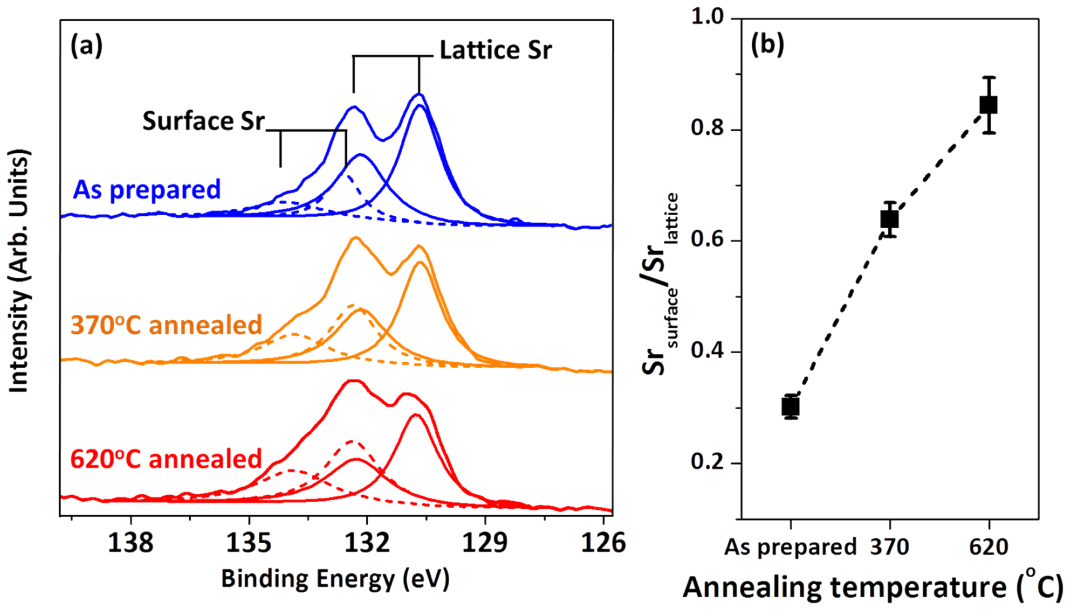

Figure S1. (a) Sr 3d photoelectron spectra, showing the evolution of the lattice and surface binding environment for Sr, and (b) the $Sr_{surface}/Sr_{lattice}$ ratio on $LSC_{113/214}$ VAN structure, at the as-prepared state and after annealing the specimen at 370°C and at 620°C in air for one hour.

Segregation and precipitation of Sr-rich phases at the surface of the $LSC_{113/214}$ VAN films upon annealing was further confirmed by the evolution of Sr 3d photoelectron spectrum (Fig S1). The Sr 3d peak was fitted by two sets of doublet peaks: $Sr_{lattice}$ and $Sr_{surface}$. The $3d_{3/2}$ and $3d_{5/2}$ doublet separation and area ratio were constrained to their theoretical values of 1.5 eV and 1:1.5, respectively. The $Sr_{lattice}$ doublet could be assigned to the lattice-bound Sr within the perovskite and Ruddlesden-Popper structures, while $Sr_{surface}$ could be attributed to the formation of species on the surface such as SrO, $Sr(OH)_2$ and $SrCO_3$.[1-3] With increasing annealing temperature, $Sr_{surface}$ peaks become more distinct, and $Sr_{lattice}$ /$Sr_{surface}$ ratio increases drastically from 0.30 to 0.85 after annealing at 620°C. This result is consistent with the AFM and AR-XPS results shown in the manuscript.

Phase	LSC_{113}	LSC_{214}
$LSC_{113/214}$ VAN (surface)	0.40±0.02	0.53±0.02
Single phase film (surface)	0.38±0.03	0.56±0.03
$LSC_{113/214}$ VAN (bulk)	0.28±0.07	0.43±0.07
Single phase film (bulk)	0.21±0.02	0.53±0.03
$LSC_{113/214}$ VAN PLD target (bulk)	0.32±0.03	0.55±0.05

Table S1. Sr/(Sr+La) ratio deduced from Auger electron spectroscopy on the LSC_{113} and LSC_{214} grains of the VAN film,on the LSC_{113} and LSC_{214} single phase films, and on the $LSC_{113/214}$ VAN PLD target. "Surface" represents the condition of the as-prepared sample surface; "Bulk" represents the measurements taken after sputtering off the surface layer and exposing the bulk. The sputtering was performed by low energy Ar^+ beam with 0.5 mA beam current, 1 kV beam voltage, and 1min duration. The value after '±' is the standard deviation within the taken set of measurements and does not include the quantification of errors arising from the system or analysis. LSC_{113} and LSC_{214} phases were well separated in the PLD target after sintered at 1300 ^oC for 10 hours in air, as well as in the VAN films.

The Sr concentration in all the as-prepared films ($LSC_{113/214}$ VAN, LSC_{113} and LSC_{214}) is compared to each other to assess whether compositional changes could contribute to the differences observed in the cathode area specific resistance (ASR). First, all samples have an Sr/(La+Sr) ratio at the as-prepared surface that is greater than the targeted 20% and 50% due to Sr segregation. After sputtering off the surface, the Sr/(Sr+La) in the subsurface (or bulk) is close to ~0.2 for LSC_{113} and ~0.5 for LSC_{214}. A small deviation of the Sr/(Sr+La) in the VAN films with respect to the single phase films is also observed, i.e. ~0.28 for LSC_{113} and ~0.43 for LSC_{214}. This is likely due to the way the VAN films are prepared – by laser ablation of a composite target during PLD which itself was sintered at elevated temperatures. However, the 10-fold decrease found in the VAN cathode ASR (Figure 9 in the manuscript) compared to single phase LSC_{113} and LSC_{214} is not likely to arise from the changes in the Sr composition in the bulk. For LSC_{113}, changing Sr/(Sr+La) from 21% to 28% is expected to lead to only 2-3 times enhancement in the surface exchange kinetics.[4] For LSC_{214}, we have shown in our ongoing work that changing Sr/(Sr+La) substantially from 50% to 25% increases the surface exchange kinetics

by 10 times.[5] Therefore, a change from 53% to 43% is not expected to give rise to nearly 10 times reduction of ASR on LSC_{214} domains of the VAN film. Furthermore, by comparing the first two rows of Table S1, we can see that, at the surface (the critical place where the oxygen reduction reactions take place), the Sr compositions on each phase in VAN and on the respective single phase films are very close to each other.

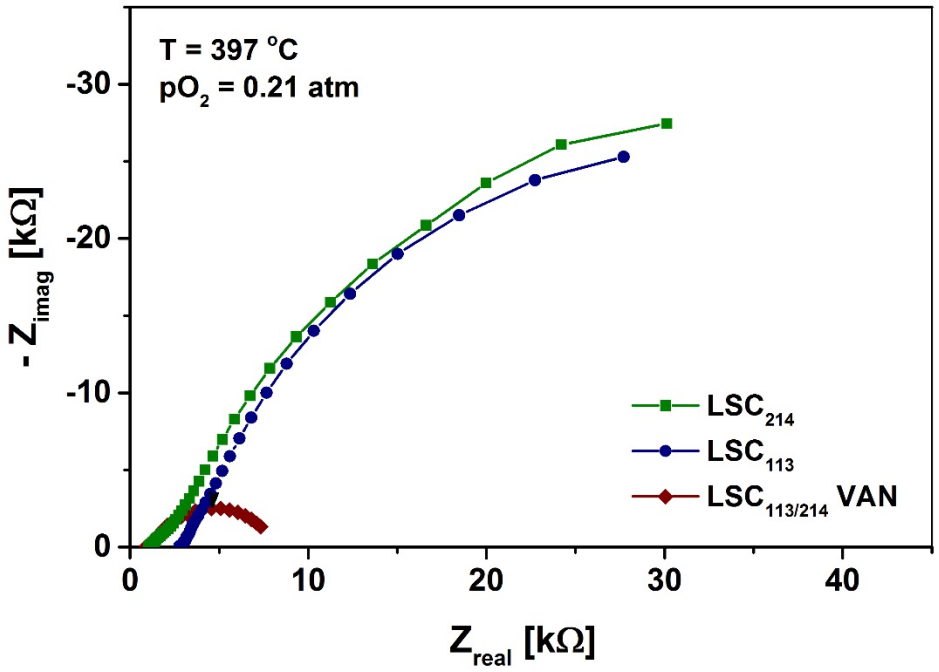

Figure S2. Typical electrochemical impedance spectra measured for an LSC_{214}, LSC_{113} and $LSC_{113/214}$ VAN phase thin film electrode on GDC/YSZ(001) at 397 °C and in air. All the impedance spectra show similar characteristics except that x-axis offset resistances may vary from sample to sample. This might come from the variation in homogeneity and/or thickness of YSZ single substrates.

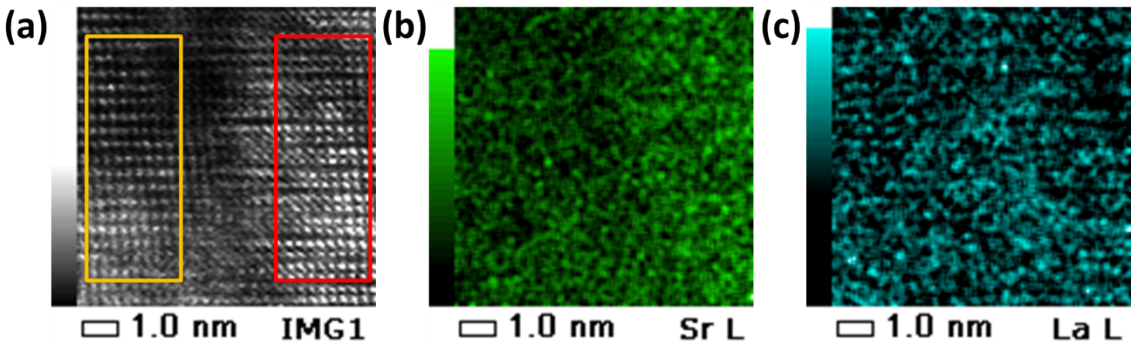

Figure S3. a) STEM-HAADF image at LSC_{113} and LSC_{214} interface. STEM-EDX mapping of b) Sr L and c) La L in the same region as a). From the quantitative EDX analysis in yellow (left) and red (right) rectangular region, we could I identify that the yellow (left) region is LSC_{113} phase and the red (right) region is LSC_{214} phase . The quantities are shown in Table S2.

Yellow (left) region in Figure S3(a) LSC_{113}			
Component	Position (keV)	Weight percentage	Atomic percentage
O K	0.525	3.33	16.93
Co K	6.924	26.22	36.17
Sr L	16.52	15.33	15.33
La L	4.65	53.93	31.57
total		100	100
Sr/(Sr+La)=0.32			
Red (right) region in Figure S3(a) LSC_{214}			
Component	Position (keV)	Weight percentage	Atomic percentage
O K	0.525	7.55	32.99
Co K	6.924	19.11	22.67
Sr L	16.52	25.26	20.15
La L	4.65	48.08	24.19
total		100	100
Sr/(Sr+La)=0.45			

Table S2. Quantitative EDX analysis of the highlighted region in Figure S3(a) for O K, Co K, Sr L, La L and Sr/(Sr+La) ratio.

References

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