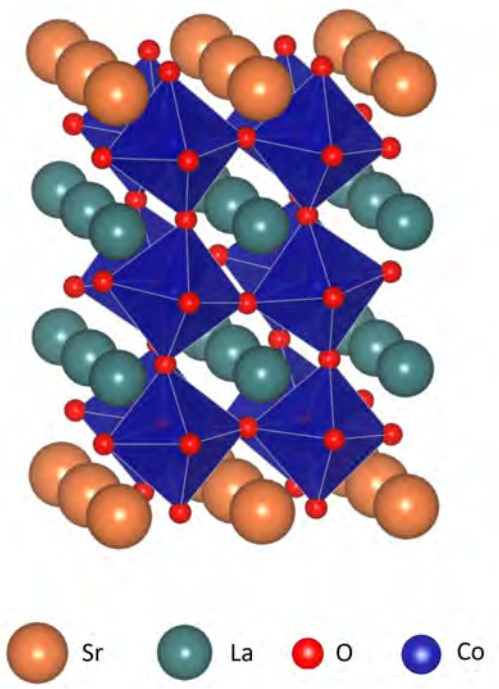
# Electronic and ionic effects of sulphur and other acidic adsorbates on the surface of an SOFC cathode material

Matthäus Siebenhofer, Andreas Nenning, George E. Wilson, John A. Kilner, Christoph Rameshan, Markus Kubicek, Jürgen Fleig, Peter Blaha

## S.I. 1. equilibrium structures

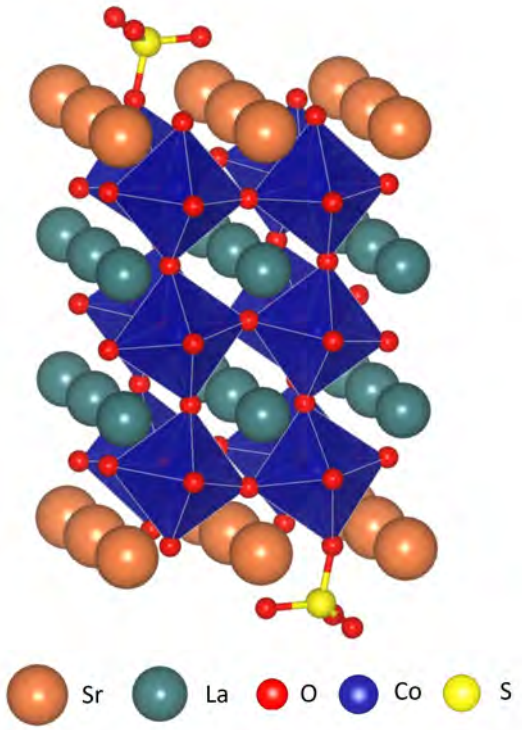
In the following section, the essential equilibrium structures used in the main manuscript are shown with the corresponding fractional coordinates. For every atom, a second counterpart atom exists on the inverse position (e.g. for 0.1/0.1/0.1, a second atom with the coordinates 0.9/0.9/0.9 exists). The supercell dimensions for most calculations were 7.66 x 7.66 x 32.62 Å.

LSC with SrO termination and no adsorbates:



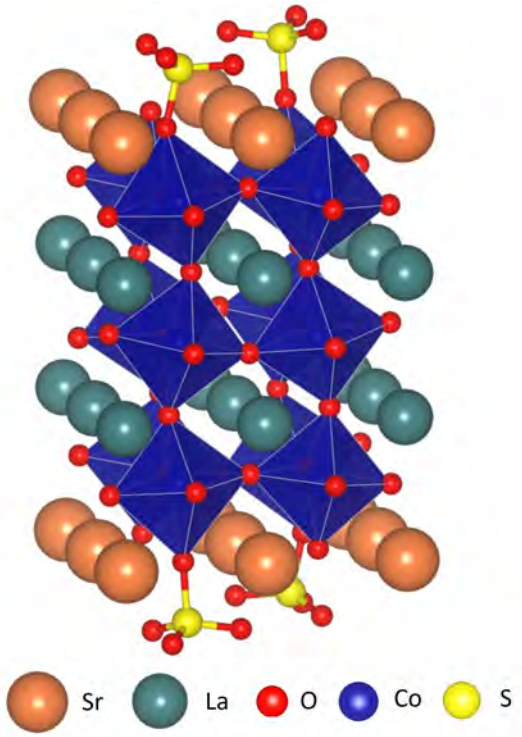

| | | | x | y | z |
|---|---|---|---|---|---|
| 1 | Sr | Sr1 | 0.99918 | 0.99834 | 0.32962 |
| 3 | Sr | Sr3 | 0.49932 | 0.0024 | 0.32923 |
| 5 | Sr | Sr5 | 0.99918 | 0.50205 | 0.32959 |
| 7 | Sr | Sr7 | 0.49932 | 0.49805 | 0.32928 |
| 9 | La | La1 | 0.00028 | 0.9972 | 0.55933 |
| 11 | La | La3 | 0.5002 | 0.00175 | 0.55972 |
| 13 | La | La5 | 0.00022 | 0.50308 | 0.55935 |
| 15 | La | La7 | 0.5003 | 0.4986 | 0.55969 |
| 17 | Co | Co1 | 0.74964 | 0.75 | 0.37996 |
| 19 | Co | Co3 | 0.24905 | 0.75002 | 0.37988 |
| 21 | Co | Co5 | 0.25066 | 0.74999 | 0.62024 |
| 23 | Co | Co7 | 0.75037 | 0.75001 | 0.62015 |
| 25 | Co | Co9 | 0.74929 | 0.75001 | 0.4999 |
| 27 | Co | Co11 | 0.25075 | 0.75 | 0.49989 |
| 29 | O | O1 | 0.99939 | 0.74938 | 0.38974 |
| 31 | O | O3 | 0.24873 | 0.00006 | 0.38555 |
| 33 | O | O5 | 0.00051 | 0.7491 | 0.62064 |
| 35 | O | O7 | 0.74999 | 0.00009 | 0.38561 |
| 37 | O | O9 | 0.50049 | 0.75066 | 0.61119 |
| 39 | O | O11 | 0.25149 | 0.50007 | 0.6145 |
| 41 | O | O13 | 0.49935 | 0.75088 | 0.37737 |
| 43 | O | O15 | 0.74983 | 0.50004 | 0.61439 |
| 45 | O | O17 | 0.75095 | 1 | 0.49989 |
| 47 | O | O19 | 0.00004 | 0.74976 | 0.48943 |
| 49 | O | O21 | 0.75033 | 0.5 | 0.50018 |
| 51 | O | O23 | 0.50004 | 0.75028 | 0.51078 |
| 53 | O | O25 | 0.76514 | 0.75017 | 0.32236 |
| 55 | O | O27 | 0.23275 | 0.74996 | 0.32232 |
| 57 | O | O29 | 0.26365 | 0.75009 | 0.67779 |
| 59 | O | O31 | 0.73739 | 0.74988 | 0.6777 |
| 61 | O | O33 | 0.78568 | 0.75033 | 0.55794 |
| 63 | O | O35 | 0.21449 | 0.74967 | 0.55794 |
| 65 | O | O37 | 0.28897 | 0.75028 | 0.44181 |
| 67 | O | O39 | 0.71107 | 0.74963 | 0.44182 |

LSC with SrO termination and one $SO_4^{2-}$ adsorbate:



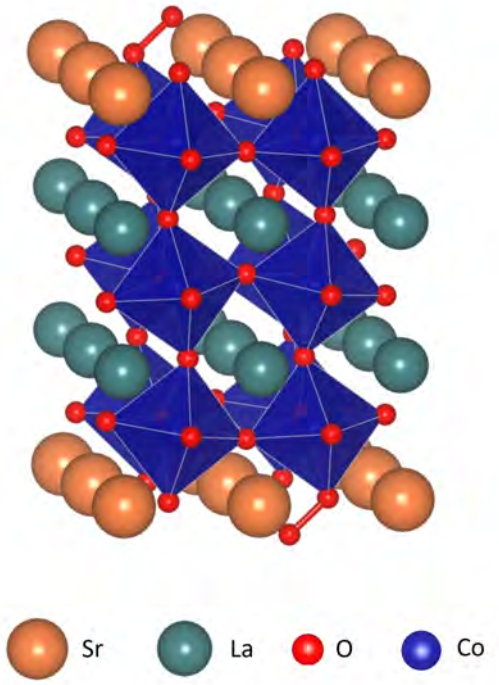

| | | | x | y | z |
|---|---|---|---|---|---|
| 1 | Sr | Sr1 | 0.99175 | 0.98657 | 0.67403 |
| 3 | Sr | Sr3 | 0.50927 | 0.99311 | 0.67463 |
| 5 | Sr | Sr5 | 0.99177 | 0.51331 | 0.67402 |
| 7 | Sr | Sr7 | 0.50923 | 0.50682 | 0.67461 |
| 9 | La | La1 | 0.99959 | 0.00464 | 0.44031 |
| 11 | La | La3 | 0.49816 | 0.00246 | 0.44007 |
| 13 | La | La5 | 0.99963 | 0.49531 | 0.44032 |
| 15 | La | La7 | 0.4981 | 0.49745 | 0.44008 |
| 17 | Co | Co1 | 0.25254 | 0.25001 | 0.61671 |
| 19 | Co | Co3 | 0.75162 | 0.25 | 0.61935 |
| 21 | Co | Co5 | 0.74808 | 0.24998 | 0.38007 |
| 23 | Co | Co7 | 0.25044 | 0.24999 | 0.38019 |
| 25 | Co | Co9 | 0.24916 | 0.24999 | 0.50045 |
| 27 | Co | Co11 | 0.74837 | 0.25 | 0.50042 |
| 29 | O | O1 | 0.001 | 0.25012 | 0.60693 |
| 31 | O | O3 | 0.74867 | 0.99982 | 0.61423 |
| 33 | O | O5 | 0.99955 | 0.25012 | 0.38046 |
| 35 | O | O7 | 0.25031 | 0.99966 | 0.61482 |
| 37 | O | O9 | 0.49967 | 0.24989 | 0.3889 |
| 39 | O | O11 | 0.74939 | 0.49964 | 0.38509 |
| 41 | O | O13 | 0.49891 | 0.24986 | 0.62827 |
| 43 | O | O15 | 0.25155 | 0.49981 | 0.38581 |
| 45 | O | O17 | 0.24957 | 0.00019 | 0.5007 |
| 47 | O | O19 | 0.99977 | 0.25004 | 0.51083 |
| 49 | O | O21 | 0.24969 | 0.49981 | 0.50054 |
| 51 | O | O23 | 0.49913 | 0.24994 | 0.48995 |
| 53 | O | O25 | 0.19851 | 0.24986 | 0.67856 |
| 55 | O | O27 | 0.78024 | 0.25005 | 0.675 |
| 57 | O | O29 | 0.73541 | 0.24986 | 0.3241 |
| 59 | O | O31 | 0.2592 | 0.25005 | 0.32225 |
| 61 | O | O33 | 0.21619 | 0.24983 | 0.44289 |
| 63 | O | O35 | 0.7816 | 0.2502 | 0.44252 |
| 65 | O | O37 | 0.70731 | 0.24986 | 0.55852 |
| 67 | O | O39 | 0.29789 | 0.2502 | 0.55984 |
| 69 | S | S1 | 0.24048 | 0.24998 | 0.72605 |
| 71 | O | O41 | 0.16166 | 0.08655 | 0.74162 |
| 73 | O | O43 | 0.16179 | 0.41357 | 0.74157 |
| 75 | O | O45 | 0.43585 | 0.24995 | 0.72902 |

LSC with SrO termination and two $SO_4^{2-}$ adsorbates:



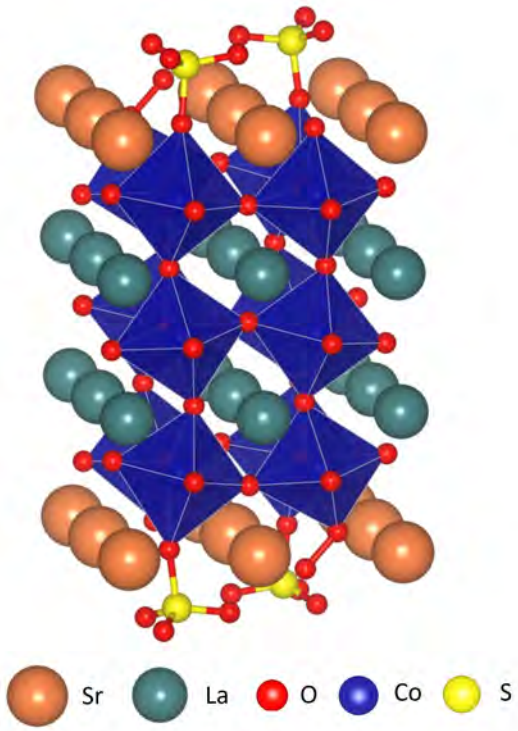

| | | | x | y | z |
|---|---|---|---|---|---|
| 1 | Sr | Sr1 | 0.9979 | 0.99323 | 0.67706 |
| 3 | Sr | Sr3 | 0.50049 | 0.99763 | 0.67562 |
| 5 | Sr | Sr5 | 0.99794 | 0.50648 | 0.67707 |
| 7 | Sr | Sr7 | 0.50034 | 0.5022 | 0.67557 |
| 9 | La | La1 | 0.99745 | 0.00147 | 0.44059 |
| 11 | La | La3 | 0.49758 | 0.00029 | 0.43982 |
| 13 | La | La5 | 0.99748 | 0.49828 | 0.44058 |
| 15 | La | La7 | 0.49753 | 0.49943 | 0.43983 |
| 17 | Co | Co1 | 0.25184 | 0.25003 | 0.61648 |
| 19 | Co | Co3 | 0.7538 | 0.25003 | 0.61864 |
| 21 | Co | Co5 | 0.75008 | 0.24994 | 0.38138 |
| 23 | Co | Co7 | 0.24617 | 0.24997 | 0.38403 |
| 25 | Co | Co9 | 0.25153 | 0.25001 | 0.50031 |
| 27 | Co | Co11 | 0.74877 | 0.25 | 0.5002 |
| 29 | O | O1 | 0.00219 | 0.25038 | 0.60683 |
| 31 | O | O3 | 0.74917 | 0.99973 | 0.61411 |
| 33 | O | O5 | 0.99922 | 0.25061 | 0.37703 |
| 35 | O | O7 | 0.25273 | 0.9999 | 0.61362 |
| 37 | O | O9 | 0.49745 | 0.24958 | 0.38999 |
| 39 | O | O11 | 0.74628 | 0.49987 | 0.3862 |
| 41 | O | O13 | 0.50037 | 0.24952 | 0.62586 |
| 43 | O | O15 | 0.25178 | 0.4997 | 0.38598 |
| 45 | O | O17 | 0.24825 | 0.00038 | 0.49988 |
| 47 | O | O19 | 0.00083 | 0.25014 | 0.51006 |
| 49 | O | O21 | 0.24852 | 0.49962 | 0.49963 |
| 51 | O | O23 | 0.49953 | 0.24983 | 0.48965 |
| 53 | O | O25 | 0.20957 | 0.24972 | 0.67826 |
| 55 | O | O27 | 0.78078 | 0.25012 | 0.67318 |
| 57 | O | O29 | 0.73623 | 0.24969 | 0.32633 |
| 59 | O | O31 | 0.25633 | 0.25018 | 0.32024 |
| 61 | O | O33 | 0.2101 | 0.24969 | 0.44145 |
| 63 | O | O35 | 0.78276 | 0.25033 | 0.44253 |
| 65 | O | O37 | 0.71229 | 0.24975 | 0.55794 |
| 67 | O | O39 | 0.29522 | 0.25037 | 0.55871 |
| 69 | S | S1 | 0.25696 | 0.24996 | 0.72672 |
| 71 | O | O41 | 0.18038 | 0.0861 | 0.74162 |
| 73 | O | O43 | 0.18006 | 0.08686 | 0.25849 |
| 75 | O | O45 | 0.18064 | 0.41411 | 0.74153 |
| 77 | O | O47 | 0.18003 | 0.41331 | 0.25847 |
| 79 | O | O49 | 0.45189 | 0.24989 | 0.72778 |
| 81 | O | O51 | 0.45921 | 0.2501 | 0.26277 |
| 83 | S | S3 | 0.26876 | 0.25012 | 0.27013 |

LSC with SrO termination, one $O_2$ adsorbate:



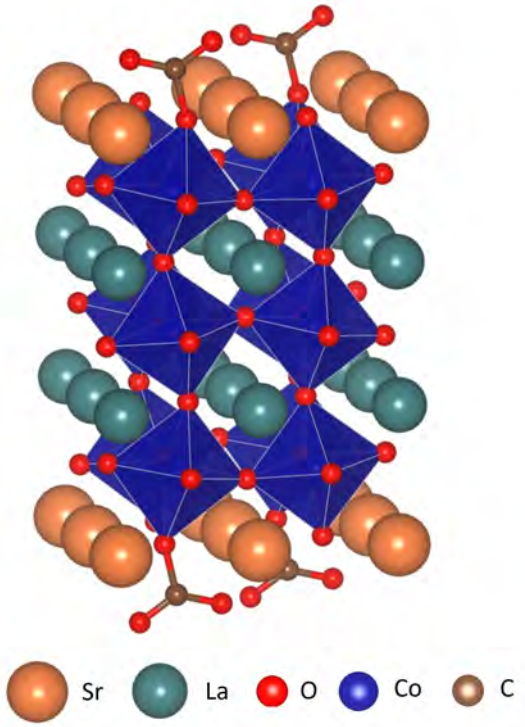

| | | | x | y | z |
|---|---|---|---|---|---|
| 1 | Sr | Sr1 | 0.98771 | 0.00901 | 0.32919 |
| 3 | Sr | Sr3 | 0.50211 | 0.00622 | 0.32697 |
| 5 | Sr | Sr5 | 0.98699 | 0.49167 | 0.32914 |
| 7 | Sr | Sr7 | 0.50167 | 0.4956 | 0.32716 |
| 9 | La | La1 | 0.00207 | 0.99643 | 0.55934 |
| 11 | La | La3 | 0.50199 | 0.99958 | 0.56 |
| 13 | La | La5 | 0.0019 | 0.50438 | 0.55934 |
| 15 | La | La7 | 0.50218 | 0.50147 | 0.55993 |
| 17 | Co | Co1 | 0.74639 | 0.75004 | 0.3799 |
| 19 | Co | Co3 | 0.24738 | 0.75011 | 0.38127 |
| 21 | Co | Co5 | 0.25467 | 0.74997 | 0.62018 |
| 23 | Co | Co7 | 0.7528 | 0.74998 | 0.62074 |
| 25 | Co | Co9 | 0.74822 | 0.75005 | 0.4996 |
| 27 | Co | Co11 | 0.25088 | 0.75002 | 0.49962 |
| 29 | O | O1 | 0.99613 | 0.7481 | 0.39079 |
| 31 | O | O3 | 0.24293 | 0.00061 | 0.38473 |
| 33 | O | O5 | 0.00382 | 0.74793 | 0.61932 |
| 35 | O | O7 | 0.74769 | 0.00035 | 0.3852 |
| 37 | O | O9 | 0.50368 | 0.75189 | 0.61186 |
| 39 | O | O11 | 0.25627 | 0.50029 | 0.61502 |
| 41 | O | O13 | 0.49479 | 0.75244 | 0.37351 |
| 43 | O | O15 | 0.75241 | 0.50058 | 0.61503 |
| 45 | O | O17 | 0.75132 | 0.0001 | 0.50002 |
| 47 | O | O19 | 0.9996 | 0.74922 | 0.48966 |
| 49 | O | O21 | 0.74936 | 0.4999 | 0.50045 |
| 51 | O | O23 | 0.49972 | 0.75099 | 0.51023 |
| 53 | O | O25 | 0.77125 | 0.75031 | 0.32278 |
| 55 | O | O27 | 0.19888 | 0.74924 | 0.32305 |
| 57 | O | O29 | 0.2612 | 0.74996 | 0.67844 |
| 59 | O | O31 | 0.74585 | 0.74955 | 0.67807 |
| 61 | O | O33 | 0.78303 | 0.75058 | 0.55775 |
| 63 | O | O35 | 0.21959 | 0.74945 | 0.55767 |
| 65 | O | O37 | 0.2896 | 0.75053 | 0.44071 |
| 67 | O | O39 | 0.70639 | 0.74948 | 0.44128 |
| 69 | O | O41 | 0.33628 | 0.75107 | 0.29325 |

LSC with SrO termination, one $O_2$ adsorbate and two $SO_4^{2-}$ adsorbates:



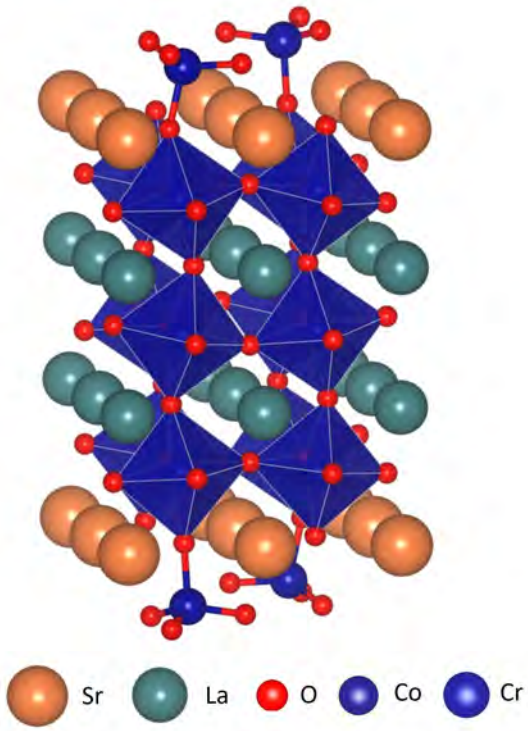

| | | | x | y | z |
|---|---|---|---|---|---|
| 1 | Sr | Sr1 | 0.98732 | 0.01965 | 0.32273 |
| 3 | Sr | Sr3 | 0.50828 | 0.00591 | 0.32205 |
| 5 | Sr | Sr5 | 0.98263 | 0.47615 | 0.32163 |
| 7 | Sr | Sr7 | 0.5066 | 0.4967 | 0.32205 |
| 9 | La | La1 | 0.00639 | 0.99714 | 0.55871 |
| 11 | La | La3 | 0.50363 | 0.99773 | 0.56077 |
| 13 | La | La5 | 0.0057 | 0.50423 | 0.55874 |
| 15 | La | La7 | 0.50404 | 0.50266 | 0.56078 |
| 17 | Co | Co1 | 0.74268 | 0.74974 | 0.38401 |
| 19 | Co | Co3 | 0.2398 | 0.7502 | 0.38432 |
| 21 | Co | Co5 | 0.25415 | 0.75008 | 0.61814 |
| 23 | Co | Co7 | 0.75709 | 0.75006 | 0.61578 |
| 25 | Co | Co9 | 0.74712 | 0.74998 | 0.49971 |
| 27 | Co | Co11 | 0.25278 | 0.74989 | 0.49971 |
| 29 | O | O1 | 0.99264 | 0.74849 | 0.3962 |
| 31 | O | O3 | 0.24839 | 0.99997 | 0.38388 |
| 33 | O | O5 | 0.00389 | 0.74776 | 0.62235 |
| 35 | O | O7 | 0.74685 | 0.99936 | 0.38579 |
| 37 | O | O9 | 0.50578 | 0.75227 | 0.61038 |
| 39 | O | O11 | 0.25782 | 0.49969 | 0.61467 |
| 41 | O | O13 | 0.49421 | 0.75131 | 0.37245 |
| 43 | O | O15 | 0.74645 | 0.50078 | 0.61431 |
| 45 | O | O17 | 0.75358 | 0.99956 | 0.49987 |
| 47 | O | O19 | 0.99928 | 0.74978 | 0.49023 |
| 49 | O | O21 | 0.75395 | 0.5005 | 0.50089 |
| 51 | O | O23 | 0.50099 | 0.75017 | 0.51118 |
| 53 | O | O25 | 0.78484 | 0.74943 | 0.32002 |
| 55 | O | O27 | 0.16929 | 0.74377 | 0.3309 |
| 57 | O | O29 | 0.28901 | 0.75765 | 0.30077 |
| 59 | O | O31 | 0.26427 | 0.75043 | 0.67447 |
| 61 | O | O33 | 0.748 | 0.7481 | 0.68068 |
| 63 | O | O35 | 0.79201 | 0.7525 | 0.55854 |
| 65 | O | O37 | 0.21929 | 0.74917 | 0.55733 |
| 67 | O | O39 | 0.29466 | 0.75175 | 0.44196 |
| 69 | O | O41 | 0.69783 | 0.74914 | 0.44134 |
| 71 | S | S1 | 0.75528 | 0.75051 | 0.27043 |
| 73 | O | O43 | 0.83765 | 0.91446 | 0.25715 |
| 75 | O | O45 | 0.82568 | 0.91215 | 0.74239 |
| 77 | O | O47 | 0.83644 | 0.58643 | 0.25678 |
| 79 | O | O49 | 0.82547 | 0.58683 | 0.74271 |
| 81 | O | O51 | 0.56349 | 0.75104 | 0.26523 |
| 83 | O | O53 | 0.54547 | 0.74945 | 0.73833 |
| 85 | S | S3 | 0.7363 | 0.74933 | 0.73078 |

LSC with SrO termination and two $CO_3^{2-}$ adsorbates:




| | | | x | y | z |
|---|---|---|---|---|---|
| 1 | Sr | Sr1 | 0.99258 | 0.99443 | 0.67627 |
| 3 | Sr | Sr3 | 0.49274 | 0.00329 | 0.67655 |
| 5 | Sr | Sr5 | 0.99234 | 0.50402 | 0.67663 |
| 7 | Sr | Sr7 | 0.49298 | 0.49518 | 0.67618 |
| 9 | La | La1 | 0.99869 | 0.00045 | 0.44022 |
| 11 | La | La3 | 0.49876 | 0.99844 | 0.44013 |
| 13 | La | La5 | 0.99875 | 0.49834 | 0.44016 |
| 15 | La | La7 | 0.49871 | 0.50032 | 0.44018 |
| 17 | Co | Co1 | 0.24958 | 0.25004 | 0.61711 |
| 19 | Co | Co3 | 0.75063 | 0.25007 | 0.61937 |
| 21 | Co | Co5 | 0.74942 | 0.24993 | 0.38062 |
| 23 | Co | Co7 | 0.25013 | 0.24995 | 0.38294 |
| 25 | Co | Co9 | 0.25011 | 0.25 | 0.50002 |
| 27 | Co | Co11 | 0.74991 | 0.25 | 0.50001 |
| 29 | O | O1 | 0.99972 | 0.25204 | 0.60763 |
| 31 | O | O3 | 0.75373 | 0.00009 | 0.61472 |
| 33 | O | O5 | 0.00118 | 0.25328 | 0.37519 |
| 35 | O | O7 | 0.24803 | 0.99981 | 0.61451 |
| 37 | O | O9 | 0.50012 | 0.24794 | 0.3922 |
| 39 | O | O11 | 0.74635 | 0.49989 | 0.38527 |
| 41 | O | O13 | 0.49862 | 0.24674 | 0.62501 |
| 43 | O | O15 | 0.25193 | 0.50016 | 0.38547 |
| 45 | O | O17 | 0.24967 | 0.00024 | 0.50014 |
| 47 | O | O19 | 0.00047 | 0.25054 | 0.51 |
| 49 | O | O21 | 0.25054 | 0.49976 | 0.4998 |
| 51 | O | O23 | 0.49956 | 0.24945 | 0.48998 |
| 53 | O | O25 | 0.20033 | 0.24953 | 0.67666 |
| 55 | O | O27 | 0.76983 | 0.25032 | 0.67493 |
| 57 | O | O29 | 0.73059 | 0.24964 | 0.32504 |
| 59 | O | O31 | 0.29742 | 0.25043 | 0.32322 |
| 61 | O | O33 | 0.20917 | 0.24948 | 0.44138 |
| 63 | O | O35 | 0.78562 | 0.25044 | 0.44206 |
| 65 | O | O37 | 0.71403 | 0.24959 | 0.55798 |
| 67 | O | O39 | 0.29112 | 0.25055 | 0.55863 |
| 69 | C | C1 | 0.24122 | 0.24978 | 0.71931 |
| 71 | O | O41 | 0.10797 | 0.24994 | 0.74128 |
| 73 | O | O43 | 0.40335 | 0.24983 | 0.72812 |
| 75 | C | C3 | 0.25852 | 0.2502 | 0.28041 |
| 77 | O | O45 | 0.09684 | 0.25018 | 0.27124 |
| 79 | O | O47 | 0.39287 | 0.25002 | 0.25881 |

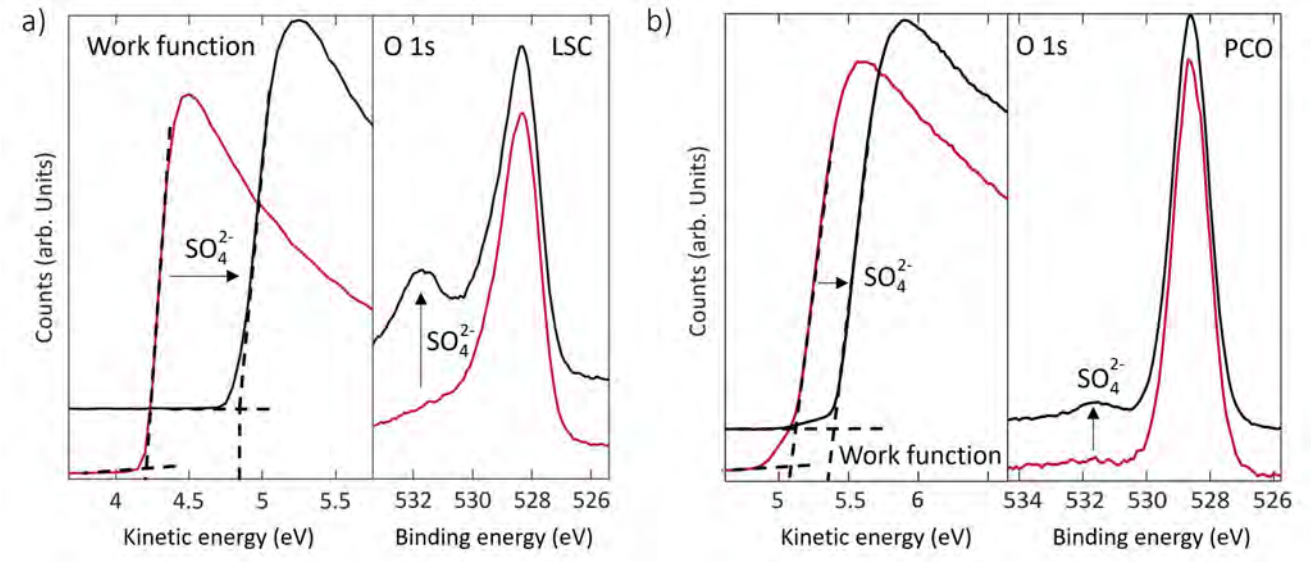
LSC with SrO termination and two $CrO_4^{2-}$ adsorbates:




| | | | x | y | z |
|---|---|---|---|---|---|
| 1 | Sr | Sr1 | 0.99847 | 0.99336 | 0.67626 |
| 3 | Sr | Sr3 | 0.50031 | 0.99786 | 0.67409 |
| 5 | Sr | Sr5 | 0.99852 | 0.50634 | 0.67628 |
| 7 | Sr | Sr7 | 0.50016 | 0.50193 | 0.67404 |
| 9 | La | La1 | 0.998 | 0.00201 | 0.44075 |
| 11 | La | La3 | 0.49769 | 0.00012 | 0.44 |
| 13 | La | La5 | 0.99804 | 0.49772 | 0.44074 |
| 15 | La | La7 | 0.49764 | 0.49958 | 0.44001 |
| 17 | Co | Co1 | 0.24871 | 0.25002 | 0.61629 |
| 19 | Co | Co3 | 0.75331 | 0.25003 | 0.61876 |
| 21 | Co | Co5 | 0.75015 | 0.24995 | 0.38136 |
| 23 | Co | Co7 | 0.24645 | 0.24998 | 0.38357 |
| 25 | Co | Co9 | 0.25135 | 0.25 | 0.50023 |
| 27 | Co | Co11 | 0.74872 | 0.25 | 0.5002 |
| 29 | O | O1 | 0.00093 | 0.25042 | 0.60639 |
| 31 | O | O3 | 0.74915 | 0.00013 | 0.61387 |
| 33 | O | O5 | 0.99863 | 0.25067 | 0.37726 |
| 35 | O | O7 | 0.25297 | 0.99961 | 0.61343 |
| 37 | O | O9 | 0.49785 | 0.24954 | 0.3902 |
| 39 | O | O11 | 0.74596 | 0.49958 | 0.38638 |
| 41 | O | O13 | 0.49961 | 0.24948 | 0.62582 |
| 43 | O | O15 | 0.25189 | 0.50011 | 0.38623 |
| 45 | O | O17 | 0.24826 | 0.00027 | 0.4999 |
| 47 | O | O19 | 0.00068 | 0.25015 | 0.51008 |
| 49 | O | O21 | 0.24855 | 0.49973 | 0.49964 |
| 51 | O | O23 | 0.49957 | 0.24982 | 0.48957 |
| 53 | O | O25 | 0.2077 | 0.2497 | 0.67487 |
| 55 | O | O27 | 0.78113 | 0.25013 | 0.67315 |
| 57 | O | O29 | 0.73575 | 0.24968 | 0.3263 |
| 59 | O | O31 | 0.25576 | 0.25019 | 0.32378 |
| 61 | O | O33 | 0.21022 | 0.24968 | 0.44163 |
| 63 | O | O35 | 0.78293 | 0.25035 | 0.44256 |
| 65 | O | O37 | 0.71225 | 0.24974 | 0.55795 |
| 67 | O | O39 | 0.29535 | 0.25039 | 0.55843 |
| 69 | Cr | Cr1 | 0.25737 | 0.24995 | 0.7273 |
| 71 | O | O41 | 0.17242 | 0.06946 | 0.74378 |
| 73 | O | O43 | 0.17146 | 0.07009 | 0.25667 |
| 75 | O | O45 | 0.17272 | 0.43077 | 0.74368 |
| 77 | O | O47 | 0.17142 | 0.43009 | 0.25664 |
| 79 | O | O49 | 0.47232 | 0.24986 | 0.7282 |
| 81 | O | O51 | 0.47844 | 0.25011 | 0.26147 |
| 83 | Cr | Cr3 | 0.26875 | 0.25013 | 0.26981 |

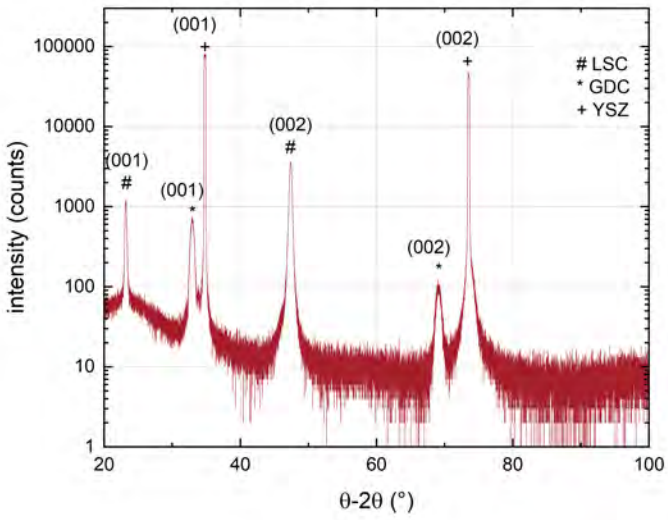
## S.I. 2. Work function shift on PCO

In addition to LSC, the effect of sulphate adsorbates on the work function was also investigated for the structurally and chemically different material $Pr_{0.1}Ce_{0.9}O_{2-\delta}$ (PCO). The same fundamental effect was observed for LSC (a) and PCO (b), namely an increase of the work function as a consequence of charge redistribution towards sulphate adsorbates on the surface. However, for PCO, the magnitude of this effect is smaller than for LSC, also the amount of sulphate adsorbates is reduced. We strongly suspect that this is due to the very basic nature of the LSC surface in comparison to the PCO surface.



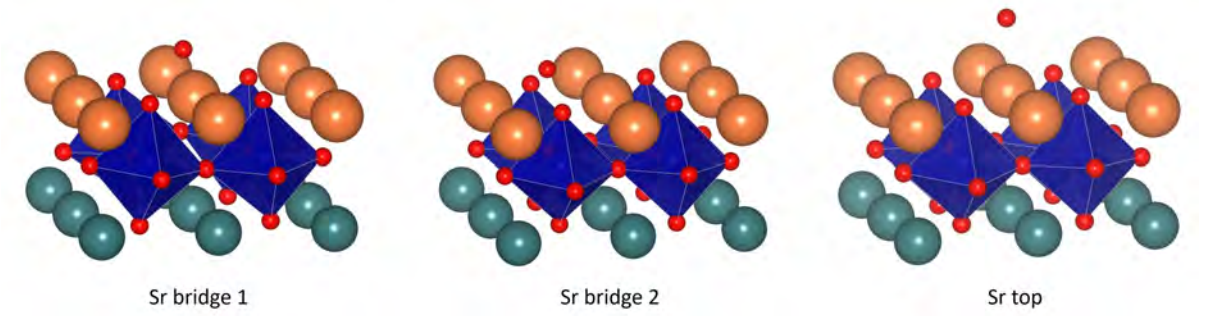

## S.I. 3. Structural analysis

The crystalline structure of an LSC thin film was investigated with X-ray diffraction with an Empyrean diffractometer (Panalytical). A 120 nm LSC thin film was deposited on a YSZ single crystal with a GDC20 buffer layer by pulsed laser deposition and the diffractogram is shown in the following figure. The diffractogram clearly shows that LSC grows well oriented in the (001) orientation on a (001) oriented YSZ single crystal with a GDC buffer layer.



## S.I. 4. $O_2$ dissociation

The dissociation of an $O_2$ molecule in a surface vacancy on LSC-S0 was investigated computationally. Three positions of the dissociated atom were examined: i) the first Sr bridge position between two surface Sr atoms, ii) the second Sr bridge position in the second lattice direction, iii) the Sr top position on top of a neighbouring Sr atom. The dissociated oxygen atom was constrained in x and y direction and structure relaxation was performed. The following figure shows the relaxed structures:




## S.I. 5. Reaction energetics

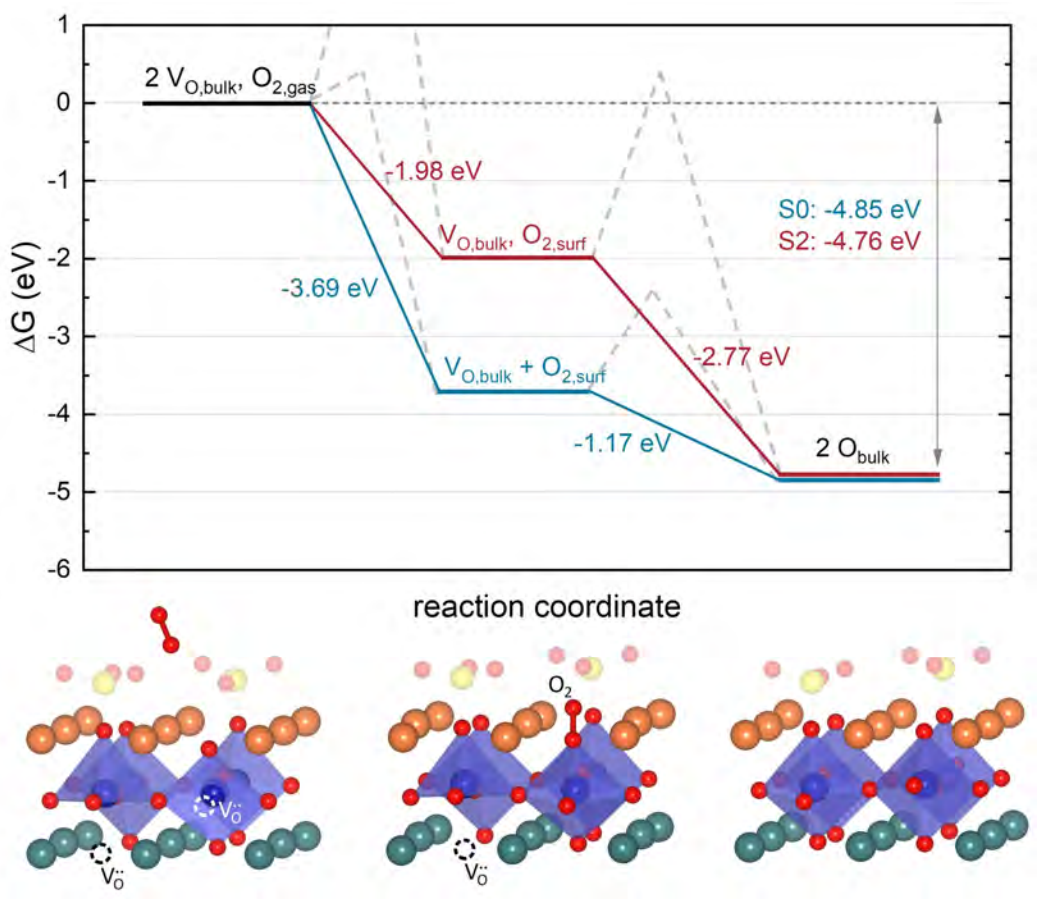
While the convolution of effects on the oxygen exchange kinetics induced by acidic adsorbates severely complicates a quantitative kinetic model for the oxygen exchange reaction rate, one may obtain further insight by approaching the problem from an energetic point of view. As an example, we calculated the start and end stages of the total oxygen exchange reaction

$$O_2(g) + 2V_{O,bulk} \leftrightarrow 2O_{latt} \tag{1}$$

as well as the energy of one reaction intermediate, LSC with an oxygen molecule adsorbed in a surface vacancy (see Fig. **??**). Usually, when the oxygen exchange reaction is discussed experimentally, a rate equation is employed to correlate the reaction rate with the concentrations of participating species [1–4]. For a mechanism in which the rate determining step of the incorporation direction follows the here calculated reaction intermediate, this would read

$$\vec{r} = \vec{k} \cdot [O_{2,surf}] \prod_i \cdot [i] \tag{2}$$

with $\vec{k}$ containing the kinetic barrier of the rate determining step as well as surface potential contributions and $[i]$ denoting additional species which might participate in the reaction step, such as oxygen vacancies or electronic charge carriers. As was already indicated by the previous discussion, the molecular adsorbate on LSC-S0 is energetically much more favourable than on LSC-S2. If one translates this into equilibrium conditions, the concentration of adsorbates will decrease correspondingly and slow down the reaction rate considerably. While this discussion does not take into account the kinetic barriers of the reaction steps (which are drawn schematically in the figure below and which are also altered substantially by $SO_4^{2-}$ adsorbate formation), the energetics of reaction intermediates before and after the rate determining step also affect the overall kinetics of the reaction and may act as a further link between experimental studies in equilibrium conditions and computational investigations of the oxygen exchange reaction. Regarding the here presented calculations, it is also noteworthy that, due to the small supercell and the selective placement of oxygen vacancies, vacancy formation and adsorption energies differ from single vacancy calculations. Hence, this examination is rather a conceptual approach than a quantitative investigation.




The figure shows the total energy of LSC with two bulk vacancies and one $O_2$ molecule, of LSC with one bulk vacancy and an oxygen molecule adsorbed in a surface vacancy and of LSC with no oxygen vacancies. The structures below the energy profile correspond to the three reaction steps. Barriers are only drawn schematically, qualitatively estimated from the previously presented results.

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