Oxygen defect engineering by the current effect assisted with temperature cycling in a perovskite-type La$_{0.7}$Sr$_{0.3}$CoO$_3$ film†

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Introducing and modulating the oxygen deficiency concentration have been received as an effective way to obtain high catalytic activity in perovskite oxides. However, it is difficult to control the oxygen vacancy in conventional oxygen defect engineering due to harsh reaction conditions at elevated temperatures and the reducing atmosphere, which make it impractical for many technological applications. Herein, we report a new approach to oxygen defect engineering based on the combination of the current effect and temperature cycling at low temperature. Our investigations revealed that the electrical conductivity of the (011)-La$_{0.7}$Sr$_{0.3}$CoO$_3$/PMN-PT film changes continuously from metallicity to insulativity under repeated transport measurements below room temperature, which indicates the transformation of the Co$^{4+}$ state to Co$^{3+}$ in the film. Further experiments and analysis revealed that oxygen vacancies can be well regulated by the combined current effect and temperature cycling in repeated measurements, which results in a decrease of Co$^{4+}$/Co$^{3+}$ and thus the remarkable variation of conductive properties of the film. Our work provides a simple and highly efficient method to engineer oxygen vacancies in perovskite-type oxides and brings new opportunities in designing high-efficiency oxidation catalysts.

Introduction

Multivalent transition metal oxides have attracted significant interest due to their intriguing physical properties based on the flexibility of transition metal charge states. In particular, oxygen-deficient perovskite oxides have received considerable attention due to their unique mixed electronic and ionic conducting properties, which make them appealing in a wide range of applications such as oxidation catalysts, gas sensors, oxygen separation membranes and electrode materials for solid oxide fuel cells. 1–4 It was previously believed that the catalytic activity is strongly associated with the binding strength of oxygen molecules and surface redox-active sites according to the so-called Sabatier’s principle. However, recent studies indicate that the surface redox center at transition metal cations cannot fully explain the catalytic behavior in oxygen-deficient perovskite oxides. 5–8 Further experimental and theoretical studies correlated oxygen electrocatalysis with the electronic structure of oxygen and metal cations such as $e_g$ band filling of transition metal ions, the O p-band center relative to the Fermi level and hybridization of the metal-3d and O-2p orbitals. 9–11 These studies provide a promising strategy to achieve highly active oxide catalysts through controlling the electronic structure of perovskite oxides. Moreover, experiments have revealed that the oxygen vacancies not only affect the electronic state between the metal-3d and O-2p but also change the metal cation valence, leading to regulation of the electronic structure of perovskite oxides. 6,9,12 As a result, oxygen defect engineering is accepted as an efficient way to obtain high catalytic activity in perovskite oxides.

Perovskite-type oxides, La$_{1-x}$Sr$^x$CoO$_3$–δ, have been viewed as an excellent platform for the study of reversible redox activity due to their characteristic properties of high oxygen ionic diffusivity, high electrical conductivity and high oxygen off stoichiometry. 12–16 It has been found that the substitution of Sr$^{2+}$ for La$^{3+}$ changes Co$^{3+}$ into Co$^{4+}$ in La$_{1-x}$Sr$^x$CoO$_3$ systems, resulting in the mixing valences Co ions. 17 As x increases, double exchange (DE) interaction in the La$_{1-x}$Sr$^x$CoO$_3$ system
becomes stronger and the La$_{1-x}$Sr$_x$CoO$_3$ system undergoes an insulator-to-metal transition. However, the high energy of the Co$^{4+}$ valence state promotes its conversion to the more stable Co$^{3+}$ or/and Co$^{2+}$ states, leaving oxygen vacancies in the CoO$_6$ octahedron. As oxygen vacancies increase in the La$_{1-x}$Sr$_x$CoO$_3$ film, the ferromagnetism becomes weaker$^{18}$ and the transport mechanism is transformed from the DE interaction effect to variable range hopping (VRH), characterized by the enhancement of overall resistivity and the emergence of insulativity.$^{19}$

More importantly, experiments revealed that the formation of oxygen vacancies from oxygen off stoichiometry, which is usually realized by annealing in a reducing atmosphere, greatly affects the redox activity of La$_{1-x}$Sr$_x$CoO$_3$. However, the possibility of a reversible redox reaction and the associated property changes of La$_{1-x}$Sr$_x$CoO$_3$ have not been systematically studied owing to the difficulty in precisely controlling the oxygen defect concentration. Although oxygen deficiency can be induced by growth or annealing in a reducing atmosphere, the strong redox property and narrow control range makes it difficult to regulate the oxygen defect structure of La$_{1-x}$Sr$_x$CoO$_3$ actively. Moreover, experiments showed that the formation of oxygen off-stoichiometric phases in perovskite-type oxides usually requires a very high annealing temperature and long annealing time,$^{23-24}$ which are impractical for many technological applications.

In this work, we revealed a low cost and highly efficient method to engineer oxygen defects in La$_{0.7}$Sr$_{0.3}$CoO$_3$ (LSCO) film by the application of an electric current and temperature cycling below room temperature. Investigations of the magnetic and transport properties in the (011)-oriented LSCO film demonstrate that the combined current effect and temperature cycling in the repeated temperature-dependent transport measurements could drive a continuous transformation of electrical conductivity from metallicity to insulativity by introducing oxygen vacancies and reducing the content of cation Co$^{4+}$ in the film. Our work provides a novel and practical method to manufacture extra oxygen defects and regulate the concentration of oxygen vacancies in the LSCO thin film through adjusting the combination of the current effect and temperature cycling, and brings new opportunities in preparing high-efficiency solid oxidation catalysts.

### Results and discussion

The $\theta$–$2\theta$ X-ray diffraction patterns of the LSCO film on the PMN-PT substrate are shown in Fig. 1(a). The result indicates...
that the LSCO/PMN-PT film is highly oriented along the [011] direction and the out-of-plane lattice constant is calculated to be 2.694 Å. Compared with bulk LSCO ($a \approx 3.82$ Å),$^{25}$ the film undergoes an out-of-plane compressive strain which was calculated to be $-0.25\%$ along the [011] direction by using the equation $\varepsilon_{[011]} = (d_{\text{film}} - d_{\text{bulk}})/d_{\text{bulk}}$. Fig. 1(b) and (c) show the X-ray reciprocal space maps collected around (222) and (013) reflections of the LSCO/PMN-PT film, respectively. By analyzing the two RSM patterns, we could obtain the lattice parameters and thus the strains along both orthogonal [100] and [01–1] directions in the deposition plane. The lattice constants of the film are determined to be 3.93 Å and 2.74 Å along the in-plane [100] and [01–1] directions, respectively. Accordingly, the in-plane strain $\varepsilon_{[100]}$ and $\varepsilon_{[01–1]}$ are calculated as 2.88% and 1.48%, respectively. The results show that the LSCO/PMN-PT film undergoes different tensile strain along [100] and [01–1] directions. Such anisotropic in-plane lattice strain would bring about a different overlap of O 2p and Co 3d electronic orbitals along [100] and [01–1], resulting in the in-plane anisotropy of the magnetic and transport properties.

Fig. 2(a) presents the temperature-dependent magnetization under a 500 Oe magnetic field along the in-plane [100] (open point) and [01–1] (solid point) directions after 500 Oe field cooling (FC) from room temperature. It is found that the Curie temperature ($T_C$) of the film, determined from both curves (215 K for [100] direction and 217 K for [01–1]), is a little bit lower than the bulk but similar to previous reports.$^{26,27}$ It is noteworthy that the difference in $T_C$ for the two directions suggests relatively weak magnetism in the [100] direction. Fig. 2(b) shows the magnetic hysteresis loops of LSCO/PMN-PT at 10 K along both in-plane directions. The image indicates that the LSCO/PMN-PT film is in a ferromagnetic state at 10 K, which is in coincidence with previous reports.$^{18,26,28}$ Meanwhile, the better squareness of the loop and the higher remnant magnetic moment along the [01–1] direction indicate that the magnetic moment prefers to align in the [01–1] direction. These results demonstrate a clear in-plane magnetic anisotropy in the LSCO/PMN-PT film, which should be ascribed to the anisotropic lattice strain field induced by the substrate. Actually, the larger strain at the [100] direction leads to weaker hybridization between the neighboring Co$^{3+}$/Co$^{4+}$ 3d orbital and O$^{2–}$ 2p orbital, resulting in a suppression of the DE interaction$^{29}$ and thus weak magnetism as shown in Fig. 2. The resistance along the in-plane [100] and [01–1] directions at a temperature range between 320 K and 20 K are also plotted in Fig. 2(a). It is seen that the resistance along both directions exhibit a metallic temperature dependence in a temperature interval below $T_C$, but insulating behavior outside the interval. At the bottom and top of the interval, two metal–insulator transitions are identified (see the Fig. 2(a)). The transition temperature at the bottom of the interval, $T_{M1}$ (211 K for both directions), is consistent with $T_C$, indicating that the metallic conduction is related to the DE interaction.$^{17,19,28}$ Meanwhile, the transition temperature at the bottom of the interval ($T_{M2}$) in the [01–1] direction is lower than the one in the [100] direction, which is ascribed to the stronger DE effect caused by the smaller tensile strain at the [01–1] direction.

The stability of the Co$^{4+}$ state was further investigated by repeatedly measuring the resistance of the LSCO film at a temperature range between 320 K and 20 K. A series of curves for two in-plane directions are plotted in Fig. 3(a) and (b). It is surprising to find that the transport characteristics of the LSCO film change steadily from metallicity to insulativity with the cycle number of measurements. The overall resistance is enhanced by the repeated measurements. Moreover, the metal–insulator transition at high temperature, which is relating to the change of magnetic order, shifts to lower temperature gradually with the cycle number of measurements. Further increases in the cycle number makes this metal–insulator transition gradually vanish. Meanwhile, in accordance with the variation of $T_{M1}$, the transition at low temperature moves towards high temperature with the increase of cycle number, suggesting the development of insulating conduction. Fig. 4(a) plots the summary of $T_{M1}$ and $T_{M2}$ for both in-plane directions against the cycle number of repeated measurements. In the beginning of the repeated measure-

![Fig. 2](image-url) (a) Temperature-dependent magnetization under a 500 Oe field (left axis, black) and resistance (right axis, red) in field cooling mode along both in-plane directions. (b) The magnetic hysteresis loops of LSCO/PMN-PT at 10 K along the in-plane [100] (black) and [01–1] (red) directions.
ments, $T_{M11}$ decreases slightly and linearly with the cycle number, $n$, at both directions. Meanwhile, $T_{M12}$ increases continuously with $n$, moving close to $T_{M11}$. As a result, the metallic conduction area shrinks with the cycle number of measurements. Moreover, a sharp drop of $T_{M11}$ is observed after $T_{M12}$ approaches $T_{M11}$, corresponding to the disappearance of both transitions and the predominance of insulating conduction in the whole temperature range. Such a remarkable variation of conductive properties indicates that the ratio of Co$^{4+}$/Co$^{3+}$, which is considered to be the determinative role in the electronic transport process, decreases continuously with the cycle number of repeated transport measurements. Previous research has revealed that the transformation of the Co$^{4+}$ state to Co$^{3+}$ in the LSCO system, either by reduction of Sr doping or incorporation of oxygen vacancies, will shift the resistive transition at $T_{M11}$ to lower temperatures, accompanied by an enhancement of the overall resistivity.$^{19,30}$

Our scanning electron microscopy and energy-dispersive X-ray spectra measurements (section I of ESI, Fig. S1†) demonstrate that no anomalous Sr cluster area appears in the surface of the film and the Sr distribution is nearly consistent with that of La and Co elements both before and after repeated transport measurements, which excludes the effect of the reduction in Sr doping. On the other hand, careful X-ray diffraction (XRD) experiments before and after repeated measurements exhibit no obvious change in the diffraction patterns, indicating that the possible structural change related to the variation in conductivity, if any, may locate in very small areas. Actually, our high-resolution transmission electron microscope experiments (section II of ESI, Fig. S2†) do observe a periodic oxygen vacancy ordering modulation in very small regions of the film after repeated transport measurements, suggesting the accumulation of oxygen vacancies in the local areas of the film. Meanwhile, soft X-ray absorption spectroscopy (XAS)

![Image](https://example.com/image1.png)

Fig. 3  Repeated temperature-dependent resistance measurements of the LSCO/PMN-PT film with a current of 1 $\mu$A applied along [01–1] (a) and [100] (b) directions. The numbers in the images represent the cycle index of measurements.

![Image](https://example.com/image2.png)

Fig. 4  (a) A summary for $T_{M11}$ and $T_{M12}$ as a function of cycle number of repeated transport measurements, $n$. The red solid (open) points represent $T_{M11}$ ($T_{M12}$) for the [01–1] direction, and the blue ones for the [100] direction. The shadow regions indicate the metallic conduction area for both directions (blue for [100] and red for [01–1], respectively). (b) Co L-edge X-ray adsorption spectra for the LSCO film before and after repeated transport measurements.
measurements at the Co L<sub>2–3</sub> absorption thresholds were carried out at the Beamline BL08U1A of Shanghai Synchrotron Radiation Facility to further examine the electronic structures and the Co valence states<sup>31</sup> in the LSCO film. The observed changes in the electronic structure of the LSCO film after repeated transport measurements strongly suggest variation in the Co valence state due to oxygen vacancy formation. Fig. 4(b) shows the comparison of the Co L-edge spectra at 300 K for the LSCO film before and after repeated transport measurements. First of all, a mixture of high-spin (HS) Co<sup>4+</sup>, HS Co<sup>3+</sup> and low-spin (LS) Co<sup>3+</sup> in the sample both before and after repeated measurements is suggested by the spectral shape at both edges, which is consistent with previous results of the LSCO film.<sup>32</sup> Moreover, it is evident that the Co L<sub>2–3</sub> spectral weights shift toward lower photon energies after repeated transport measurements. Such a shift suggests a lower Co valence in the LSCO film after measurements, evidencing the changes in the Co valence state toward Co<sup>3+</sup>. Previous spectral research has shown that Co<sup>3+</sup> ions induced by Sr-doping in the strained La<sub>0.7</sub>Sr<sub>0.3</sub>CoO<sub>3</sub> film prefers to have a HS configuration (3t<sub>2g</sub>2eg) due to the Jahn–Teller (JT) splitting of t<sub>2g</sub> resulting from Sr-doping and epitaxial strain.<sup>32,33</sup> This JT splitting of t<sub>2g</sub> could be stabilized by the strong in-plane strain in the present LSCO/PMN-PT, resulting in the maintenance of the HS configuration in Co<sup>3+</sup> ions.

Based on the above results, one could speculate, naturally, that the electric current applied during repeated measurements probably plays a key role in the presented unusual evolution of the electrical conductivity, which may introduce oxygen vacancies near the electrical channels in the LSCO/PMN-PT film, and thus reduces the content of Co<sup>4+</sup>. Usually, considerable oxygen loss in the LSCO film occurs at temperatures higher than 470 K in a vacuum or in an air environment.<sup>19,37</sup> Recent studies<sup>18,19</sup> on the La<sub>2/3</sub>Sr<sub>1/3</sub>MnO<sub>3</sub> film have revealed that Joule heating by an applied voltage/current can temporarily raise the temperature of the manganite oxide film and modify the oxygen vacancies doping condition. Theoretical simulations and spectroscopic experiments<sup>38</sup> show that Joule heating by a current of ~50 μA (produced by a short triangular voltage pulse with 0.1 s duration) can generate a temperature gradient with a maximum temperature of >600 K around the electrical contact and result in an electro-thermal redistribution of oxygen vacancies, inducing the oxygen deficient brownmillerite phase in the La<sub>2/3</sub>Sr<sub>1/3</sub>MnO<sub>3</sub> thin film (in submicrometer level).<sup>38</sup> Considering the high oxygen ionic diffusivity and the instability of the Co<sup>4+</sup> ions of LSCO, it is reasonable to expect the occurrence of a similar current effect in the present experiments, which may activate the formation of oxygen deficiencies around the current channel and increase the concentration of oxygen vacancy in the film. Moreover, the strong tensile strain in the present LSCO film can lower the formation energy of the oxygen vacancies, facilitating the accommodation of oxygen vacancies in the

![Fig. 5](Image) The magnetic hysteresis loops of the LSCO/PMN-PT film at 10 K after repeated temperature-dependent resistance measurements (red) compared with the original one (black) along the in-plane [01–1] (a) and [100] (b) directions. The insets are the temperature-dependent moment under 500 Oe for the corresponding direction.
however, the resistance approaches a constant after several repeated measurements \((n \geq 4)\), unlike the case of repeated measurements with temperature cycling where the overall resistance increases continuously. This result indicates that the individual current effect cannot totally account for the observed conductivity variation. To fully understand the origin of the unusual conductivity transformation, the role of temperature cycling should also be considered. To verify such an assumption, further experiments were performed: three purely temperature cycles without the application of an electric current were inserted between normal repeated measurements of the temperature-dependent resistance. The measured results at the [01–1] direction are plotted in Fig. 6(b). One could find that the increased amount of the overall resistance after 3 extra temperature cycles is markedly larger than those between neighboring repeated measurements without extra temperature cycling in between. This result exemplifies that temperature cycling is indispensable in this novel conductivity transformation. Although the exact mechanism of temperature cycling in the evolution of conductivity is unclear at the moment, one could expect that the lattice changes induced by the temperature variation may contribute to the accumulation of oxygen vacancies by reducing its forming or/and migration energy.40,41,45,46 It’s patently obvious that both the current effect and the temperature cycling have their own specific role in oxygen vacancy formation and neither of them can be dispensed in the observed novel conductivity transformation. Anyway, our present results have shown that oxygen vacancies could be introduced into the LSCO film simply by utilizing the combined current effect and temperature cycling below room temperature. Moreover, the concentration of oxygen vacancies in the LSCO film could be well regulated by adjusting the combination of the current effect and temperature cycling. Compared with the general route of annealing at high temperature in a reducing atmosphere, this newly developed oxygen defect engineering project is novel and highly effective.

It is worthwhile to note that the development of insulating conduction is different for two in-plane directions. One can
find from Fig. 4(a) that the metallic conduction area for the [100] direction (blue shadow region) is much smaller than the one for the [01−1] direction (red shadow region). Accordingly, the vanishing point of both metal–insulator transitions appears earlier in the [100] direction (the passing point for curves of $T_{M1}$ and $T_{M2}$, $n \sim 35$ for [100] and $n \sim 65$ for [01−1]). Moreover, the resistivity at an individual temperature along the [100] direction increases much faster with the number of repeated measurements than the one along the [01−1] direction (see Fig. 6(a)). These results indicate that the accumulation of oxygen vacancies and thus the transformation of Co$^{4+}$ to Co$^{3+}$ are much easier in the [100] direction, which could be ascribed to the anisotropic in-plane lattice strain-field in the LSCO/PMN-PT film. Previous research$^{40,41,45}$ has shown that the tensile strain can lower the oxygen vacancy formation energy by increasing the ionic radius associated with the reduction reactions in the expanded lattice. Meanwhile, the larger tensile strain weakens orbit hybridization and charge transfer between the O-atom and the neighboring Co-atom, leading to a smaller formation and migration energy of the oxygen vacancy. As a result, the oxygen deficiencies can be formed more easily in the [100] direction, leading to the quick decrease of the Co$^{4+}$/Co$^{3+}$ ratio and thus the quick transformation from metallicity to insulativity in the [100] direction. Moreover, repeated transport measurements were also performed on the bulk sample of La$_{0.9}$Sr$_{0.1}$CoO$_3$. No obvious change of transport properties was observed after repeated measurements (see Fig. S3 in the ESI†), demonstrating that no conductivity transformation caused by the current effect assisted with temperature cycling occurs in the bulk sample. Obviously, such distinct conductivity response to the temperature cycling-assisted current effect in bulk and the thin film of LSCO should be closely relative to the tensile strain in the thin film, evidencing the important role of the lattice strain in oxygen vacancy formation.

**Conclusions**

We present the first experimental observation for oxygen defect engineering by the combined current effect and temperature cycling in cobaltite films. A continuous conductivity transformation from metallicity to insulativity was observed in the (011)-oriented LSCO/PMN-PT film during repeated measurements of the temperature-dependent transport properties. Further experiments demonstrated that the oxygen vacancies induced by the combined current effect and temperature cycling in the repeated measurements should be the main cause for the conductivity transformation. Meanwhile, it was found that the oxygen vacancy concentration in the film could be well regulated by adjusting the combination of the current effect and temperature cycling. Our work reveals a novel and highly effective method to introduce oxygen vacancies in the perovskite-type oxide La$_{1-x}$Sr$_x$CoO$_3$ film and provides a new avenue to design highly efficient catalysts.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**