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# Solid-State Electrochemical Thermal Transistors

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Thermal transistors that electrically control heat flow have attracted growing attention as thermal management devices and phonon logic circuits. Although several thermal transistors are demonstrated, the use of liquid electrolytes may limit the application from the viewpoint of reliability or liquid leakage. Herein, a solid-state thermal transistor that can electrochemically control the heat flow with an on-to-off ratio of the thermal conductivity ( $\kappa$ ) of  $\approx$ 4 without using any liquid is demonstrated. The thermal transistor is a multilayer film composed of an upper electrode, strontium cobaltite (SrCoO<sub>x</sub>), solid electrolyte, and bottom electrode. An electrochemical redox treatment at 280 °C in air repeatedly modulates the crystal structure and  $\kappa$  of the SrCoO<sub>x</sub> layer. The fully oxidized perovskite-structured SrCoO<sub>3</sub> layer shows a high  $\kappa \approx 3.8$  W m<sup>-1</sup> K<sup>-1</sup>, whereas the fully reduced defect perovskite-structured SrCoO<sub>2</sub> layer shows a low  $\kappa \approx 0.95$  W m<sup>-1</sup> K<sup>-1</sup>. The present solid-state electrochemical thermal transistor may become next-generation devices toward future thermal management technology.

# 1. Introduction

Thermal transistors,<sup>[1–3]</sup> which can electrically control heat flow, have attracted growing attention as thermal management devices<sup>[4]</sup> and phonon logic circuits.<sup>[5,6]</sup> A thermal transistor is composed of an active material and a switching material.

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### DOI: 10.1002/adfm.202214939

The active material shows nonlinear heat transport properties upon a phase change, while the switching material controls the phase of the active material repeatedly. Thus, switching electrically modulates the thermal conductivity ( $\kappa$ ) of the active material.

History of thermal transistor development is short, only less than 10 years. In 2014, Ben-Abdallah and Biehs theoretically predicted a thermal transistor that uses the metal-to-insulator transition (MIT) of  $VO_2^{[7]}$  as the active layer. According to the Wiedemann-Frantz law, metallic  $VO_2$  exhibits  $\kappa$  that is at least  $\approx 1 \text{ W m}^{-1} \text{ K}^{-1}$  higher than the insulator  $VO_2$  due to the electron contribution. That is,  $\kappa_{\text{ele}} = L \cdot \sigma \cdot T$ , where *L* is the Lorentz number (2.44 × 10<sup>-8</sup> W  $\Omega$  K<sup>-2</sup>),  $\sigma$  is the electrical conductivity ( $\approx 1500 \text{ S cm}^{-1}$ for metal phase  $VO_2^{[8]}$ ), and *T* is the abso-

lute temperature. Since the MIT occurs at  $\approx 68$  °C in the bulk state, they predicted that  $\kappa$  of the VO<sub>2</sub> layer can be switched by Joule heating of the VO<sub>2</sub> layer above 68 °C. However, in 2017, Lee et al.<sup>[9]</sup> reported that the Wiedemann-Franz law was not applicable to VO<sub>2</sub> and the  $\kappa$  values of VO<sub>2</sub> before and after the MIT were almost the same<sup>[10]</sup>. Although Zhu et al.<sup>[11]</sup> demonstrated a thermal rectification in VO<sub>2</sub> beams, the value is not sufficient for thermal transistor applications. Consequently, the thermal transistor described in ref. [7] is impossible to realize.

Recently, electrochemical control of  $\kappa$  for materials using liquid electrolytes has attracted attention. Cho et al.<sup>[12]</sup> realized the first thermal transistor in 2014. They measured  $\kappa$ of a LiCoO<sub>2</sub> thin film before and after electrochemical delithiation using the time-domain thermo-reflectance (TDTR) method.  $\kappa$  of the LiCoO<sub>2</sub> film can be reversibly modulated in the range of  ${\approx}5.4{\text{--}}3.7~\text{W}~\text{m}^{\text{--}1}$  K date, several similar thermal transistors have been proposed. In 2018, Sood et al.<sup>[13]</sup> demonstrated the electrochemical Li intercalation/deintercalation using a liquid electrolyte modulates  $\kappa$  of MoS<sub>2</sub>. In 2020, transition metal oxide (TMO)-based thermal transistors using an ionic liquid as the electrolyte have been reported.  $^{\left[ 14,15\right] }$  Lu et al.<sup>[15]</sup> used SrCoO<sub>x</sub> as the active layer. The  $\kappa$  ratio of oxidized SrCoO<sub>3</sub> ( $\kappa$  = 4.33 ±1.62 W m<sup>-1</sup> K<sup>-1</sup>) versus protonated HSrCoO<sub>2.5</sub> ( $\kappa = 0.44 \pm 0.06$  W m<sup>-1</sup> K<sup>-1</sup>) is 10 ± 4. Very recently, Zhou et al.<sup>[16]</sup> reported a heat conductor-insulator transition in electrochemical hybrid superlattices composed of MoS<sub>2</sub> and an organic molecule. These thermal transistors utilize the change in  $\kappa$  of the active material when ions are intercalated/deintercalated electrochemically. Although these materials show suitable thermal transistor characteristics, the use of liquids (electrolyte,

ionic liquid) may limit the application because such devices must be placed in containers and sealed. Thus, the development of solid-state thermal transistors is crucial.

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To realize solid-state thermal transistors, we used a solid electrolyte, yttria-stabilized zirconia (YSZ), though the operation temperature is a bit high ( $\approx$ 300 °C) compared to the liquid electrolyte. We choose YSZ from the following reasons. YSZ is an oxide (O<sup>2–</sup>) ion conductor and has been applied as the solid electrolyte for solid oxide fuel cells.<sup>[17]</sup> Additionally, rather large-sized YSZ single crystals are commercially available. Most importantly, many perovskite-related TMOs are heteroepitaxially grown on YSZ single-crystal substrates.<sup>[18–20]</sup>

In this study, we focus on  $SrCoO_x$  ( $2 \le x \le 3$ ) as the active material for a solid-state electrochemical thermal transistor.  $\mathrm{SrCoO}_x$  is known as an oxygen sponge, and the  $\mathrm{O}^{2-}$  ion concentration of SrCoO<sub>x</sub> can be controlled at relatively low temperatures.<sup>[21-24]</sup> Our preliminary studies (Supporting Information Section S1, Figures S1–S6, Table S1) reveal that a SrCoO<sub>25</sub> film with a brownmillerite (BM) structure grown on YSZ is electrochemically oxidized into a perovskite (P-) SrCoO<sub>3</sub> film, which shows a high  $\sigma$  of  $\approx$ 1400 S cm<sup>-1.[25]</sup> Moreover, we found that a SrCoO<sub>2.5</sub> film on YSZ can be electrochemically reduced into a defect perovskite (DP-) SrCoO<sub>2</sub> film that is highly insulating. Generally,  $\kappa$  of material is expressed as the summation of  $\kappa$  due to the quantized lattice vibration (phonon) and  $\kappa$  due to the electron.<sup>[26]</sup> The former depends on the crystal structure and quality. The latter is given by the Wiedemann-Franz law as described above. From these observations, we expect that  $\kappa$  of P-SrCoO<sub>3</sub> is higher than that of DP-SrCoO<sub>2</sub>, as schematically illustrated in Figure 1.

Here, we demonstrate a solid-state electrochemical thermal transistor. The thermal transistor consists of a multilayered structure composed of a Pt upper electrode, a  $SrCoO_{2.5}$  active layer, a solid electrolyte Gd-doped  $CeO_2$  layer on a YSZ substrate, and a Pt bottom electrode on the backside of the YSZ. The multilayer sample is placed on a heater stage and heated to 280 °C in air. Then electrochemical oxidation/ reduction treatment at 280 °C in air repeatedly modulates the crystal structure and  $\kappa$  of the SrCoO<sub>x</sub> layer. The fully oxidized P-SrCoO<sub>3</sub> layer shows a high  $\kappa \approx 3.8$  W m<sup>-1</sup> K<sup>-1</sup>. By contrast, the fully reduced DP-SrCoO<sub>2</sub> layer shows a low  $\kappa \approx 0.95$  W m<sup>-1</sup> K<sup>-1</sup>. Consequently, a solid-state thermal transistor electrochemically controls the heat flow with an on-to-off  $\kappa$  ratio of  $\approx 4$ .

# 2. Results and Discussion

First, we fabricated solid-state electrochemical thermal transistors (Supporting Information Section S2, Figures S7 and S8). Then, a fabricated solid-state electrochemical thermal transistor (5 mm × 5 mm) was set on a Pt-coated glass substrate (Supporting Information Section S3, Figure S9). After heating to 280 °C in air, an electrochemical redox treatment was performed by applying a constant current of  $-50 \ \mu$ A for reduction and  $+50 \ \mu$ A for oxidation. We controlled the current application time by monitoring the flown electron density  $Q = (I \cdot t)/(e \cdot V)$ , where *I* is the flown current, *t* is the applied time, *e* is the electron charge, and *V* is the volume of the SrCoO<sub>2.5</sub> film (5 mm × 5 mm × ≈50 nm). After applying the current, the device was immediately cooled to room temperature.

The electrochemical redox treatment began by applying a negative current to reduce BM-SrCoO<sub>2.5</sub> into DP-SrCoO<sub>2</sub> (**Figure 2a**). Initially, the DC voltage in the electrochemical reduction was  $\approx$ -5.1 V, which was close to that expected from the DC resistance of the YSZ substrate ( $\approx$ 100 kΩ, 5 mm × 5 mm × 0.5 mm) (Supporting Information Section S3, Figure S10). Two semicircles of  $\approx$ 100 and  $\approx$ 25 kΩ were observed when we measured the impedance spectroscopy (Cole-Cole plot, data not shown). The former indicates resistance of YSZ substrate and the latter indicates the YSZ/ Pt interface resistance. As *Q* increased, the absolute value of the voltage gradually increased and became saturated around -5.7 V. Then it jumped to -6.1 V and became saturated again when *Q* was  $\approx$ 1.7 × 10<sup>22</sup> cm<sup>-3</sup>. This change in the voltage



**Figure 1.** Design of a solid-state electrochemical thermal transistor. (Left) Off state. Oxygen defects are generated in the  $SrCoO_x$  layer via the electrochemical reduction treatment. Resultant  $SrCoO_2$  layer (defect perovskite) contains 1/3 oxygen defects against  $SrCoO_3$ , and the defects scatter the heat flow, reducing the thermal conductivity. (Right) On state. Electrochemical oxidation treatment causes the oxygen defects to disappear, increasing the thermal conductivity.

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Figure 2. Operation of a solid-state thermal transistor. a,d) Changes in the observed DC voltage of the thermal transistor during a) reduction from SrCoO2, to SrCoO2 and d) oxidation from SrCoO2 to SrCoO3. Dotted lines indicate the theoretical electron density for the redox reaction of SrCoO2/ SrCoO<sub>2.5</sub>/SrCoO<sub>3</sub>. If Q exceeds  $\approx 3 \times 10^{22}$  cm<sup>-3</sup>, the voltage drops due to the reduction of GDC. b,e) Changes in the TDTR decay curves of the thermal transistor after b) reduction and e) oxidation treatments. c,f) Changes in the thermal conductivity of the SrCoO, layer after c) reduction and f) oxidation. Thermal conductivity of the SrCoO<sub>2.5</sub> layer for as-fabricated thermal transistor (0 cm<sup>-3</sup>) is  $\approx$ 1.8 W m<sup>-1</sup> K<sup>-1</sup>. TDTR decay is gradually suppressed as the electron density increases. Thermal conductivity of the SrCoO<sub>x</sub> layer gradually decreases with Q and becomes constant ( $\approx$ 1 W m<sup>-1</sup> K<sup>-1</sup>) when Q exceeds 1.7 × 10<sup>22</sup> cm<sup>-3</sup>. c,d) Changes in c) the TDTR decay curves and d) the thermal conductivity of a thermal transistor with oxidation. Thermal conductivity changes from  $\approx 1$  to  $\approx 3.5$  W m<sup>-1</sup> K<sup>-1</sup>.

corresponds to the electrochemical reduction of BM-SrCoO<sub>2.5</sub> as  $SrCoO_{2.5} + e^- \rightarrow SrCoO_2 + 0.5O^{2-}$ , which was confirmed by the change in the X-ray diffraction (XRD) patterns (Figure 3a-c). Afterward, the voltage gradually increased with

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Figure 3. Topotactic crystal structure change of the SrCoO<sub>x</sub> film upon electrochemical reduction/oxidation treatment. a,c,e) Out-of-plane XRD patterns for a) the as-grown SrCoO<sub>2.5</sub>, c) reduced SrCoO<sub>2</sub>, and e) oxidized SrCoO<sub>3</sub>. a) Intense diffraction peaks of 00/ (*l* = 2, 4, 8, and 10) brownmillerite (BM) SrCoO<sub>2.5</sub> are seen together with those of 002 GDC, 002 YSZ (\*), and 111 Pt. c) Intense diffraction peaks of 00/ (I = 1 and 2) defect perovskite (DP) SrCoO<sub>2</sub> are seen together with 002 GDC, 002 YSZ (\*), and 111 Pt. e) Intense diffraction peaks of 00/ (l = 1 and 2) perovskite (P) SrCoO<sub>3</sub> are seen together with 002 GDC, 002 YSZ (\*), and 111 Pt. b,d) Changes in the out-of-plane XRD patterns of b) SrCoO<sub>2.5</sub> upon reduction and d) SrCoO<sub>2</sub> upon oxidation. b) Diffraction peaks of BM disappear when Q exceeds  $0.8 \times 10^{22}$  cm<sup>-3</sup> and the intermediate phase appears (arrows). Intermediate phase peaks disappear and 002 DP-SrCoO<sub>2</sub> with defect perovskite structure appears. d) Diffraction peaks of DP disappear when Q exceeds  $1.0 \times 10^{22}$  cm<sup>-3</sup>, while the intermediate phase appears (arrows). Then these intermediate phase peaks disappear and the BM phase appears. Finally, P-SrCoO<sub>3</sub> appears when Q exceeds  $2.4 \times 10^{22}$  cm<sup>-3</sup>.

Q but dramatically decreased once Q exceeded  $\approx 3.2 \times 10^{22}$  cm<sup>-3</sup>. Electrochemical reduction of GDC<sup>[27]</sup> occurred after the overreduction treatment (data not shown). It should be noted that GDC is easily oxidized during electrochemical oxidation.

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Separately, we measured the  $\kappa$  of the SrCoO<sub>x</sub> layer by the TDTR method using the top Pt electrode as the transducer (Figures S15 and S16, Supporting Information). The TDTR measurement was performed at room temperature in air. Figure 2b shows the TDTR decay curves upon electrochemical reduction (see also Figure S17, Supporting Information). Compared to the as-grown state (0 cm<sup>-3</sup>), the decay slowed as Q increased, suggesting a decrease of  $\kappa$  of the SrCoO<sub>x</sub> layer. Figure 2c plots the estimated  $\kappa$  as a function of Q.  $\kappa$  of as-grown BM-SrCoO<sub>2.5</sub> was  $\approx$ 1.9 W m<sup>-1</sup> K<sup>-1</sup> but gradually decreased with Q. When Q reached  $\approx$ 1.7  $\times$  10<sup>22</sup> cm<sup>-3</sup>,  $\kappa$  became saturated at  $\approx$ 1 W m<sup>-1</sup> K<sup>-1</sup>.

Next the device was oxidized electrochemically (Figure 2d). The initial DC voltage was  $\approx$ 4.0 V. As *Q* increased, the voltage increased gradually and became saturated at  $\approx$ 4.2 V. When *Q* exceeded  $\approx$ 1.7 × 10<sup>22</sup> cm<sup>-3</sup>, the voltage dramatically increased and became saturated at  $\approx$ 4.8 V when *Q* reached  $\approx$ 3.4 × 10<sup>22</sup> cm<sup>-3</sup>.

The change in the crystalline phases is as follows

 $(\text{Up to} \approx 1.7 \times 10^{22} \text{ cm}^{-3}) \text{SrCoO}_2 + 0.5 \text{O}^{2-} \rightarrow \text{SrCoO}_{2.5} + \text{e}^{-}$  (1)

$$(Up \text{ to} \approx 3.4 \times 10^{22} \text{ cm}^{-3}) \text{ SrCoO}_{2.5} + 0.5\text{O}^{2-} \rightarrow \text{SrCoO}_3 + \text{e}^{-}$$
 (2)

The XRD patterns confirmed these changes (Figure 3c–e). These results reveal that the x value in SrCoO<sub>x</sub> can be controlled electrochemically between 2 and 3 without destroying the crystal structure.

The TDTR decay became faster as *Q* increased (Figure 2e), suggesting  $\kappa$  of the SrCoO<sub>x</sub> layer increased. Figure 2f shows two stepwise increases of  $\kappa$  of the SrCoO<sub>x</sub> at  $Q \approx 1.7 \times 10^{22}$  and  $\approx 3.4 \times 10^{22}$  cm<sup>-3</sup>. These stepwise increases of  $\kappa$  correspond to the oxidation from DP-SrCoO<sub>2</sub> to BM-SrCoO<sub>2.5</sub> and

from BM-SrCoO<sub>2.5</sub> to P-SrCoO<sub>3</sub>. The  $\kappa$  of fully oxidized P-SrCoO<sub>3</sub> was  $\approx$ 3.5 W m<sup>-1</sup> K<sup>-1</sup>. These results reveal that  $\kappa$  of the SrCoO<sub>x</sub> layer can be controlled electrochemically between  $\approx$ 1 and  $\approx$ 3.5 W m<sup>-1</sup> K<sup>-1</sup> using YSZ as the solid electrolyte.

Finally, we examined the repeatability of the thermal transistor. Figure 4 shows the change in the crystal lattice of  $SrCoO_x$ layer on the redox treatment. In the out-of-plane XRD patterns, the diffraction peak around 5.05 nm<sup>-1</sup> was 008 for the as-grown BM-SrCoO<sub>25</sub>. The reduction treatment shifted the diffraction peak to  $\approx 5.4 \text{ nm}^{-1}$  (002 DP-SrCoO<sub>2</sub>), while the oxidation treatment shifted it to  $\approx 5.25$  nm<sup>-1</sup> (002 P-SrCoO<sub>3</sub>). Repeating the redox treatments ten times did not change the peak position or shape except for the first reduction and oxidation treatments. Similarly, the applied voltage was almost unchanged in each redox cycle except for the first reduction and oxidation treatments (Figure S11, Supporting Information). Figure 4b shows the change in the *d*-value of reduced DP-SrCoO<sub>2</sub> and oxidized P-SrCoO<sub>3</sub> layers upon redox cycles. The extracted lattice parameter c was 0.3706 nm for reduced DP-SrCoO<sub>2</sub> and 0.3795 nm for oxidized P-SrCoO<sub>3</sub>. These results reveal that the crystal structure is maintained after redox cycling.

Figure 5 shows the change in the TDTR decay curves of the redox-cycled device. The TDTR decay of oxidized P-SrCoO<sub>3</sub> was always faster than that of reduced DP-SrCoO<sub>2</sub>. Using these TDTR decay curves, the change in  $\kappa$  of reduced DP-SrCoO<sub>2</sub> and oxidized P-SrCoO<sub>3</sub> layers was simulated in the redox cycles (see Figure S18, Supporting Information). The average  $\kappa$  values were 0.95 W m<sup>-1</sup> K<sup>-1</sup> for reduced DP-SrCoO<sub>2</sub> and 3.8 W m<sup>-1</sup> K<sup>-1</sup> for oxidized P-SrCoO<sub>3</sub>, indicating an on-tooff thermal conductivity ratio for the  $SrCoO_x$  layer of 4. If we assume the electron contribution of the  $\kappa_{\rm ele}$  of P-SrCoO3 in the cross-plane direction by the Wiedemann-Frantz law using the in-plane electrical conductivity (≈590 S cm<sup>-1</sup>, Section S1.3, Supporting Information), the value is  $\approx 0.43$  W m<sup>-1</sup> K<sup>-1</sup> ( $\approx 11\%$  of the observed  $\kappa$ ). These results indicate the on-to-off thermal conductivity ratio mainly comes from the difference between DP and P structure of SrCoO<sub>x</sub>.



**Figure 4.** Repeatable change in the crystal lattice of  $SrCoO_x$  layer on the redox treatment. a) Change in the out-of-plane XRD patterns in the  $q_z/2\pi$  range of 4.8–5.6 nm<sup>-1</sup>. Diffraction peak around 5.05 nm<sup>-1</sup> is 008 of  $SrCoO_{2.5}$ . Diffraction peak shifts to  $\approx$ 5.4 nm<sup>-1</sup> (002  $SrCoO_2$ ) after the reduction treatment, while oxidation treatment shifts to  $\approx$ 5.25 nm<sup>-1</sup> (002  $SrCoO_3$ ). Upon repeating the redox treatments ten times, the peak position and shape are unchanged except for the 1st reduction and oxidation treatments. b) Change in the *d*-value of the reduced  $SrCoO_2$  and oxidized  $SrCoO_3$  layers upon redox cycles. Extracted lattice parameter *c* is 0.3706 nm for reduced  $SrCoO_2$  and 0.3795 nm for oxidized  $SrCoO_3$ .

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**Figure 5.** Repeatable change in the thermal conductivity of  $SrCoO_x$  layer on the redox treatment. a) Change in the TDTR decay curves. TDTR decay of oxidized  $SrCoO_3$  is always faster than that of reduced  $SrCoO_2$ . Good repeatability is seen. b) Change in the thermal conductivity of reduced  $SrCoO_2$  and oxidized  $SrCoO_3$  layers upon redox cycles. Average thermal conductivity is 0.95 W m<sup>-1</sup> K<sup>-1</sup> for reduced  $SrCoO_2$  and 3.8 W m<sup>-1</sup> K<sup>-1</sup> for oxidized  $SrCoO_3$ . On/off thermal conductivity ratio of  $SrCoO_x$  layer is 4.

Here, we compare the characteristics of the present solidstate electrochemical thermal transistor with the reported liquid-based electrochemical thermal transistors (**Table 1**). The present solid-state thermal transistor shows comparable characteristics except that the operating temperature is high due to low oxide ion conductivity of YSZ crystal. In order to overcome this problem, reduction of the resistance of the solid electrolyte is crucial.

If we except the problem of high operating temperature, the present solid-state electrochemical thermal transistor has several advantages compared to liquid-based electrochemical thermal transistors. First, it does not need to be placed in a container and sealed. Second, it shows stable operations after repeated cycles. Third, it has a good reproducibility. The multilayered structure composed of Pt, SrCoO<sub>x</sub>, GDC, and YSZ is maintained after the redox cycles (Figures S12 and S13, Supporting Information), and the crystal structure of SrCoO<sub>x</sub> maintains the perovskite structure upon the redox reaction (Figure S14, Supporting Information). We fabricated many thermal transistors (>20 pieces) and tested the cycle properties. And we confirmed that all the devices show the on/off ratio of  $\approx$ 4 between the fully oxidized perovskite SrCoO<sub>3</sub> versus the reduced defect perovskite SrCoO2. Fourth, the device operations obey Faraday's law of electrolysis without current leakage. Thus, controlling Q can realize on/off control of the device. In the present device, the solid electrolyte (0.5 mm thick YSZ crystal) and the solid electrolyte/Pt interface dominate the current flow. In other word, use of a solid electrolyte with a higher  $O^{2-}$  ion conductivity or reducing the thickness of a solid electrolyte is effective to reduce the operating temperature and switching time of the device.

## 3. Conclusions

In summary, we demonstrated a solid-state electrochemical thermal transistor without any liquid that can control the heat flow using the change in the thermal conductivity of the SrCoO<sub>x</sub> layer. The on-to-off ratio of the thermal conductivity ( $\kappa$ ) was  $\approx$ 4. The solid-state electrochemical thermal transistor was composed of the upper electrode, SrCoO<sub>x</sub>, the solid electrolyte, and the bottom electrode. The electrochemical redox treatment at 280 °C in air turned the thermal transistor on and off and repeatedly modulates the crystal structure and  $\kappa$  of the SrCoO<sub>x</sub> layer. When the thermal transistor was on,  $\kappa$  of the SrCoO<sub>3</sub> layer was  $\approx$ 3.8 W m<sup>-1</sup> K<sup>-1</sup>. By contrast,  $\kappa$  of the SrCoO<sub>2</sub> layer was  $\approx$ 0.95 W m<sup>-1</sup> K<sup>-1</sup> when it was off. Additionally, we confirmed the cycle properties of the thermal transistor (10 cycles).

Although the present solid-state thermal transistor shows comparable characteristics with liquid-based thermal transistors ever reported, the operating temperature is high due to low oxide ion conductivity of YSZ crystal. In order to develop

Table 1. Thermal transistor characteristics of the reported electrochemical thermal transistors. Compared with the liquid electrolyte or ionic liquidbased thermal transistors, the present solid-state thermal transistor shows comparable characteristics except that the operating temperature is high.

Active material	Electrolyte	On/off ratio	Operating temperature [°C]	Operating voltage [V]	Switching time	Ref.
LiCoO <sub>2</sub> /Li <sub>0.6</sub> CoO <sub>2</sub>	LiClO <sub>4</sub> -EC/DMC (Liquid)	≈1.5	RT	4.2	≈1.5 h	[12]
MoS <sub>2</sub> /LiMoS <sub>2</sub>	LiPF <sub>6</sub> -EC/DEC (Liquid)	≈10	RT	3	7 min	[13]
La <sub>5</sub> Ca <sub>9</sub> Cu <sub>24</sub> O <sub>41</sub>	DEME-TFSI (Ionic liquid)	≈4	RT	2	≈0.5 h	[14]
SrCoO <sub>3</sub> /HSrCoO <sub>2.5</sub>	HMIM-TFSI (Ionic liquid)	≈10	RT	4	≈0.5 h	[15]
MoS <sub>2</sub> /MoS <sub>2</sub> -C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> Br	C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> Br -NMP (Liquid)	≈80	RT	≈3	≈2.3 min	[16]
SrCoO <sub>3</sub> /SrCoO <sub>2</sub>	GDC/YSZ (Solid-state)	≈4	280	≈6.5	≈3 min	This work

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practical thermal transistors, reduction of the resistance of the solid electrolyte is crucial. When this problem is solved, the present solid-state electrochemical thermal transistor may become next-generation devices toward future thermal management technology such as electric heat shutters.

# 4. Experimental Section

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Fabrication of the Thermal Transistors: SrCoO<sub>25</sub> films were heteroepitaxially grown on 10%-Gd-doped CeO2 (GDC) buffered (001)-oriented YSZ substrates by pulsed laser deposition (PLD) technique. First, ≈10 nm thick GDC was heteroepitaxially grown on a YSZ (10 mm  $\times$  10 mm  $\times$  0.5 mm, double-sided polished, Crystal Base) substrate at 750 °C in an oxygen atmosphere (10 Pa). Focused KrF excimer laser pulses ( $\lambda = 248$  nm, fluence  $\approx 2$  J cm<sup>-2</sup> pulse<sup>-1</sup>, repetition rate = 10 Hz) were irradiated onto the ceramic target of GDC. Subsequently, an  $\approx$ 50 nm thick SrCoO<sub>2.5</sub> film was heteroepitaxially grown on the GDC film at 750 °C in an oxygen atmosphere (10 Pa). The laser fluence was  $\approx 2$  J cm<sup>-2</sup> pulse<sup>-1</sup>. After film growth, the sample was cooled to room temperature in the PLD chamber in an oxygen atmosphere (10 Pa). Then ≈60 nm thick Pt film was sputtered on the top surface of the SrCoO<sub>2.5</sub> epitaxial film followed by  $\approx$ 40 nm thick Pt film sputtering on the backside of the YSZ substrate. Pt sputtering was performed at room temperature. Finally, the sample was cut into four squares  $(5 \text{ mm} \times 5 \text{ mm}).$ 

*Electrochemical Redox Treatments*: The thermal transistor (5 mm  $\times$  5 mm) was put on a Pt-coated glass substrate, which was heated at 280 °C in air. Then the electrochemical redox treatment was performed by applying a constant current of  $\pm$ 50  $\mu$ A. After applying the current, the sample was immediately cooled to room temperature.

Crystallographic Analyses: The crystalline phase, orientation, and lattice parameters of the resultant films were analyzed by high-resolution XRD (Cu K $\alpha_h$ ,  $\lambda = 1.54059$  Å, ATX-G, Rigaku). The out-of-plane and in-plane Bragg diffraction patterns as well as the rocking curves were measured at room temperature to clarify the changes in the crystalline phase of SrCoO<sub>x</sub>. The lattice parameters were calculated from the diffraction peaks. Atomic force microscopy (AFM, Nanocute, Hitachi Hi-Tech Sci. or MFP-3D Origin, Oxford Instruments) was used to observe the surface morphology of the films at room temperature. The atomic arrangement of the SrCoO<sub>x</sub> films was visualized using scanning transmission electron microscopy (STEM, JEM-ARM200CF, JEOL) operating at 200 keV.

X-Ray Absorption Spectroscopy (Figure S6, Supporting Information): Soft X-ray absorption spectroscopy (XAS) of the Co L- and O K-edges was performed at the 2A beamline in the Pohang Accelerator Laboratory. The direction of the incident X-rays was normal to the sample plane, and a circular polarization was used. The XAS spectra of these samples were measured in the total electron yield mode at room temperature. The base pressure of the system was  $10^{-9}$  Torr.

Measurements of the Optical and Electrical Properties (Figure S5, Table S1, Supporting Information): After mechanically removing the Ag paste film from the backside of the YSZ substrate, the optical transmission spectra of the samples were acquired at room temperature using a UV-vis–NIR spectrometer (SolidSpec-3700, Shimadzu). The electrical resistivities of the resultant films were measured by the DC four-probe method with van der Pauw electrode configuration.

Measurements of the Thermal Conductivity:  $\kappa$  of the SrCoO<sub>x</sub> films perpendicular to the substrate surface was measured by TDTR (PicoTR, PicoTherm). The top Pt film was used as the transducer. The decay curves of the TDTR signals were simulated to obtain  $\kappa$ . The specific heat capacities of the layers used for the TDTR simulation were Pt, 132 J kg<sup>-1</sup> K<sup>-1</sup>; SrCoO<sub>x</sub>, 485 J kg<sup>-1</sup> K<sup>-1</sup>; and YSZ, 460 J kg<sup>-1</sup> K<sup>-1</sup>. Details of the TDTR method are described in the Supporting Information (Section S4) and elsewhere.<sup>[28-30]</sup> Regarding the treatment of the thermal conductivity values, since there were several uncertainties such as position of the baseline, position of the time zero, and noise of the signal, the error bars of  $\pm 10\%$  of the obtained values were used.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

# Acknowledgements

This research was supported by Grants-in-Aid for Scientific Research A (22H00253) and Innovative Areas (19H05791 and 19H05788) from the Japan Society for the Promotion of Science (JSPS). Part of this work was supported by the Crossover Alliance to Create the Future with People, Intelligence and Materials, and by the Network Joint Research Center for Materials and Devices. Part of this work was supported by the Advanced Research Infrastructure for Materials and Nanotechnology Japan (grant number JPMXP1222UT0055) by Ministry of Education, Culture, Sports, Science and Technology (MEXT). Q.Y. was supported by a Grant-in-Aid for JSPS Fellows (21J10042). Z.B. was supported by Hokkaido University DX Doctoral Fellowship.

# **Conflict of Interest**

The authors declare no conflict of interest.

# **Data Availability Statement**

The data that support the findings of this study are available in the Supporting Information of this article.

# Keywords

electrochemistry, redox treatment, solid state, thermal conductivity, thermal transistors, transition metal oxides

Received: December 23, 2022 Revised: January 20, 2023 Published online:

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