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Citation	ACS Applied Electronic Materials, 3(7), 3296-3300 https://doi.org/10.1021/acsaelm.1c00505
Issue Date	2021-07-27
Doc URL	http://hdl.handle.net/2115/86381
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Type	article (author version)
File Information	Revised Manuscript_HxSrCoO ₂ _clean.pdf



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**Solid-State Electrochemical Protonation of SrCoO_{2.5} into H_xSrCoO_{2.5}
($x = 1, 1.5$ and 2)**

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KEYWORDS: solid-state electrochemical protonation, brownmillerite, H_xSrCoO_{2.5}, SrCoO_{2.5}, optical property, magnetic property

ABSTRACT: Among many transition metal oxides (TMOs), strontium cobalt oxide (SrCoO_x) is a promising active material for advanced memory devices due to the

versatile valence state of cobalt ion. Several SrCoO_x -based electrochemical devices have been proposed, but solid-state protonation from $\text{SrCoO}_{2.5}$ to $\text{H}_x\text{SrCoO}_{2.5}$ ($x = 1, 1.5, \text{ and } 2$) at room temperature has not been demonstrated thus far due to the absence of appropriate solid electrolyte. Here we demonstrate a solid-state electrochemical protonation of $\text{SrCoO}_{2.5}$ using mesoporous amorphous $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (CAN) film as the solid electrolyte. The crystalline phase discretely changed from $\text{SrCoO}_{2.5}$ to $\text{HSrCoO}_{2.5}$ (phase A), $\text{H}_{1.5}\text{SrCoO}_{2.5}$ (phase B), and $\text{H}_2\text{SrCoO}_{2.5}$ (phase C) through formation of an intermediate phase of $\text{H}_{1.25}\text{SrCoO}_{2.5}$. The $\text{H}_{1.5}\text{SrCoO}_{2.5}$ (phase B) was colorless-transparent and showed weak ferromagnetism. The present results indicate that the CAN film can be used as the solid electrolyte for the protonation treatment of TMOs.

INTRODUCTION

Due to the recent explosive increase in the stored volume of information, advanced memory devices that store multiple information are highly demanded¹. Materials that show non-volatile control of the optical, electrical, and magnetic properties would be useful as the active material of these advanced memory devices. In this regard, transition metal oxides (TMOs) are promising active materials of such memory devices

since many TMOs show the transition from one crystalline phase to another by electrochemical protonation/reduction/oxidation method, resulting in the changes in optoelectronic and magnetic properties²⁻⁶.

Among many TMOs, we focused on SrCoO_x film in this study because SrCoO_x film is known as an oxygen sponge⁷; where the topotactic redox reaction of SrCoO_x easily occurs⁸. There are several crystalline phases associated with the valence state of Co ions: brownmillerite (BM) SrCoO_{2.5} (Co³⁺), perovskite SrCoO₃ (Co⁴⁺), and protonated BM-H_xSrCoO_{2.5} (Co²⁺) ($x = 1, 1.5, \text{ and } 2$)^{5,9}. BM-SrCoO_{2.5} is a brown-colored antiferromagnetic insulator, and SrCoO₃ is a black-colored ferromagnetic metal.

Further, protonated H_xSrCoO_{2.5}, which is almost transparent in the visible region, is an electrical insulator and shows a weak ferromagnetic behavior⁵. In addition, the thermal conductivity of SrCoO_x also can be modulated by the electrochemical protonation/oxidation treatment¹⁰. Thus, we can control the optical, electrical, magnetic, and thermal properties of SrCoO_x, which can be utilized in the active material for the electrochemical memory device.

In 2017, Lu *et al.*⁵ firstly demonstrated the electrochemical protonation/oxidation of

SrCoO_x and successfully controlled the optical, electrical, and magnetic properties.

They used residual water in the ionic liquid as the electrolyte. Since there is a possibility of liquid leakage from the device, utilization of liquid electrolyte^{5, 11} is not appropriate for the requirement for the practical application. To overcome this problem, the use of the solid electrolyte is essential for realizing a leakage-free device. In 2016, Katase *et al.*¹² used a porous amorphous NaTaO₃ film as the solid electrolyte and successfully converted SrCoO_{2.5} film to SrCoO₃ film at room temperature. In our preliminary experiment, we tried the protonation of SrCoO_{2.5} film using NaTaO₃ film as the solid electrolyte but failed, probably due to the strong alkalinity of NaTaO₃ containing NaOH¹²⁻¹³.

In this study, we focused on the solid-state electrochemical protonation of SrCoO_{2.5} into H₂SrCoO_{2.5}. We choose a mesoporous amorphous 12CaO·7Al₂O₃ (CAN)¹⁴⁻¹⁵ film as the solid electrolyte. CAN contain ultrapure water in the mesopores (~40 vol.%) and shows the electrical conductivity of $2.2 \times 10^{-9} \text{ S cm}^{-1}$, which is ~4% of that of ultrapure water ($5.5 \times 10^{-8} \text{ S cm}^{-1}$) at room temperature¹⁶. Katase *et al.* demonstrated that VO₂¹⁷⁻¹⁸ and WO₃¹⁹ can be protonated electrochemically using CAN as the solid electrolyte at room temperature. Thus, we expected that solid-state electrochemical protonation of SrCoO_{2.5}

is possible by using CAN as the solid electrolyte. As a result of this study, we successfully modulated the crystalline phase discretely from $\text{SrCoO}_{2.5}$ to $\text{HSrCoO}_{2.5}$ (phase A), $\text{H}_{1.5}\text{SrCoO}_{2.5}$ (phase B), and $\text{H}_2\text{SrCoO}_{2.5}$ (phase C) through the formation of an intermediate phase of $\text{H}_{1.25}\text{SrCoO}_{2.5}$. $\text{H}_{1.5}\text{SrCoO}_{2.5}$ (phase B) was colorless-transparent and showed weak ferromagnetism. The present results indicate that the CAN film can be used as the solid electrolyte for the protonation treatment of TMOs.

EXPERIMENTAL SECTION

Sample preparation: Two-terminal electrochemical cells were fabricated by a pulsed laser deposition (PLD) technique with stencil masks (**Fig. 1a**). First, ~30-nm-thick 10 mol% Nb-doped SrTiO_3 films were heteroepitaxially grown on (001)-oriented SrTiO_3 substrate (10 mm \times 10 mm \times 0.5 mm) at the substrate temperature of 900 °C in an oxygen atmosphere (1×10^{-3} Pa). Second, ~50-nm-thick $\text{SrCoO}_{2.5}$ active layers were heteroepitaxially grown on the Nb-doped SrTiO_3 films with stencil mask (2.25 mm \times 2.25 mm) at the substrate temperature of 850 °C in an oxygen atmosphere (10 Pa). Then, ~300-nm-thick mesoporous CAN containing ~40 vol.% water was deposited on the $\text{SrCoO}_{2.5}$ film at room temperature as the solid electrolyte. Finally, ~30-nm-thick

ITO film was deposited as the top electrode at room temperature. Details of the PLD condition of each layer have been published elsewhere^{12, 14-15, 17, 19-22}.

Electrochemical oxidation and protonation: Electrochemical protonation of SrCoO_{2.5} films was performed at room temperature in air as schematically shown in **Fig. 1**. When a constant voltage of +10 V was applied using a source meter (Model 2450, Keithley), the SrCoO_{2.5} film was converted into H_xSrCoO_{2.5} film within several hours.

Crystallographic analyses: The crystallographic phase and orientation were analyzed using a high-resolution X-ray diffractometer with Cu K α_1 ($\lambda = 1.54059 \text{ \AA}$) radiation (ATX-G, Rigaku Co.). Out-of-plane Bragg diffraction pattern and reciprocal space mapping of the samples were measured at room temperature. *In-situ* monitoring of the out-of-plane XRD patterns during the electrochemical reduction was performed using a high-resolution X-ray diffractometer with Cu K α_1 ($\lambda = 1.54059 \text{ \AA}$) radiation (D8 Advance, Bruker) and a source meter (Model 2450, Keithley). After applying the bias voltage using gold-coated probes, all the *in-situ* XRD patterns were measured at room temperature in air. Each scan took about 5 minutes and was plotted in a two-dimensional contour diagram.

Magnetic properties: The magnetic moments of the protonated/as-grown/oxidized samples were measured at 10–300 K with 100 Oe field cooling using a SQUID magnetometer (MPMS3, Quantum Design). To check the change in magnetic properties, magnetic hysteresis loops (M vs. H curves) were measured up to 7 T at 10 K.

Optical property measurements: The optical transmission spectra of the two-terminal memory devices were measured at room temperature using UV-Vis-NIR spectrometer (SolidSpec-3700, Shimadzu) and FT-IR (Model IRPrestige-21, Shimadzu).

Proton concentration: We conducted secondary-ion mass spectrometry (SIMS) to obtain the hydrogen concentration in the protonated sample (Front Side SIMS, PHI, 6800). Cs^+ primary ion beam (2 keV) was scanned, and data were collected in an area of $40 \times 40 \mu\text{m}$. The Hydrogen concentration of H^+ ions was quantitatively analyzed by profiling proton-embedded silica with known H^+ doses.

RESULTS AND DISCUSSION

During the protonation, we *in-situ* monitored the out-of-plane XRD pattern of the device as shown in **Fig. 2a**. We also recorded the flowing current density (J) to the solid-state electrochemical cell during the voltage application (**Fig. 2b**). Before the protonation (0 min), 008 diffraction peak of BM-SrCoO_{2.5} (008_{BM}) is seen together with 002 SrTiO₃ substrate (002_s). Approximately 40 min after starting the protonation treatment, 008 diffraction peak of HSrCoO_{2.5} (008_A) appears and the intensity of 008_{BM} becomes weak. The J dropped from $\sim 5 \text{ mA cm}^{-2}$ to $\sim 4 \text{ mA cm}^{-2}$ simultaneously. Approximately 100 min after starting the protonation treatment, 008 diffraction peak of H_{1.5}SrCoO_{2.5} (008_B) appears together with a diffraction peak of the intermediate phase. Details of the intermediate phase are described later. Approximately 260 min after starting the protonation treatment, 008 diffraction peak of H₂SrCoO_{2.5} (008_C) appears. Simultaneously, diffraction peaks of 008_A and intermediate phase disappear. The J gradually decreased from $\sim 3.6 \text{ mA cm}^{-2}$ to $\sim 0.3 \text{ mA cm}^{-2}$. These results indicate that solid-state protonation is possible by using CAN as the solid electrolyte.

In order to clarify the diffraction peak of the intermediate phase, we measured out-of-plane XRD patterns of the solid-state electrochemical cell (another cell) after protonation treatment (**Fig. 2c**). At 0 min, 00 l diffraction peaks of BM-SrCoO_{2.5} are

seen together with 00 l SrTiO₃ substrate, indicating strong c -axis orientation of the BM-SrCoO_{2.5} film. After starting the protonation treatment, the diffraction peak position changes discretely from $q_z/2\pi = (0.6346 \times l) \text{ nm}^{-1}$ (BM-SrCoO_{2.5}) to $(0.6091 \times l) \text{ nm}^{-1}$ (HSrCoO_{2.5}, A), $(0.5968 \times l) \text{ nm}^{-1}$ (H_{1.5}SrCoO_{2.5}, B), and $(0.5845 \times l) \text{ nm}^{-1}$ (H₂SrCoO_{2.5}, C) through formation of an intermediate phase of H_{1.25}SrCoO_{2.5} ($q_z/2\pi = 1.822, 3.046, 4.253, 5.484, \text{ and } 6.699 \text{ nm}^{-1}$). **Figure 2d** summarizes schematic modification of the crystal structure upon protonation treatment. The lattice parameter c of BM-SrCoO_{2.5} is 1.5751 nm, which agrees well with the reported value (1.5745 nm)²³. The lattice parameter c of phase B is 1.6756 nm, which agrees well with that of H_{1.5}SrCoO_{2.5} (1.675 nm)⁹. The intermediate phase H_{1.25}SrCoO_{2.5} is a half-filled state of the oxygen vacancy site of HSrCoO_{2.5} (phase A) with an H₂ dimer. Thus, the lattice parameter c is double of phases A and B.

In order to further clarify the formation of H_{1.5}SrCoO_{2.5} (phase B) after 240 min protonation treatment, we measured the hydrogen concentration by SIMS (**Figure S1**). The hydrogen concentration of the H_{1.5}SrCoO_{2.5} (phase B) sample is $\sim 2 \times 10^{22} \text{ cm}^{-3}$. For comparison, we also prepared oxidized SrCoO₃ samples by applying negative voltage (-10 V) to the solid-state electrochemical cell for 1 h in air. Compared to the as-

grown $\text{SrCoO}_{2.5}$ sample and oxidized SrCoO_3 samples, the $\text{H}_{1.5}\text{SrCoO}_{2.5}$ (phase B) sample is an order of magnitude higher in the hydrogen concentration. The quantitative hydrogen concentration was estimated to be 1.5 H per chemical formula of $\text{SrCoO}_{2.5}$, which is close to the reported phase $\text{H}_{1.5}\text{SrCoO}_{2.5}$ ⁹.

Then, we measured the optical transmission spectra of the as-grown BM- $\text{SrCoO}_{2.5}$ sample, the protonated $\text{H}_{1.5}\text{SrCoO}_{2.5}$ (phase B, 240 min) sample, and the oxidized SrCoO_3 sample (**Figure 3**). Compared to the BM- $\text{SrCoO}_{2.5}$ sample, the $\text{H}_{1.5}\text{SrCoO}_{2.5}$ (phase B) sample is more transparent in the visible region, whereas the oxidized SrCoO_3 sample shows lower transmissivity. The as-grown BM- $\text{SrCoO}_{2.5}$ samples are brown, the oxidized SrCoO_3 sample is black, and the protonated $\text{H}_{1.5}\text{SrCoO}_{2.5}$ (phase B) sample is colorless transparent, respectively, as shown in the inset photograph. Note that the low transmission in the IR region is due to the absorption of Nb-doped SrTiO_3 film. The overall tendency of the color change in the electrochemical cells is similar to the previously reported tendencies in literature^{5, 24}.

The magnetic properties of the solid-state electrochemical cell were measured (**Figure 4**). The magnetism of SrCoO_x is closely linked to the concentration of oxygen in the

lattice possibly due to the formation of oxygen holes²⁵⁻²⁶. The clear magnetic transition was observed from the M versus T curve with 100 Oe of the magnetic field through a SQUID magnetometer (**Fig. 4a**). The as-grown BM-SrCoO_{2.5} sample did not show any magnetic transition due to its antiferromagnetic ground state. On the other hand, a clear transition is observed in the oxidized SrCoO₃ sample. The transition temperature (T_c) is estimated to be ~240 K, which is comparable to the reported T_c of the nearly stoichiometric perovskite SrCoO₃^{5, 7-8}. Further, the protonated H_{1.5}SrCoO_{2.5} (phase B) sample showed a weak ferromagnetic behavior with T_c ~130 K, which is consistent with the reported value⁵. We also measured the field-dependent magnetization measurements at 10 K (**Fig. 4b**). The oxidized SrCoO₃ sample showed a clear ferromagnetic signal, where the hysteresis loop is clearly seen. The coercive field is estimated to be 500 Oe, which is ~1/4 of the data from the ionic-liquid case (~2000 Oe⁵). Since the SrCoO₃ film releases oxygen even at room temperature in air, the measured saturation magnetization is smaller than the references, while the magnetic transition temperature is 240 K, which is close to the transition temperature of nearly stoichiometric SrCoO_{3- δ} . Note that the coercive field of our film is comparable to that of SrCoO₃ single crystal. In contrast, the protonated H_{1.5}SrCoO_{2.5} (phase B) sample has a comparable magnetic moment to ionic-liquid gated HSrCoO_{2.5}⁵. These results clearly show that the optical and magnetic

properties can be controlled electrochemically at room temperature in air by using the solid-state electrochemical cells composed of $\text{SrCoO}_{2.5}$ and CAN solid electrolyte.

Compared to the use of ionic liquid as the electrolyte, our solid-state electrochemical cell has an advantage in terms of being free from the liquid leakage problem. In addition, these results also suggest that the CAN film can be used as the solid electrolyte for the memory device utilizing electrochemical protonation/oxidation of TMOs.

CONCLUSIONS

In summary, we demonstrated a solid-state electrochemical protonation of $\text{SrCoO}_{2.5}$ films at room temperature in air. We prepared solid-state electrochemical cells of $\text{SrCoO}_{2.5}$ using mesoporous amorphous $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (CAN) film as the solid electrolyte. The electrochemical protonation was performed by applying constant positive voltage (+10 V) to the electrochemical cells. During the protonation treatment, the crystalline phase discretely changed from $\text{SrCoO}_{2.5}$ to $\text{HSrCoO}_{2.5}$ (phase A), $\text{H}_{1.5}\text{SrCoO}_{2.5}$ (phase B), and $\text{H}_2\text{SrCoO}_{2.5}$ (phase C) through formation of an intermediate phase of $\text{H}_{1.25}\text{SrCoO}_{2.5}$. The $\text{H}_{1.5}\text{SrCoO}_{2.5}$ (phase B) sample was colorless-transparent

and showed weak ferromagnetism with $T_c \sim 130$ K. The present results suggest that the CAN film can be used as the solid electrolyte for the protonation treatment of TMOs.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge via the Internet at

<https://pubs.acs.org/doi/10.1021/acsaelm.XXXXXXX>.

Depth profiles of H, Ti, and Co ions of the multilayer samples measured by SIMS (40 $\mu\text{m} \times 40 \mu\text{m}$).

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Author Contributions

Q.Y. performed the sample preparation and measurements. J.L. and H.J. measured the in-situ XRD patterns and magnetic properties. Q.Y. and H.O. planned and supervised the project. All authors discussed the results and commented on the manuscript.

Funding Sources

Qian Yang received funding from Grants-in-Aid for JSPS Fellows (21J10042).

Hirofumi Ohta received funding from Grants-in-Aid of the JSPS (19H05791).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This research was supported by Grants-in-Aid for Innovative Areas (19H05791) from the JSPS. Q.Y. was supported by Grants-in-Aid for JSPS Fellows (21J10042) from the JSPS. H.J.J was supported by PNU-RENovation (2020-2021). A part of this work was supported by Dynamic Alliance for Open Innovation Bridging Human, Environment, and Materials, and by the Network Joint Research Center for Materials and Devices.

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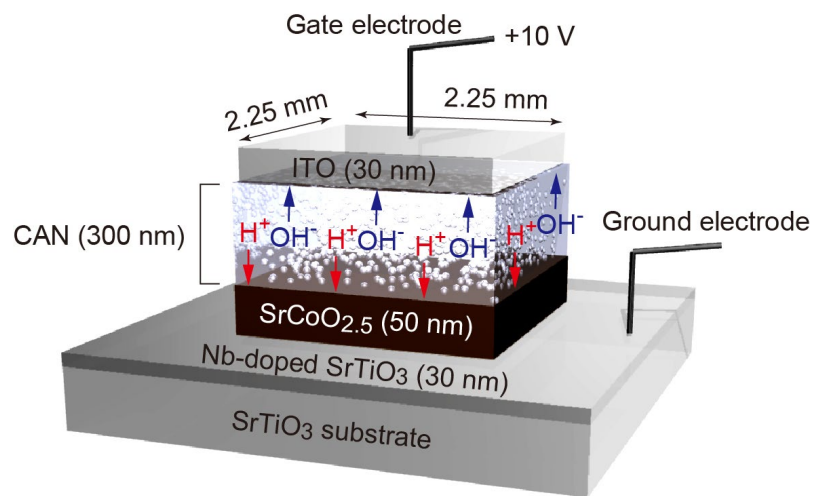


Figure 1. Schematic illustration of solid-state electrochemical protonation of $\text{SrCoO}_{2.5}$ film. The active area of the electrochemical cell is $2.25 \text{ mm} \times 2.25 \text{ mm}$. +10 V was applied for the protonation. Since CAN film contains ultrapure water, protonation of $\text{SrCoO}_{2.5}$ and oxidation of ITO films occurs during +10 V application.

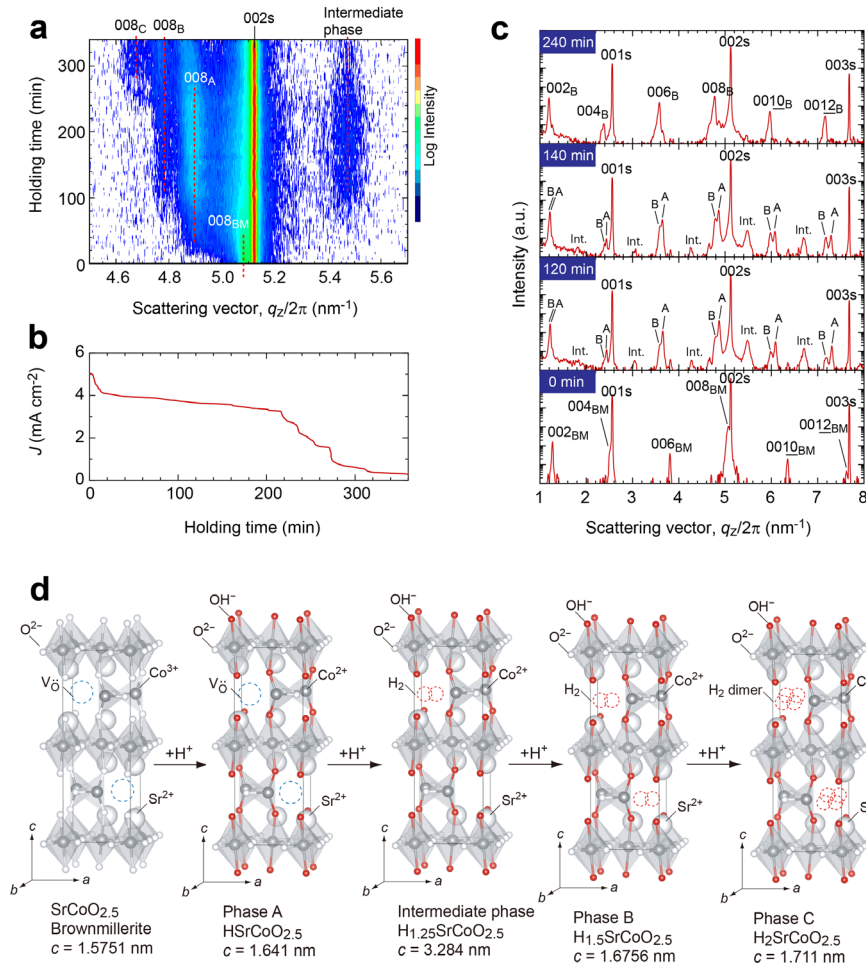


Figure 2. Crystal phase modulation during the protonation. (a) Change in the out-of-plane XRD pattern of the solid-state electrochemical cell during the electrochemical protonation treatment. The XRD patterns were taken every 5 min in situ. (b) Change in the current density (J) with holding time. (c) Out-of-plane XRD patterns of the solid-state electrochemical cell (another sample) after the electrochemical protonation treatment. A, B, and Int. denote HSrCoO_{2.5} (phase A), H_{1.5}SrCoO_{2.5} (phase B), and H_{1.25}SrCoO_{2.5} (intermediate phase), respectively. (d) Schematic crystal structure change upon protonation.

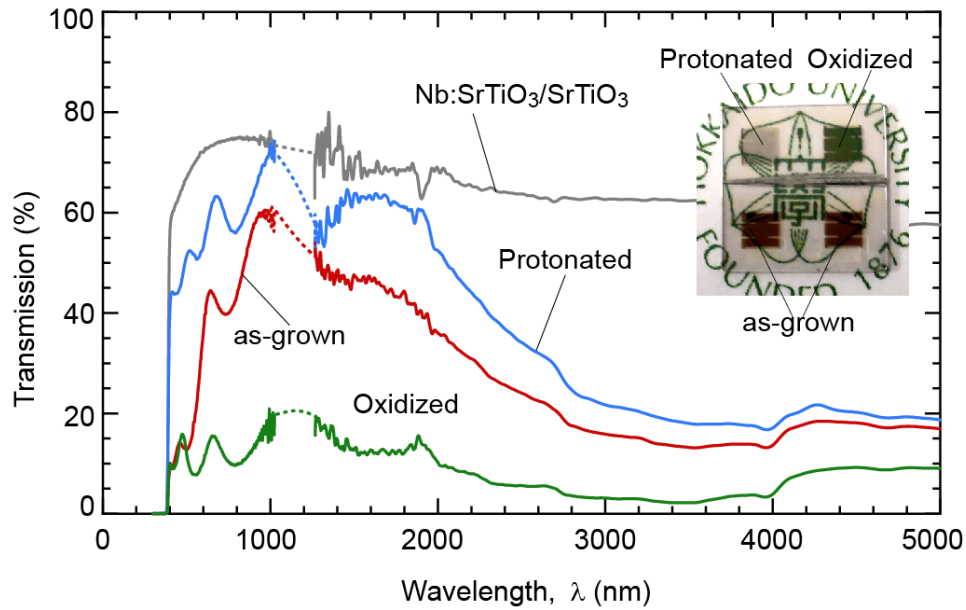


Figure 3. Optical transmission spectra of the solid-state electrochemical cells. As-grown: BM-SrCoO_{2.5} sample, Protonated: H_{1.5}SrCoO_{2.5} sample (240 min, **Fig. 2c**), Oxidized: SrCoO₃ sample. The gray line is the reference of Nb:SrTiO₃-coated SrTiO₃ substrate. The dotted lines were used to connect two different spectrometer results. (Inset) Photograph of the devices. The as-grown BM-SrCoO_{2.5} samples are brown, the protonated H_{1.5}SrCoO_{2.5} sample (240 min) is colorless transparent, and the oxidized SrCoO₃ sample is black, respectively. The logomark is reprinted with permission from Hokkaido University.

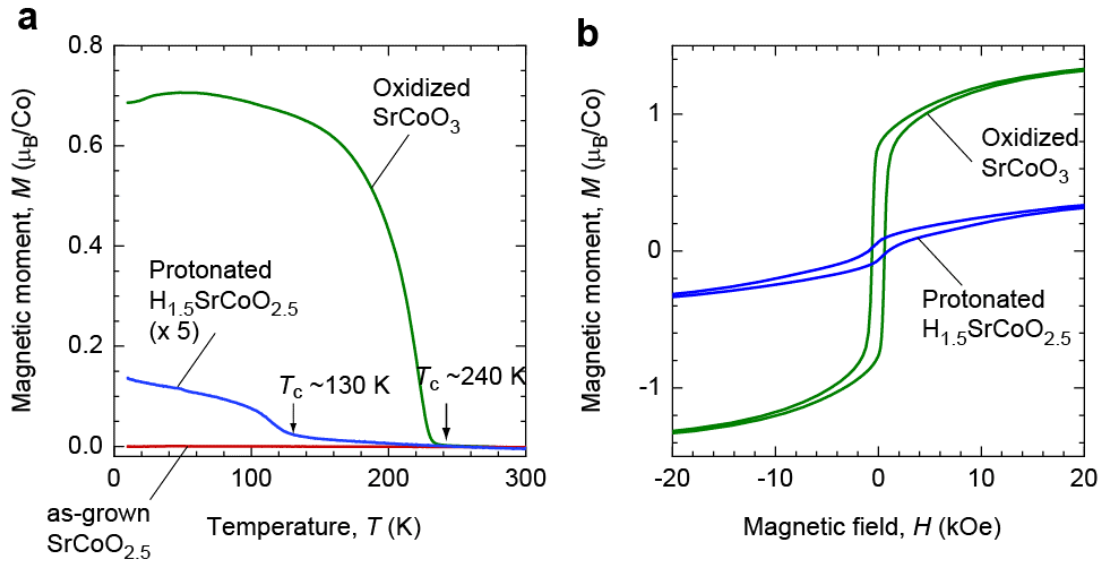
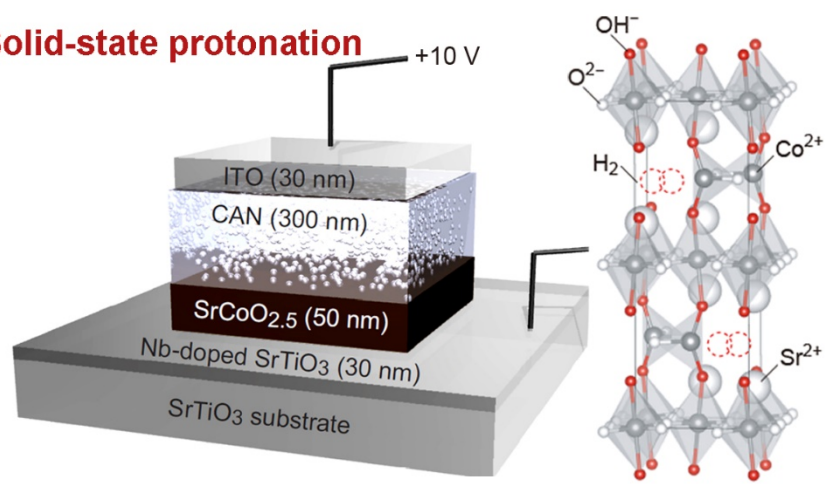


Figure 4. (a) Temperature dependence of the magnetization of SrCoO_x layer measured with the magnetic field of 100 Oe. The oxidized SrCoO_3 sample shows clear magnetic transition with $T_c \sim 240$ K. The protonated $\text{H}_{1.5}\text{SrCoO}_{2.5}$ sample (240 min, **Fig. 2c**) shows $T_c \sim 130$ K. Both T_c values are comparable to the reported values⁵. (b) $M-H$ curves of the oxidized SrCoO_3 sample and the protonated $\text{H}_{1.5}\text{SrCoO}_{2.5}$ sample measured at 10 K.

Solid-state protonation



Supporting Information

**Solid-State Electrochemical Protonation of SrCoO_{2.5} into H_xSrCoO_{2.5}
(*x* = 1, 1.5 and 2)**

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KEYWORDS: solid-state electrochemical protonation, brownmillerite, H_xSrCoO_{2.5}, SrCoO_{2.5}, optical property, magnetic property

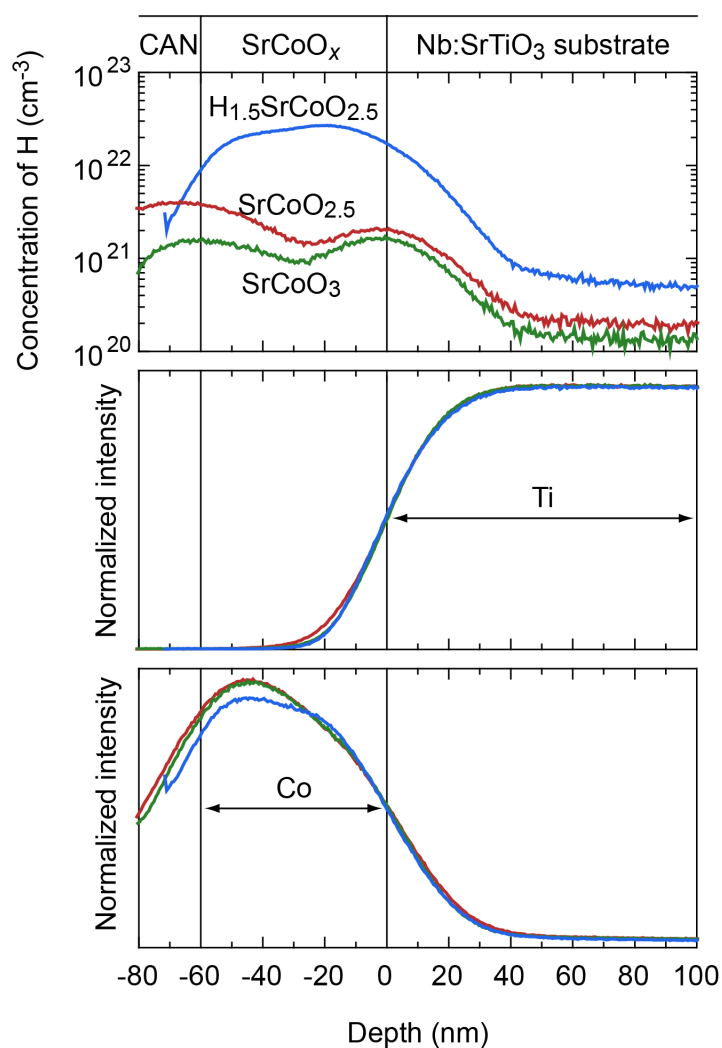


Figure S1. Depth profiles of H, Ti, and Co ions of the multilayer samples measured by SIMS ($40\ \mu\text{m} \times 40\ \mu\text{m}$). The hydrogen concentration of the protonated $\text{H}_{1.5}\text{SrCoO}_{2.5}$ sample is $\sim 2 \times 10^{22}\ \text{cm}^{-3}$, confirmed that $\text{H}_{1.5}\text{SrCoO}_{2.5}$ was formed. SIMS results do not show a flat profile. This is due to the film surface of ITO/CAN is rough. Since high-density hydrogen is contained in the CAN layer, the H signals of $\text{SrCoO}_{2.5}$ and SrCoO_3 possibly affected by the CAN layer. Therefore, the large H signal of $\text{SrCoO}_{2.5}$ and SrCoO_3 would not be a real value.