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Title	Solid-State Electrochemical Protonation / Redox reaction induced Control of Physical Properties of SrCoOx and SrFeOx [an abstract of dissertation and a summary of dissertation review]
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Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第15074号
Issue Date	2022-03-24
Doc URL	https://hdl.handle.net/2115/85276
Rights(URL)	https://creativecommons.org/licenses/by/4.0/
Type	doctoral thesis
File Information	Qian_Yang_abstract.pdf, 論文内容の要旨

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学　位　論　文　内　容　の　要　旨

博士の専攻分野の名称　　博士（工学）　　氏名　楊 倩

学　位　論　文　題　名

Solid-State Electrochemical Protonation / Redox reaction induced Control of Physical Properties of $SrCoO_x$ and $SrFeO_x$

（固体電気化学的プロトン化/酸化還元反応による $SrCoO_x$ および $SrFeO_x$ の物理的性質の制御）

Transition metal oxides (TMOs) have been widely studied thus far due to their controllable physical properties by controlling the oxygen content. For example, strontium cobalt oxide ($SrCoO_x$) has been extensively studied because its physical properties are dramatically changed; $SrCoO_{2.5}$ (Co^{3+}) with brownmillerite (BM) crystal structure is brown colored antiferromagnetic insulator, $SrCoO_3$ (Co^{4+}) with perovskite structure is black colored ferromagnetic metal, and $H_xSrCoO_{2.5}$ (Co^{2+}) (x = 1, 1.5, and 2) is colorless-transparent weak ferromagnetic insulator [1,2]. Thus, $SrCoO_x$ would be a good candidate active material of a nonvolatile memory device if the oxygen content is modulated electrically while keeping the solid state.

In 2016, Katase *et al*. reported a solid-state electrochemical redox device based on $SrCoO_x$ [3]. Using $NaTaO_3$ nanopillar film as the electrolyte, the authors reversibly oxidized/reduced $SrCoO_{2.5}$/$SrCoO_3$ by applying ±3 V at room temperature. However, the authors did not observe the formation of protonated $H_xSrCoO_{2.5}$, probably due to the strong alkalinity of $NaTaO_3$ nanopillar film. On the other hand, in 2017, Lu *et al*. reported protonation of $SrCoO_{2.5}$ into $H_xSrCoO_{2.5}$ by using residual water in the ionic liquid as the electrolyte [2]. Thus, neutral water would be better to protonate $SrCoO_x$.

In order to realize the electrochemical protonation of $SrCoO_{2.5}$ while keeping solid-state, I choose a mesoporous amorphous $12CaO{\cdot}7Al_2O_3$ (CAN)[4] film as the solid electrolyte. CAN contains ultrapure water in the mesopores (40 vol.%) and shows the electrical conductivity of 2.2×10^{-9} S cm^{-1}, which is 4% of that of ultrapure water (5.5×10^{-8} S cm^{-1})[4] at room temperature. Then, I used an oxide ion conductor yttria-stabilized zirconia (YSZ) single-crystal as the solid electrolyte. I fabricated $SrCoO_{2.5}$ films on the YSZ substrate and performed the electrochemical redox treatment of $SrCoO_{2.5}$ film at 300 °C in air. In order to expand this all solid redox method on other materials, finally, I tested $SrFeO_x$ active layer because it also exhibits a clear phase transition like $SrCoO_x$. This thesis is mainly composed of the following sections:

In chapter 1, the background and purpose of this research are explained.

In chapter 2, experimental methods are introduced.

In chapter 3, I report on unusually large thermopower change from +330 μV K^{-1} to –185 μV K^{-1} of

brownmillerite $SrCoO_{2.5}$ [5]. I measure the thermopower of $SrCoO_{2.5}$ epitaxial films grown on several lattice-mismatched substrates at room temperature in the air. Although the differences of the electronic structure and the oxidation states among the samples are extremely small, the thermopower obviously changed from +330 μV K^{-1} to –185 μV K^{-1} with a slight increase of lattice and/or absorbed oxygen in the $SrCoO_{2.5}$ films, clearly demonstrating the effectiveness of thermopower to analyze the electronic structure and the oxidation states of TMOs.

In chapter 4, I report on solid-state electrochemical protonation of $SrCoO_{2.5}$ into $H_xSrCoO_{2.5}$ (x = 1, 1.5 and 2) [6]. I demonstrate a solid-state electrochemical protonation of $SrCoO_{2.5}$ using mesoporous amorphous CAN film as the solid electrolyte. The crystalline phase discretely changed from $SrCoO_{2.5}$ to $HSrCoO_{2.5}$, $H_{1.5}SrCoO_{2.5}$, and $H_2SrCoO_{2.5}$ through formation of an intermediate phase of $H_{1.25}SrCoO_{2.5}$. The $H_{1.5}SrCoO_{2.5}$ was colorless-transparent and showed weak ferromagnetism.

In chapter 5, I report on macroscopic visualization of the fast electrochemical reaction of $SrCoO_x$ oxygen sponge [7]. $SrCoO_x$ epitaxial films with various oxidation states were prepared by the electrochemical oxidation of $SrCoO_{2.5}$ film. Steep decrease of both resistivity and the absolute value of thermopower of electrochemically oxidized $SrCoO_x$ epitaxial films indicated the columnar oxidation firstly occurred along with the oxidation direction and then spread perpendicular to the oxidation direction. Further, I directly visualized the phenomena using the conductive AFM.

In chapter 6, I report on solid-state electrochemical redox control of the optoelectronic properties for $SrFeO_x$ thin films [8]. I fabricated $SrFeO_{2.5}$ film on the YSZ substrate and modulated the oxygen content by the electrochemical redox treatment. The phase gradually changed from $SrFeO_{2.5}$ to $SrFeO_{2.5+x}$, and $SrFeO_{3-x}$. The color of the film changed from yellowish-transparent to dark brown. Although as-grown $SrFeO_{2.5}$ film showed high resistivity ($\rho \geq 10^1$ Ω cm), the ρ dramatically decreased ($\sim 10^{-2}$ Ω cm) when oxidized. Simultaneously, the thermopower decreased dramatically from +200 μV K^{-1} to –10 μV K^{-1}.

In chapter 7, the above researches are summarized.

In a word, the present results of solid-state electrochemical redox treatment of $SrCoO_x$ and $SrFeO_x$ would provide a design concept for future TMOs-based solid-state multifunctional memory devices.

References

[1] H. Jeen *et al.*, *Nat. Mater.* 12, 1057 (2013).
[2] N. Lu *et al.*, *Nature* 546, 124 (2017).
[3] T. Katase *et al.*, *Adv. Electron. Mater.* 2, 1600044 (2016).
[4] H. Ohta *et al.*, *Nat. Commun.* 1, 118 (2010).
[5] Q. Yang *et al.*, *ACS Appl. Electron. Matter.* 2, 2250 (2020).

[6] Q. Yang *et al*., *ACS Appl. Electron. Mater.* 3, 3296 (2021).
[7] Q. Yang *et al*., *Adv. Mater. Interfaces* 6, 1901260 (2019).
[8] Q. Yang *et al*., *J. Appl. Phys.* 129, 215303 (2021).