酸素スポンジ $SrCoO_{2.5}$ 薄膜の固体電気化学的プロトン化/酸化

Solid-State Electrochemical Protonation/Oxidation of Oxygen Sponge $SrCoO_{2.5}$ Films

北大院情報[1]，東大総研[2]，釜山大物理[3]，北大電子研[4] ○(D)楊 倩[1]，馮 斌[2]，幾原 雄一[2]，
ジン ヒョンジン[3]，ジョ ヘジュン[1,4]，太田 裕道[1,4]
IST-Hokkaido U.[1], U. Tokyo[2], Pusan Nat'l U.[3], RIES-Hokkaido U.[4] ○Qian Yang[1], Bin Feng[2],
Yuichi Ikuhara[2], Hyoungjeen Jeen[3], Hai Jun Cho[1,4], Hiromichi Ohta[1,4]
E-mail: yangqian@eis.hokudai.ac.jp

Due to the flexibility of the valence state of cobalt ion, brownmillerite $SrCoO_{2.5}$ can be protonated/oxidized by an electrochemical reaction with H^+ / OH^- ions. Owing to the electrochemical protonation / oxidation, the physical properties of $SrCoO_{2.5}$ can be modulated from antiferromagnetic insulator ($SrCoO_{2.5}$, Co^{3+}) to ferromagnetic insulator ($HSrCoO_{2.5}$, Co^{2+}) / ferromagnetic metal ($SrCoO_3$, Co^{4+}).[1,2] Further, the color of $SrCoO_{2.5}$ can be modulated from colorless transparent (Co^{2+}) to brown (Co^{3+}) and black (Co^{4+}).[2] To utilize these changes in practical device applications, the solid-state device is favorable compared to liquid-state devices. In 2016, Katase *et al*. demonstrated electrochemical Redox reaction between $SrCoO_{2.5}$ and $SrCoO_3$ using amorphous $NaTaO_3$ film as the solid-electrolyte.[3] However, there is no report on the solid-state protonation/deprotonation reaction between $SrCoO_{2.5}$ and $HSrCoO_{2.5}$. Here we demonstrate that solid-state electrochemical protonation/deprotonation of $SrCoO_{2.5}$ for the first time. We used mesoporous amorphous C12A7 (CAN) film as the solid electrolyte.[4] We fabricated two-terminal thin-film device composed of (gate electrode) ITO / CAN / $SrCoO_{2.5}$ / (bottom electrode) Nb:$SrTiO_3$ on (001) $SrTiO_3$ substrate. When positive 10 V was applied as the gate voltage, the color of the $SrCoO_{2.5}$ became colorless transparent. The XRD pattern of the resultant film revealed the formation of $HSrCoO_{2.5}$ phase. The provided electron density was ~1.5 × 10^{22} cm^{-3}, which corresponds well with the proton concentration in $HSrCoO_{2.5}$. In addition, we succeeded the electrochemical oxidation of $SrCoO_{2.5}$ into $SrCoO_3$. These results indicate that the CAN film can be utilized as the solid electrolyte in the solid-state electrochemical protonation/oxidation of $SrCoO_{2.5}$ films (**Fig.**).

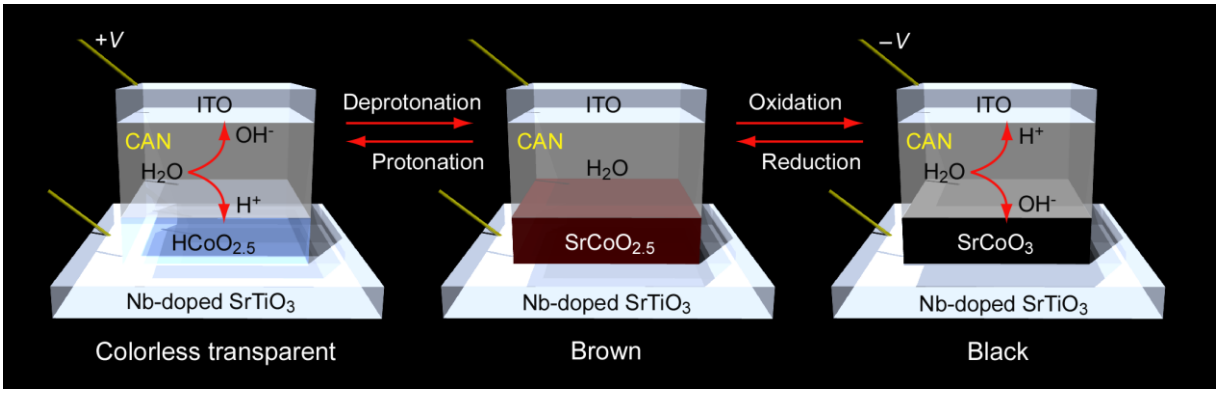

Fig. Solid-state electrochemical protonation/oxidation of oxygen sponge $SrCoO_{2.5}$ film. We performed protonation/deprotonation and oxidation/reduction of the $SrCoO_{2.5}$ layer using CAN as the solid electrolyte.

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).