

Oxygen Reduction Activity and Interfacial Structures of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ at Initial Electrochemical Process in an Alkaline Solution

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Supporting Information

S1. Electrochemical activity of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (100) film synthesized on MgO (100)

Fig. S1 shows the cyclic voltammograms of a 30 nm-thick $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (100) film synthesized on MgO (100), measured in 1 M KOH aqueous solution using an *in-situ* electrochemical cell. Here, Pt electrodes were used as a counter electrode and quasi-reference electrode (PtQRE), and the potential was swept between 0.6 and -0.6 V vs. PtQRE. Oxygen evolution and reduction reactions were observed during anodic and cathodic scans, respectively. This result confirms the OER and ORR activities of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (100) film deposited on MgO (100). The $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (001) film showed a decrease in the cathodic current, which indicates deterioration of the ORR activity. This behavior agrees with the results observed for the (001) film fabricated on Nb:SrTiO₃(001). Thus, the $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (100) / MgO (100) can be used for in situ XRD analyses to investigate the deterioration mechanism of the ORR activity at the initial cycle.

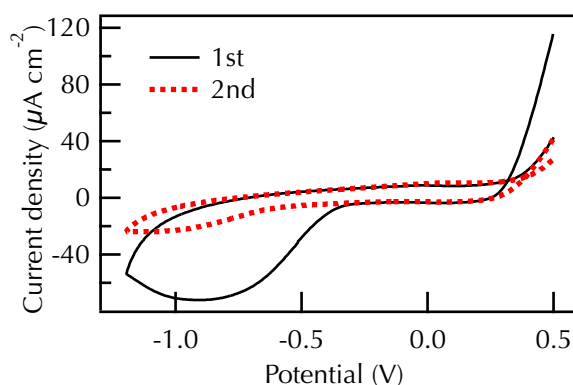


Fig. S1 Cyclic voltammograms of a 30 nm-thick $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (001) film synthesized on MgO (100) and measured in 1 M KOH aqueous solution.

S2. Crystal structure changes in $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (001) along the $\langle h0h \rangle$ direction

Fig. S2 shows the *in-situ* XRD patterns, d -values, and peak intensities of the out-of-plane 202 reflections for the 30 nm-thick $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (001) film. No significant changes were observed after cell construction (the open-circuit voltage (OCV) condition). Under the first OER condition (0.7 V vs. PtQRE), the peak intensity decreased with no change in the peak position. In the first ORR (-0.5 V), the peak intensity increased with a peak shift to lower angles. Although the 002 peak shifted back to higher angles in the second OER (0.7 V), the angle remained below that in the first OER. These peak changes are similar to those observed for the 002 reflection, as shown in **Fig.**

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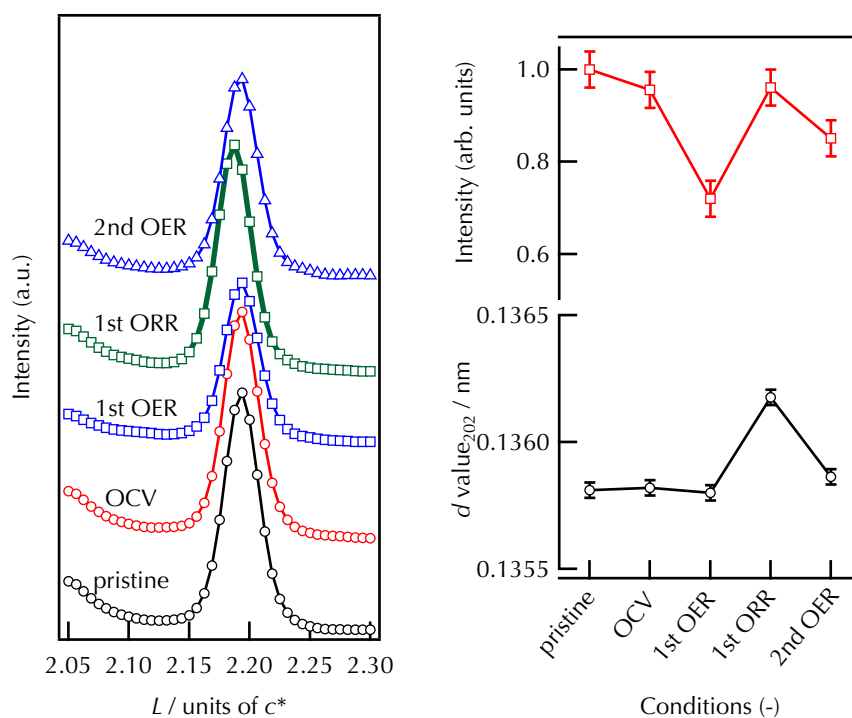


Fig. S2 *In-situ* XRD patterns, d -values, and peak intensities of out-of-plane 202 reflection for $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (001) film under various conditions: pristine (dry), OCV, 1st OER, 1st ORR, and 2nd OER.

S3. Changing oxidation states of cobalt ions in $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (001) during the OER and ORR processes

Fig. S3 shows the normalized bulk XANES spectra of the Co-K edge for $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (001)/MgO(001) under the pristine condition and after the OER and ORR processes. The OER sample showed no significant change in the absorption edge compared to that of the pristine sample. In contrast, the absorption edge of the ORR sample was located at lower energies. XANES spectra can reflect the coordination environment of Co ions because of their high sensitivity to the arrangement of nearest-neighbor atoms. When the Co ion is in a more oxidized state, the greater overlap between the Co and O orbitals causes the energies of these outer orbital levels to increase relative to those of the core levels, resulting in a higher threshold absorption energy. The XANES spectra indicate that Co exists in a low oxidation state under the ORR conditions. This result suggests that the reduction of Co induces the formation of oxygen vacancies for charge compensation under the ORR conditions, as detected by *in-situ* XRD measurements.

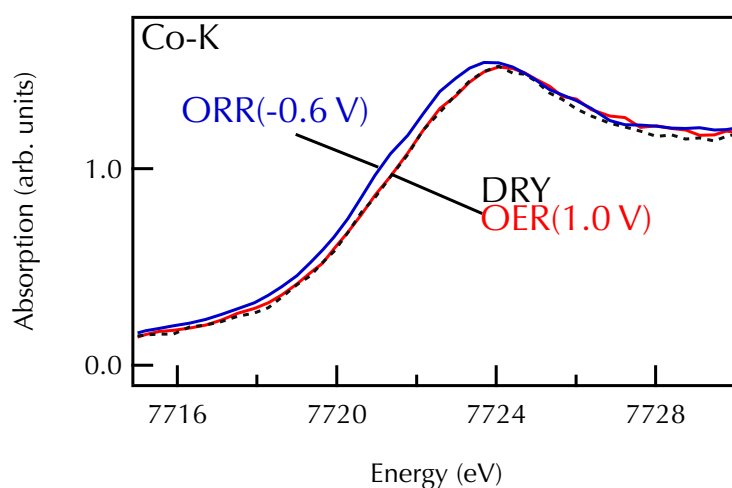


Fig. S3 Co-K edge XANES spectra of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (001) collected under pristine (dry) conditions and after OER and ORR.