In situ examination of oxygen vacancy dynamics in epitaxial LaCoO3 thin films

Dr. Seung Jo Yoo[1], Mrs. Ji-Hyun Lee[1], Mr. Sang-Gil Lee[1], Dr. Hyung Joong Yun[1]
[1]Korea Basic Science Institute, Deajeon, Republic of Korea

Background incl. aims
Understanding the coupling effect between lattice strain and the energy required to create oxygen vacancies is crucial for the rational optimization of the catalytic performance of thin film perovskite electrocatalysts. However, contradictory results have been reported regarding the impact of lattice strain on both the oxygen vacancy content and formation energy, differing in terms of extent, direction, and mechanism. Theoretical studies have indicated that oxygen vacancy defects may either increase or decrease with increasing tensile strain. Additionally, the formation energy of oxygen vacancies has been observed to follow either a curved or nearly linear trend as the strain state transitions from compression to tension. These theoretical findings suggest that the energetics of oxygen vacancy formation could be highly complex and material dependent. Therefore, our study aimed to experimentally investigate the concentration and distribution of oxygen vacancies in epitaxial thin films of LaCoO3 (LCO), a highly active perovskite oxide material, for both the oxygen reduction reaction and the oxygen evolution reaction. We observed the formation behavior of oxygen vacancies at the atomic level in real time using in situ transmission electron microscopy (TEM) with an electron beam exposure function. This technique allowed us to study the dynamic behavior of oxygen vacancies under compressive and tensile lattice strains. Additionally, we utilized high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images to directly analyze the local mapping and visualization of oxygen vacancies at the unit cell level in the LCO thin films.

Methods
On (001) LaAlO3 (LAO) and SrTiO3 (STO) substrates, LCO thin films were synthesized using the sol-gel technique. Cross-sectional TEM specimens were prepared using a focused ion beam (Quanta 3D FEG, FEI), and HAADF STEM images were acquired using TEM (Mono ARM 200F, JEOL) operating at 200 kV. The beam convergence semi-angle was set to 23.81 mrad, and the collection semi-angles ranged from 68 to 280 mrad. A consistent electron dose rate was maintained during electron beam irradiation. Wiener filtering, implemented via the HREM-Filters software package (HREM Research), was utilized to enhance image clarity.

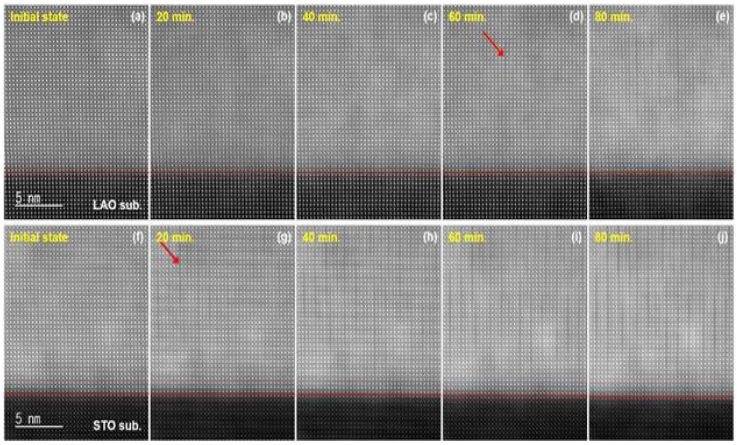
Results
Atomic-scale HAADF STEM images depicting the initial conditions of the LCO thin films on the LAO and STO substrates are presented in Figs. 1 (a) and (f), respectively. A 15 × 15 nm region within the LCO thin film was monitored for changes in lattice parameters, encompassing 1,444 unit cells. HAADF STEM images were obtained from identical pristine regions of the LCO thin film at various time intervals as the electron beam irradiation time was increased. Figs. 1 (b–e) and (g–j) exhibit high-resolution HAADF STEM images selected at 20-minute intervals in the LCO thin film on the LAO and STO substrates, respectively. The time series of the HAADF STEM images for both LCO thin films revealed the appearance of dark strip patterns over time. The modulated contrast patterns observed in the HAADF STEM images of the LCO thin films are attributed to the ordering of oxygen vacancies, leading to localized lattice expansion and the formation of modulated dark stripe patterns. The onset time of the first dark-strip pattern differed between the two LCO thin films. Specifically, the first dark strip pattern emerged after approximately 60 minutes of continuous electron beam exposure in the LCO thin film on the LAO substrate and after 20 minutes in the LCO thin film on the STO substrate. The red arrows indicate the first dark-strip pattern in Figs. 1 (d) and (g). Subsequently, dark-

strip patterns emerged at various positions and continued to grow in the out-of-plane direction. The maximum growth of dark strip patterns in the two LCO thin films occurred after 80 minutes. Furthermore, the distribution of dark strip patterns was observed more frequently in the LCO thin films on STO substrates.

Conclusions

HAADF STEM images confirm uniform thickness and initial conditions of LCO thin films on LAO and STO substrates. With increasing electron beam irradiation time, distinctive dark strip patterns emerge, indicating oxygen vacancy ordering. Variations in pattern appearance and behavior are noted between substrates, with higher tensile strain accelerating pattern onset and distribution frequency. Quantitative analysis of lattice parameter changes corroborates these observations, confirming expanded unit cells associated with oxygen vacancies. Notably, films under higher tensile strain exhibit more uniformly distributed enlarged unit cells and significantly higher oxygen vacancy concentration. These findings support previous studies suggesting reduced formation energy of oxygen vacancies under tensile strain. Overall, this research provides valuable experimental insights into oxygen vacancy formation and distribution mechanisms in LCO thin films under strain, advancing our understanding and informing tailored material design for electrochemical applications.

Graphic:



Keywords:

Oxygen vacancies, Strain states

Reference:

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