Atomic-scale perturbation of oxygen octahedra via surface ion exchange in perovskite nickelates boosts water oxidation

Jumi Bak1, Hyung Bin Bae2 & Sung-Yoon Chung1

A substantial amount of interest has been focused on $\text{ABO}_3$-type perovskite oxides over the past decade as oxygen electrocatalysts. Despite many studies on various compositions, the correlation between the structure of the oxygen octahedra and electrocatalytic property has been overlooked, and there accordingly have been a very limited number of attempts regarding control of atomistic structure. Utilizing epitaxial $\text{LnNiO}_3$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$) thin films, here we demonstrate that simple electrochemical exchange of Fe in the surface region with several-unit-cell thickness is notably effective to boost the catalytic activity for the oxygen evolution reaction by different orders of magnitude. Furthermore, we directly establish that strong distortion of oxygen octahedra at the angstrom scale is readily induced during the Fe exchange, and that this structural perturbation permits easier charge transfer. The findings suggest that structural alteration can be an efficient approach to achieve exceptional electrocatalysis in crystalline oxides.
Oxygen evolution and reduction are the major electrochemical reactions in electrolyzers, metal-air batteries, fuel cells, and water-splitting devices, and facilitating these reactions has been a central issue for effective fuel generation and higher energy conversion/storage efficiency.\(^2\)\(^-\)\(^5\) It is generally accepted that the activation barrier of the oxygen evolution and reduction reactions is fundamentally large and that multiple intermediate steps of electron transfer are necessarily involved during the reactions. Adequate electrocatalysts are thus essential for promoting the reactions at lower overpotentials. In particular, since both the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) in metal-air batteries and water-splitting devices take place at room temperature,\(^1\)\(^-\)\(^3\) enhancing the oxygen electrocatalysis has a crucial impact not only on the efficiency of such devices, but on their longevity and ultimate performance.

Since the milestone works by Bockris and Otagawa,\(^6\)\(^,\)\(^7\) in the early 1980s, substantial attention has been paid to employing perovskite oxides as OER electrocatalysts with the aim of replacing expensive precious-metal-based materials such as IrO\(_2\) and RuO\(_2\).\(^8\)\(^-\)\(^9\) Furthermore, sparked by recent findings on the notably high OER catalytic activity of a multiple-cation perovskite\(^1\)\(^0\) there has been strong interest in ABO\(_3\)-type perovskite oxides as alternative OER catalysts.\(^1\)\(^1\)\(^-\)\(^2\)\(^0\) Plausible mechanisms have been reasonably suggested, based on the B-OH bond strength (where B is a transition metal)\(^2\)\(^1\)\(^-\)\(^2\)\(^3\)\(^-\)\(^2\)\(^5\), the 3d-shell electronic configuration\(^1\)\(^0\), the position of the O 2p band center in the electronic band structure,\(^1\)\(^1\) the degree of hybridization between B-site metal and oxygen orbitals,\(^1\)\(^4\)\(^-\)\(^2\)\(^4\) and the charge-transfer energy between B and O.\(^1\)\(^8\)\(^,\)\(^2\)\(^5\) Although there is no single universal descriptor for OER electrocatalysis using perovskite oxides,\(^9\) it is recognized in general that the electronic structure of the O 2p and metal 3d bands strongly correlates with the OER catalytic activity.

A significant change can be induced in the electronic structure of both the metals and the oxygen in many oxides by varying their physical structure, including by lattice strain.\(^2\)\(^6\) Accordingly, one of the crucial initial steps toward establishing the link between the crystal structure, the electronic configurations, and the overall OER catalytic performance is the precise identification of changes in the surface structure by direct observation at the atomic scale.\(^2\)\(^7\)\(^-\)\(^2\)\(^9\) From a structural viewpoint, the ABO\(_3\) perovskite framework consists of corner-sharing [BO\(_6\)] octahedral units, which are catalytically active sites,\(^7\) together with A-centered dodecahedra. Consequently, identifying variations in the shape of the [BO\(_6\)] octahedra and understanding under what circumstances structural change takes place remain key issues for the accurate prediction of electronic structure and subsequent OER activity. In particular, since the shape of the [BO\(_6\)] octahedra is determined largely by the location of oxygen anions in the lattice, visualization of the oxygen positions is an essential aspect of the direct observation of structure, despite being very challenging.

By utilizing (001) epitaxial thin films of lanthanide nickelate perovskites, LnNiO\(_3\) (where Ln is La, Pr, and Nd), in this work we demonstrate that the structural perturbation of metal-oxygen octahedra via simple electrochemical Fe exchange at the surface is particularly efficient at enhancing OER activity, by an order of magnitude. To conduct atomic-column resolved observation of oxygen displacement, we used integrated differential phase-contrast (iDPC) scanning transmission electron microscopy (STEM)\(^3\)\(^0\)\(^,\)\(^3\)\(^1\), a recently developed phase-contrast imaging technique,\(^3\)\(^0\)\(^,\)\(^3\)\(^1\) in addition to well-known annular bright-field (ABF) STEM. Electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDS) were also carried out to verify the chemical exchange of the Fe for the Ni site. Combined with ab initio density functional theory (DFT) calculations, the experimental findings in the present study provide significant evidence showing that a high density of states of O 2p and transition-metal 3d orbitals near the Fermi level can be achieved by the strong distortion of the oxygen octahedra, boosting the OER activity in the perovskite nickelates.

### Results

**Fe incorporations in LaNiO\(_3\) thin films.** As demonstrated in Ni-based oxides and (oxy)hydroxides, Fe is known to be an effective solute cation that can significantly enhance OER activity.\(^3\)\(^2\)\(^-\)\(^3\)\(^4\) We accordingly prepared two different types of (001) thin-film LaNiO\(_3\) samples for comparison. One was a simple solid-solution homogeneously containing Fe in the lattice by high-temperature annealing during film fabrication. Figure 1a shows a Fe-doped LaNiO\(_3\) solid-solution film deposited on a (001) SrTiO\(_3\) single-crystal substrate. Both the high-angle annular dark-field (HAADF) STEM image and a set of EDS chemical maps in Fig. 1a clearly verify the homogeneous distribution of Fe over the entire film, in addition to epitaxial growth with high crystallinity (see Supplementary Fig. 1 for a series of X-ray diffraction patterns and atomic EDS maps showing the solid-solution of Fe and the epitaxial growth). The other type are LaNiO\(_3\) thin films that contain Fe exclusively in the surface region, induced via electrochemical ion exchange, which will be described in more detail below. Both sets of EDS maps in the middle column of Fig. 1b, c show the presence of Fe confined to the surface region. Atomic-scale HAADF images also reveal that there is no structural decomposition at the film surface, indicating that the Fe has been substituted for Ni as solute atoms. To more precisely determine the depth of Fe exchange, we obtained electron-energy loss spectrum images using the Fe-L\(_3\) peak during the EELS analysis. Based on the Fe maps shown in the right-hand column of Fig. 1b, c, a distinct amount of Fe is detectable above the background noise from several unit cells below the surface, not merely from the topmost surface (see Supplementary Fig. 2 for two series of Fe-L\(_3\) peaks).

**Surface Fe exchange.** The Fe exchanges demonstrated in Fig. 1b, c were achieved by electrochemical methods at room temperature. One approach adopted for the sample shown in Fig. 1b is schematically depicted in Fig. 2. Ni\(^{3+}\) is strongly driven to become Ni\(^{2+}\) under reducing conditions in a KOH aqueous solution far below 1.23 V vs. reversible hydrogen electrode (RHE), thereby resulting in the exsolution of Ni from the perovskite lattice. Indeed, when the reduction reaction was repeated many times, we could identify the formation of a sufficiently Ni-deficient amorphous surface layer, directly demonstrating the Ni extraction (see Supplementary Fig. 3a). At the same time, nanoscale Ni-based oxide (or hydroxide) precipitates, possibly in the form of Ni(OH)\(_2\) (or NiO) (see Supplementary Fig. 3b) were also found on the surface after 20-cycle reduction reactions down to 0.62 V vs. RHE. As a result, if the number of reactions was adequately controlled at five cycles, Ni vacancies could be created in the surface region without collapsing the crystalline perovskite framework in the surface region. As Ni vacancies are effectively negatively charged defects (V\(_{Ni}^{−}\)), electron holes (h\(^+\)) confined in the O 2p orbitals hybridized with the Ni 3d orbitals are anticipated to form in order to satisfy the overall charge neutrality during the pre-reduction reaction (see Supplementary Note 1 for more details, including the Mulliken electronic population analysis). After this pre-reduction, a cyclic potential between 1.27 and 1.75 V vs. RHE was applied to the sample in a Fe-containing KOH solution so that Fe\(^{3+}\) would fill the empty Ni sites, as illustrated in Fig. 2a. The high-magnification HAADF image and
the Fe EELS map in Fig. 1b demonstrate that this pre-reduction step is very efficient at promoting ion exchange with Fe.

The other approach to achieve Ni extraction is based on oxidation reactions. We experimentally found that Ni cations from LaNiO₃ thin films could dissolve into a KOH electrolyte solution at high oxidation potentials. Like the previous pre-reduction, a remarkably Ni-deficient amorphous layer could be identified at the film surface after 20-cycle oxidation reactions up to 1.85 V vs. RHE (see Supplementary Fig. 4). As before, when this pre-oxidation step was limited to several cycles to preserve the crystalline framework of the films, Fe exchange could be effectively achieved by filling empty Ni sites with Fe³⁺ from the electrolyte solution. This process is schematically described in Fig. 2b and was experimentally verified by STEM, as shown in Fig. 1c. Oxygen anions in the lattice can evolve at a high overpotential under the oxidizing condition, resulting in the formation of oxygen vacancies. It is thus reasonably anticipated that the negatively charged Ni vacancies (V_Ni⁻⁻) originating from the Ni dissolution are compensated by the positively charged oxygen vacancies (V_O⁺⁺) as Schottky-type defects during the pre-oxidation reaction (see Supplementary Note 2 for more details). Additional evidence obtained by EDS showing the surface Fe exchange through the pre-reduction and the pre-oxidation steps is provided in Supplementary Fig. 5.

As the Ni-L₃ peak in EELS considerably overlaps with the La-M₄ peak, it is fairly difficult to track variations in the Ni-L₃ peak intensity in LaNiO₃ without rigorous deconvolution of the two peaks. Although a detectable amount of Fe was clearly probed ~3 unit cells beneath the surface in Fig. 1b and ~5 unit cells in Fig. 1c using EELS, it was not possible to verify the change in Ni content in the LaNiO₃ thin films. We therefore fabricated epitaxial thin films of other nickelates, PrNiO₃ and NdNiO₃, on (001) SrTiO₃ substrates (see Supplementary Fig. 6 for details on the films). Figure 2c shows two series of Fe-L₃ and Ni-L₃ peaks acquired in the epitaxial PrNiO₃ film following Fe exchange via the pre-oxidation method. As denoted by numbers in the atomic-scale HAADF image in the right-hand column, each peak was collected approximately at a unit-cell interval. The two sets of EELS peaks demonstrate the increase in Ni intensity and a simultaneous decrease in Fe intensity with the peak collection below the surface. This directly proves the replacement of Ni with Fe. Consistent sets of Fe-L₃ and Ni-L₃ peaks obtained in the epitaxial NdNiO₃ film are also provided in Supplementary Fig. 7.
Fe-exchange samples is nearly an order of magnitude higher than that of the Fe-doped solid-solution film. This strongly implies that there is another crucial contribution in addition to the Fe addition. To compare the OER activities of other Fe-containing perovskite oxides with those of our thin-film samples, we also provide an additional bar graph in Supplementary Fig. 9 based on the results of previous reports.

This same significantly higher activity following the ion exchange was also consistently found in both the PrNiO₃ and NdNiO₃ epitaxial films, as demonstrated in Fig. 3b, c, respectively. Therefore, the electrochemical Fe exchange appears to be a very effective way of achieving high OER activity in nickelate perovskites in general. As denoted by an arrow in the middle panel in Fig. 3a, the appearance of a small Ni²⁺/Ni³⁺ anodic peak between 1.45 and 1.5 V in the pre-reduction sample confirms the presence of NiO on the surface. This is in good agreement with the schematic illustration shown in Fig. 2a and the EDS results in Supplementary Fig. 3b (see Supplementary Fig. 10 for verification of the anodic peak in other pre-reduction nickelate films). The Tafel plots as well as the values of the Tafel slope for each nickelate are also provided in Supplementary Fig. 11.

Electrochemical impedance spectroscopy (EIS) was carried out to examine the electrical charge transfer behavior between the thin films and electrolyte solutions. Figure 4 shows three sets of Nyquist plots obtained by EIS for the LaNiO₃, PrNiO₃, and NdNiO₃ thin films. As these nickelates are metallic⁴³, the diameter of the first semicircle in the high-frequency range, which corresponds to the uncompensated resistance (Rₑ), between the working electrode and the reference electrode⁴⁴, is very short in all three nickelates, showing Rₑ merely at an ohm·cm² scale, as demonstrated in each of the insets (see Supplementary Fig. 12 for more details on the high-frequency arcs). Moreover, the Rₑ does not significantly vary, irrespective of whether the surface ion exchange has been conducted. In stark contrast, the thin-film samples following the Fe exchange show a huge difference in the diameter of the low-frequency second semicircle representing the resistance of charge transfer (Rₜₜ) at the interface between the film and the electrolyte²³. As clearly revealed in each Nyquist plot, this remarkable reduction in Rₜₜ is observed for all the Fe-exchange samples. This notable decrease in charge-transfer barrier at the interface also agrees very well with the exceptionally high OER activity of the thin films following the surface Fe exchange. While there is no Rₑ variation, a substantially lower Rₜₜ with increasing overpotential (η) was also observed in each sample (see Supplementary Fig. 13), resulting in a Butler–Volmer type exponential increase in the OER current density as a function of η.

Direct observations with STEM. The added Fe clearly has a beneficial influence on the OER catalysis. However, the OER current density of the surface Fe-exchange LaNiO₃ films was much higher than that of the Fe solid-solution film. This implies that the structural variation that occurs during the Fe exchange reactions may significantly enhance the catalytic activity. Investigating this using STEM at atomic resolution, we observed the surface region of the LaNiO₃ films after pre-oxidation and pre-reduction. A striking structural feature was identified during the STEM observation: the oxygen anions were seriously displaced from their original positions, resulting in a remarkable distortion of the oxygen octahedra. Figure 5a provides a representative example of the distorted octahedra captured by ABF imaging near the surface of a LaNiO₃ film after eight cycles of pre-oxidation treatment. A series of magnified ABF images (lower panel) for five unit cells, denoted by yellow squares in the low-magnification
**Fig. 3** Comparison of OER current densities. **a** Remarkably high OER activities were obtained in the LaNiO$_3$ films following the surface Fe exchange that occurred with the pre-reduction and pre-oxidation reactions. Note the much larger OER current values of the surface-Fe-exchange films compared with the current value of the La(Ni$_{1-x}$Fe$_x$)$_3$O$_5$ solid-solution film, as specifically compared in the bar graph. The small peak indicated by a black arrow in the blue curve in the middle column represents the occurrence of the Ni$^{2+}/$Ni$^{3+}$ oxidation reaction. **b, c** Remarkably enhanced OER activities were consistently identified in both PrNiO$_3$ and NdNiO$_3$ films following the surface Fe exchange. HAADF images also demonstrate the epitaxial growth of the films along with high crystallinity.

**Fig. 4** Electrochemical impedance spectroscopy. In contrast to the low-frequency arcs of pristine films, considerably small arcs with very short diameters are noted for the surface-Fe-exchange films, and as a common feature in all three nickelates, indicating remarkably low charge-transfer resistance ($R_{CT}$) between the films and electrolytes. As can be seen in each magnified inset for the high-frequency range, denoted by a gray shadow, the electrolyte resistance ($R_E$) values hardly differ between the samples in each of the nickelates.

image, were compared with the unit-cell image showing four oxygens placed immediately at the corners of a white rhombus for a Ni octahedron in the bulk (upper right panel). The comparison directly shows that most oxygens have been considerably displaced from their original positions in the bulk, as indicated by a distorted yellow rhombus in each of the images (see Supplementary Fig. 14 for the unfiltered raw images). Altogether with the ABF image obtained from the bulk film in Supplementary Fig. 15, an additional set of ABF images for the surface region from the pristine sample without pre-oxidation or pre-reduction is provided in Supplementary Fig. 16 to confirm the undistorted oxygen octahedra as a standard.

ABF-STEM is one of the imaging techniques commonly used for visualizing the position of light elements including oxygen.

However, because atomic columns are imaged in this STEM mode using a dark contrast with a bright background, the position uncertainty of light elements is sometimes not negligible when a specimen is comparatively thick and its tilting angle is high.

Therefore, to achieve a better signal-to-noise ratio, we used an imaging method, iDPC-STEM, where four-quadrant
Fig. 5 Atomic-scale direct evidence of oxygen-octahedron distortion. The surface region of the LaNiO$_3$ films after pre-oxidation and pre-reduction was observed in scanning transmission electron microscopy (STEM). a The unit-cell image with the indication of a white diamond was acquired from the bulk region for reference. A series of annular bright-field (ABF) STEM images are provided in the lower panel for the unit cells denoted by a yellow square in the low-magnification image. As indicated by a yellow rhombus, each oxygen octahedron is substantially distorted. b Integrated differential phase-contrast (iDPC) STEM shows consistent image features. As indicated by arrows on the image captured from the film surface, serious displacement of oxygen atoms is clarified. c iDPC images exemplifying the oxygen displacement are demonstrated for both pre-oxidation and pre-reduction cases.
segmented STEM detectors are utilized for differential phase-contrast image acquisition\(^30,31\) (see Supplementary Fig. 17 for more details on iDPC-STEM). Figure 5b shows typical iDPC images taken of LaNiO\(_3\) thin-film samples after the pre-oxidation reactions. In contrast to the well-ordered pseudocubic array of oxygens in the bulk, denoted by a red diamond in the unit-cell image, the arrows in the iDPC image of the surface region directly indicate considerable displacements of oxygen anions. Two series of enlargements along with the indication by yellow rhombuses shown in Fig. 5c provide compelling evidence of the serious distortion of the oxygen octahedra. Based on these two independent STEM imaging methods, it appears that the Ni extraction is inevitably accompanied by perturbation of the oxygen-anion framework during the pre-oxidation and pre-reduction reactions, resulting in serious displacement of oxygens. It is noted that oxygen distortion, in fact, should not be negligible along the z-axis, although the images in Fig. 5b merely demonstrate two-dimensional distortions in the x-y plane. As strong z-axis distortion indicates that the displaced oxygen is no longer on the focal plane during the STEM image acquisition, substantially weak column intensity cannot be avoided. As a consequence, it is very likely that z-axis distortion of oxygen is responsible for the low intensity of some oxygen columns, for example, in the last image in Fig. 5c.

DFT calculations. Since the first publication of the Jahn-Teller theorem in 1937 (ref. 53), it has been widely understood that structural perturbation in transition-metal compounds strongly correlates with changes in the energy state of electrons. Therefore,
we carried out ab initio DFT calculations to examine how the density of states (DOS) of the O 2p and Ni/Fe 3d orbitals in the (001) LaNiO₃ surface would be affected by the oxygen-octahedron distortion. The atomic illustration shown in Fig. 6a presents part of the (001) surface layer in a Fe-doped LaNiO₃ supercell after geometric optimization. As denoted by the dark gray shadow in the Ni/Fe DOS in Fig. 6a, one noteworthy aspect regarding the Fe addition to LaNiO₃ is that the Fe 3d states make a substantial contribution to the DOS in the range from −1 to 0 eV, where the number of DOS in the pristine LaNiO₃ surface is significantly small (see Supplementary Fig. 18a for a set of the DOS plots of the pristine (001) surface without Fe).

More importantly, we identified notable variations in the DOS of both the O 2p and Ni/Fe 3d orbitals when a subangstrom scale of displacement was introduced in the oxygen anions in each of the supercells. Figure 6b shows four different cases of oxygen displacements and corresponding DOS plots of O 2p and Ni/Fe 3d levels, demonstrating vertical (cases 1 and 2) and lateral (cases 3 and 4) displacements of oxygens (light pink spheres) with neighboring Ni (blue sphere) and Fe (orange sphere). Specific values for each of the oxygen displacements are provided in Supplementary Fig. 19. Compared with the DOS of the (001) surface shown in Fig. 6a, several significant features can be recognized in these sets of DOS with the oxygen displacements. First, as denoted by the red and blue shadows in the O 2p and Ni/Fe 3d DOS plots, respectively, there is a considerable increase in electronic states in the range from −2 to +1 eV. For example, a much higher density of the O 2p states between −2 and 0 eV is easily observed in cases 1 and 3. A rise in the Fe 3d states between −1 and 0 eV caused by the vertical shift of oxygens (cases 1 and 2) is another feature that highlights the effect of oxygen displacements. Further, cases 3 and 4 demonstrate that the lateral shift of oxygens can lead to a substantial increase in the Fe 3d states between 0 and +1 eV above the Fermi level, while also contributing to the increase in the Ni 3d states between −2 and −1 eV. This high density of Fe 3d states near the Fermi level appears to be more dominant compared with the Ni-3d DOS variation induced by the oxygen displacements without Fe, as shown in Supplementary Fig. 18b.

**Discussion**

Although various factors are involved in oxygen electrocatalysis performance, the charge transfer between transition metals and oxygen appears to be one of the more critical steps. Indeed, as rate-limiting reactions with large activation barriers are usually involved in the formation of intermediate adsorbates of OH* and O* during the OER, facilitating the transfer of electrons between transition metals and adsorbates via oxygen is an important issue. The charge transfer from transition metals to adsorbates via oxygen (e.g., Ni³⁺:O(OH)⁻ → Ni⁴⁺:O₂⁻) would be much easier and more likely to occur if a larger number of density of O 2p and metal 3d bonding states were placed near the Fermi level rather than far below it. Consequently, as has already been suggested in previous reports, an O 2p band center with a higher position and a higher degree of covalency between metals and oxygen are both beneficial for the OER. Similarly, electron transfer from the O 2p band to the empty metal 3d band (e.g., Ni⁴⁺:O₂⁻ → Ni³⁺:O(OH)⁻) can also be remarkably facilitated if a large number of metal 3d antibonding states are present as close as possible to the Fermi level, so that the charge transfer energy (the energy difference between the unoccu pied Ni 3d and occupied O 2p band centers) is drastically reduced. In this regard, our DFT calculations for the series of DOS in Fig. 6 directly demonstrate that the distortion of oxygen octahedra is a very effective approach for improving charge transfer between transition metals and oxygen. These results are also in excellent agreement with the exceptional order-of-magnitude improvement in the OER activity of the Fe-exchange samples.

Although more rigorous and extensive investigations are required to precisely understand the changes in DOS induced by the distortion of octahedra, the Jahn-Teller theorem can be applied to qualitatively explain this notable change. Each of the degenerate tumor (dₓ²−ᵧ², dₓz, and dᵧz) and eg (dₓ²−z² and dᵧ²) orbitals discreetly splits under the cubic symmetry of oxygen ligands, constructing an equally degenerate upper eg level and a triply degenerate lower tumor level. However, when the ligands are strongly distorted, such degeneracy is significantly removed in each level, thereby resulting in the nondegenerate five orbitals with various splitting energy gaps. Therefore, the energy range of the bonding states below the Fermi level can be widened, as can be seen in cases 3 and 4 in Fig. 6b. At the same time, a higher DOS may be induced near the Fermi level as a consequence of the narrower gap between the bonding and antibonding states, as denoted by the blue shadows in the Ni/Fe 3d DOS plots in Fig. 6b.

Many previous studies on the OER catalysis of oxides have attempted to relate the observed variation in OER activity with the electronic structure of the bulk and the structural change of the overall polycrystals, even though there is substantial crystallographic anisotropy in the catalytic activity, which strongly depends on both electronic and atomic structures near the surface. To move past these previous limitations, our study employed a combination of (001) epitaxial thin films, atomic-scale structure and composition analyses, and DFT calculations using more realistic supercells from direct observation. We were thus able to reliably demonstrate a solid correlation among the structural perturbation, the electronic structure, and the resultant OER property in nickelate perovskites. In addition to providing evidence that the Fe exchange has a rather general impact on the exceptional increase in OER activity in nickelate perovskites, the findings in the present work show that symmetry-breaking configurational control of atoms on the surface can offer an important platform toward exceptional oxygen electrocatalysis in perovskite oxides.

We have demonstrated that Fe exchange via selective Ni extraction in the surface region of (001) thin-film nickelate perovskites by electrochemical oxidation and reduction reactions is a remarkably efficient method of achieving exceptional OER activity. In particular, we probed the strong distortion of oxygen octahedra induced by the Ni extraction during the pre-oxidation and pre-reduction steps. A systematic series of DFT calculations showed that this atomic-scale structural perturbation resulted in a significant variation in the O 2p and Ni/Fe 3d states, especially near the Fermi level, leading to much easier charge transfer between metals and oxygen. Our work highlights the impact of symmetry-broken oxygen geometry on electronic structure and the resulting oxygen electrocatalysis in perovskite oxides.

**Methods**

**Thin-film fabrication.** Epitaxial LnNiO₃ (Ln = La, Pr, Nd) thin films were fabricated by using a sol-gel process. First, La(NO₃)₃·6H₂O (99.999%, Aldrich), Pr (NO₃)₃·6H₂O (99.999%, Aldrich), Nd(NO₃)₃·6H₂O (99.999%, Aldrich), Ni(ClO₄)₂·6H₂O (99.999%, Aldrich), and Ni(CH₃COO)₂·4H₂O (99.998%, Aldrich) were used as starting materials for the preparation of precursor solutions. Each of the lanthanide nitrates and the nickel acetate were first dissolved in 2-methoxyethanol under a constant stirring condition to prepare precursor solutions with 0.2 M. For complete dissolution of the source materials, refluxing was carried out at 80 °C for 1 h. Each of the precursor solutions was deposited on (001) SrTiO₃ single-crystal substrates by a spin-coating method at 5000 rpm for 10 s. The wet films were dried at 150 °C for 10 min on a hot plate, subsequently heat-treated at 400 °C for 10 min for pyrolysis, and finally annealed at 800 °C for 1 h in air for LaNiO₃ films, and at 700 °C for 30 min in an O₂ flow (400 sccm) atmosphere for PrNiO₃ and NdNiO₃ films for crystallization. The epitaxy of the grown films was confirmed by X-ray diffractometry (XPERT-PRO MRD, PANalytical) with Cu-Kα radiation and STEM observation.
Scanning transmission electron microscopy, energy-dispersive X-ray spectroscopy, and electron energy-loss spectroscopy. Samples for STEM observation were prepared by lift-out via ion-beam milling in a focused ion-beam system (Quanta 3D FEG and Helios G4 UX, Thermo Fisher Scientific). Protective amorphous carbon and thin Pt layers were applied over the region of interest before milling. To minimize the sidewall damage and sufficiently thin the specimen for electron transparency, final milling was carried out at a voltage of ~2 kV. Conventionally, imaging and elemental mapping were taken with a tilted sample (titanium cubed G2 at 300 kV with a spherical aberration (Cs) corrector (CEOS GmbH). The optimum size of the electron probe was ~1 Å with a convergence semiangle of 19 mrad. The collection semiangles of the STEM detectors were set to 67.6–200 mrad for HAADF imaging and 12.1–67.6 mrad for ABF imaging. IDCPC images were obtained using a four-quadrant segmented detector attached in TitanThemis Z (Thermo Fisher Scientific) with a Cs corrector at 300 kV. The obtained raw images were band-pass filtered to reduce background noise. Chemical mapping with EDS was carried out in the Titan cubed G2 at 300 kV along with four integrated silicon-drift EDS detectors (ChemiSTEM technology) at a collection solid angle of 0.7 srad. La- down to 0.62 V vs. RHE, which belongs to the stable range of Ni2+ oxidation potential, was monitored with an electron probe at 0.1 M KOH aqueous solution (pH = 12.9) prepared by using the Milli-Q water (18.2 MΩ cm) and KOH pellets (Sigma Aldrich, 99.999%) to achieve sufficiently high purity. According to the chemical analysis by inductively coupled plasma–optical emission spectrometry (ICP-OES), the Fe impurity in our electrolyte solutions was identified to be less than 5 ppm. Furthermore, when we carried out the oxidation reactions up to 1.85 V several times, we found that the OER current density continuously decreased (see Supplementary Fig. 20), directly demonstrating the absence of an Fe-inpurity effect in the electrolyte. A Pt counter electrode and a saturated Ag/AgCl reference electrode were used. The measured potential values vs. the Ag/AgCl reference electrode were converted to the RHE scale by using the following equation at 25 °C:

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + E_{\text{Ag/AgCl}} \]  

(1)

where \( E_{\text{Ag/AgCl}} \) is the converted potential vs. RHE, \( E_{\text{Ag/AgCl}} \) is the measured potential against the Ag/AgCl reference electrode, and \( E_{\text{Ag/AgCl}} \) is the standard potential of Ag/AgCl (KCl 3 M) at 25 °C, i.e., 0.21 V. Pre-reduction reactions (up to five cycles) were conducted before each OER measurement. A potential range from 1.30 down to 0.62 V vs. RHE, which belongs to the stable range of Ni3+ (approximately 0.1–1.3 V vs. RHE at pH = 12.9)57, at a sweeping rate of 10 mV/s. Pre-oxidation reactions (up to six cycles) were also conducted in an identical manner in a KOH solution. All electrochemical reactions and measurements were conducted with a potentiostat (Biologic SP-300) in a 0.1 M KOH aqueous solution (pH = 12.9) prepared by using the Milli-Q water (18.2 MΩ cm) and KOH pellets (Sigma Aldrich, 99.999%) to achieve sufficiently high purity.

Data availability

The data that support the findings of this study are available from the corresponding author (S.-Y.C.) upon reasonable request.

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Author contributions
S.-Y.C. conceived and designed the project, carried out the STEM analysis and the DFT calculations, and wrote the paper. J.B. carried out all the experiments, electrochemical measurements, and specimens preparation. H.B.B. performed the STEM observations and contributed the acquisition of image data. All the authors discussed the results and commented on the manuscript.

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