Supplementary Information

Methods

Preparation of thin films. All of the heteroepitaxial nickelate films in this study were fabricated via a typical sol-gel process by using La(NO₃)₃·6H₂O (99.999%, Sigma Aldrich), Pr(NO₃)₃·6H₂O (99.99%, Sigma Aldrich), Nd(NO₃)₃·6H₂O (99.9%, Sigma Aldrich), and Ni(CH₃COO)₂·4H₂O (99.998%, Sigma Aldrich). For Fe solid-solution La(Ni,Fe)O₃ films, Fe(NO₃)₃·9H₂O (99.95%, Sigma Aldrich) was also used as a starting material. To prepare 0.2-M precursor solutions for $LnNiO_3$ (Ln = La, Pr, Nd) and $La(Ni,Fe)O_3$, each of the lanthanide nitrates and the nickel/iron acetates were first dissolved in 2-methoxyethanol under a constant stirring condition. Refluxing was carried out at 80°C for 1 h for complete dissolution of the source materials. Each of the precursor solutions was deposited on (001) LaAlO₃ or (001) SrTiO₃ single-crystal substrates by spin-coating at 5000 rpm for 10 sec. After the deposition. the film specimens were dried at 150°C for 10 min on a hot plate and subsequently heat-treated at 400°C for 10 min for pyrolysis. Final annealing was carried out at different temperatures in air for LaNiO₃ and in an O₂-flow (400 sccm) atmosphere for PrNiO₃ and NdNiO₃ for 1 h to control the crystallinity; 400–500°C for amorphous films and 700–800°C for crystalline films. Phase identification to determine whether the films are crystalline or amorphous was directly performed by cross-sectional STEM observations in addition to X-ray diffractometry (X'Pert-PRO MRD, PANalytical) with Cu- K_{α} radiation.

Electrochemical measurements and Fe exchange. The OER specific currents of the film samples were measured with a potentiostat (Biologic SP-300) in an alkaline aqueous solution of 0.1 M KOH (pH =12.9) prepared from Milli-Q water (18.2 MΩ·cm) and KOH pellets (Sigma Aldrich, 99.99%). This high-purity solution was also verified to be at a few parts-per-billion (ppb) level of the Fe impurity on the basis of a chemical analysis by inductively coupled plasma optical emission spectrometry (ICP-OES720, Agilent). All electrolyte solutions were presaturated by bubbling O₂ gas for 30 min before OER current measurements. A saturated Ag/AgCl (KCl 3M) reference electrode with 0.21 V of the standard potential (E°Ag/AgCl) at 25°C and a Pt counter electrode were used in a three-electrode beaker cell. To expose the films only, the substrate and the connecting copper wire were completely covered with chemically inert insulating epoxy resin after application of silver paint on the back side of a thin-film sample. For the Fe-ion exchange process, anodic cyclic potential was applied (ten cycles) to the samples in a range from 1.27 to 1.75 V vs. RHE in a 0.1 M KOH aqueous solution containing 0.1 mM Fe(NO₃)₃·9H₂O. Samples after ten anodic cycles were used for sufficient Fe exchange at the surface, as shown in Supplementary Figure S18. Before the ion exchange, pre-reduction reactions (three cycles) were conducted to activate the film surface and thereby easily induce Ni vacancy formation in a 0.1 M KOH aqueous solution in a potential range from 1.30 down to 0.62 V vs. RHE at a sweeping rate of 10 mV/sec. DL capacitance was also measured in a non-faradaic potential range (0.97-1.17 V vs. RHE) by recording the current values as a function of the scan rate to take the comparative surface roughness into account in each sample.

Therefore, the OER specific current normalized by the DL capacitance could be compared among the samples. Electrochemical impedance spectroscopy was carried out to investigate both the uncompensated series resistance (R_u) for iR_u correction of the applied potential and the interface charge-transfer resistance in a frequency range from 0.1 Hz to 1 MHz with an amplitude of 10 mV. For chronoamperometry measurement in a 0.1 M KOH aqueous solution containing 0.1 mM Fe(NO₃)₃·9H₂O, a crystalline LaNiO₃ thin-film sample attached on a rotating disc was used. The current values were recorded as a function of time under a constant potential, 1.63 V vs. RHE at a rotation speed of 2400 rpm. To remove O₂ bubbles adsorbed on the film during the measurement, the speed of the rotation disc was intermittently raised up to 6000 rpm.

Atomic-scale STEM and XPS. As our samples are in the form of thin films on single-crystal substrates, an efficient and appropriate way of preparing the specimen for STEM observation is a lift-out method by 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 sidewall damage and sufficiently thin the specimen for electron transparency, final milling was carried out at a voltage of ~2 kV. All the chemical analyses and atomic-column imaging in STEM were performed with a transmission electron microscope (Titan cubed G2 60-300, Thermo Fisher Scientific) at 300 kV with a spherical aberration (Cs) corrector (CEOS GmbH). The collection semiangles of the STEM detectors were set to 40-200 mrad for HAADF imaging and 10.1-19.1 mrad for ABF imaging. The atomic-resolution raw images were band-pass filtered to reduce background noise. Chemical composition EDS maps were acquired in the Titan cubed G2 at 300 kV and a Talos F200X (Thermo Fisher Scientific) at 200 kV along with four integrated silicon-drift EDS detectors at a collection solid angle of 0.7 srad. The La- L_{α} (4.6 keV), Pr-L_{α} (5.0 keV), Nd-L_{α} (5.2 keV), Ni-K_{α} (7.5 keV), and Fe-K_{α} (6.4 keV) lines were selected during elemental mapping. The probe current values in Titan cubed G2 and in Talos F200X were adjusted to be 100 pA and 1.0 nA with a scanning time of <300 sec, respectively. The EDS maps were low-pass filtered using Bruker ESPRIT software after reduction of background noise for better visualization. An EELS analysis was performed with a Gatan Image Filter (GIF Quantum 965, Gatan Inc.) in the Titan cubed G2. Electron energy-loss spectra for the O-K, Ni-L, and Fe-L edges were acquired for spectrum imaging with a dispersion of 0.25 eV per channel and a collection aperture of 5 mm diameter. XPS was carried out using an X-ray photoelectron spectroscope (K-Alpha XPS, Thermo Scientific) with monochromatic Al- K_{α} radiation (1486.7 eV) and flood gun emission of 150 μ A. No significant chemical shift or broadening of the Ni 2p peaks was found during the analysis.

MD simulations and DFT calculations. *Ab initi*o molecular dynamics (AIMD) simulations were utilized to construct reasonable supercells representing the distorted lattice and the amorphous disordered phase in agreement with the atomic-scale STEM observation. Rapid heating of an initial supercells containing Fe to 3500 K and subsequent dynamic relaxation were conducted in the isothermal–isobaric (NPT) ensemble with the Langevin thermostat and

the Anderson barostat in a time step of 1.5 fs to induce displacement of each atom by thermal agitation. Appropriate MD steps were performed so that the displacement of atoms does not exceed 0.8 A, which is 20% of the cubic lattice parameter of LaNiO₃ (3.83 Å), under preservation of the perovskite framework, as demonstrated in Supplementary Figure S8(a). The spin-polarized local density approximation (LDA) functional for exchange correlation and the ultrasoft pseudopotentials for ionic cores were employed in the CASTEP code (Biovia Inc.). The plane-wave basis set for the kinetic energy cutoff was 400 eV with k-space integration of a Γ -point (1 × 1 × 1). After the optimal MD steps at 3500 K, the cell was guenched to 50 K at a cooling rate of 10 K per step. For the amorphous structure, this typical melt-quenching (MQ) method was applied in an identical manner. More than 6000 MD steps at 3500 K for melting were carried out until the overall lattice energy was stabilized, followed by guenching to 50 K. To acquire the DOS variation at the surface of a (001)-surface slab along with a 10-Å vacuum layer in each case, DFT caclautaions were also carried out, using the LDA functional in the same software package. To account for the electron localization around Ni and Fe ions, the LDA + U method with the Hubbard U parameter (4.0 eV for both Ni 3d and Fe 3d states) was employed. Low-spin $(t_{2g}^{6})(e_{g}^{1})$ for d^{7} Ni³⁺ and high-spin $(t_{2g}^{3})(e_{g}^{2})$ for d^{5} Fe³⁺ configurations were assumed, respectively. The plane-wave basis set for the kinetic energy cutoff was 500 eV for geometry optimization. Relaxation of the internal coordinates for each atom was performed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm with convergence tolerances of 0.1 eV/Å for the maximum ionic force, 5×10^{-5} eV/atom for the total energy, and 0.005 Å for the maximum ionic displacement.



Figure S1. X-ray diffraction patterns and cross-sectional overview of LaNiO₃ films. (**a**) As indicated by a red arrow in each pattern, the 002 Bragg peak is clearly observed in the epitaxial crystalline films annealed at 600–800°C. See Figure S2 for more details on the Bragg reflections from the substrates and the heteroepitaxially grown films. (**b**) This series of ADF-STEM images demonstrates the evolution from an amorphous to crystalline phase with annealing temperature. At 450°C, the crystallization is observed at the interface between the films and the substrate, typically showing heterogeneous nucleation and subsequent growth. As denoted by white arrows at 600°C, residual amorphous phases remain at the surface. Therefore, annealing at \geq 700°C is necessary to acquire a crystalline film.



Figure S2. Heteroepitaxial LaNiO₃ thin film. (**a**) These ADF-STEM images clarify the heteroepitaxial growth of a crystalline film on a LaAlO₃ substrate. (**b**) The X-ray diffraction peaks, showing the (00*l*) Bragg reflections only, verify the epitaxy of the LaNiO₃ film on a (001) LaAlO₃ single-crystal substrate. The high-intensity diffraction peaks originate from the substrate and their satellite shoulder peaks (red arrows) are from the LaNiO₃ film.



Figure S3. EDS maps visualizing the compositional distribution in $LaNiO_3$ films. All the films are deposited on $LaAlO_3$ substrates. Homogeneous distribution of La and Ni in each of the films is clarified in the maps. As the amorphous phase is more easily thinned by a focused ion beam than the dense crystalline phase during specimen preparation, the lower intensity in the amorphous regions in the EDS maps originates from the different thickness of the STEM sample.



Figure S4. X-ray diffraction data of $LaNiO_3$ thin films. No substantial 002 Bragg reflections are identified in the amorphous films (left). In contrast, as indicated by a red arrow, the 002 peaks from the films are apparently observed in the patterns (right), confirming the heteroepitaxial crystalline films.



Figure S5. Comparison of X-ray diffraction data acquired from $LaNiO_3$ thin films after the surface Fe exchange. Because the Fe exchange takes place exclusively in the surface region, the overall diffraction patterns are not affected by the surface ion exchange in either (**a**) amorphous or (**b**) crystalline LaNiO₃ films. The broken vertical line in (b) indicates the 002 peak from the crystalline films.



Figure S6. DL capacitance measurements of LaNiO₃ films. As exemplified for the samples annealed at (a) 450°C and (b) 800°C, cyclic voltammograms were first obtained in a non-faradaic potential region (0.98–1.18 V *vs*. RHE) at different scan rates. The DL anodic charging currents are plotted as a function of scan rate in each case. Specific values of the capacitance for the films are 134 μ F/cm² (450°C), 214 μ F/cm² (500°C), 84 μ F/cm² (750°C), and 71 μ F/cm² (800°C), showing the higher surface roughness in the amorphous films.



Figure S7. Tafel plots of pristine and Fe-exchanged LaNiO₃ films. Four different annealing temperatures are noted; (**a**) 450°C, (**b**) 500°C, (**c**) 750°C, and (**d**) 800°C. Significantly lower values of Tafel slopes (less than 36 mV/decade) are obtained in the Fe-exchanged crystalline films in (c) and (d). Note that the Tafel slopes of the Fe-exchanged amorphous films (50–55 mV/decade) are higher than those of the Fe-exchanged crystalline films (34–36 mV/decade), even though they are much lower than those of the pristine amorphous films (139–170 mV/decade). Therefore, a substantial reduction in the activation barrier of the OER rate-limiting step in the Fe-exchanged crystalline films is anticipated in good agreement with the exceptional OER activity.



Figure S8. XPS results for the Ni 2p peaks. Because the added Fe³⁺ ion has an identical valence state to that of Ni³⁺ in LaNiO₃, neither the variation of the valence state of Ni nor the creation of charged defects should be identified in the films. To examine the valence state variation of Ni, an XPS analysis was carried out. As shown in this series of spectra, no shift of Ni $2p_{1/2}$ and $2p_{3/2}$ peaks is identified in the amorphous and crystalline films.



Figure S9. Determination of Fe concentration from the surface ion exchange. EDS spectra for composition quantification can be readily extracted from the composition maps. Two sets of EDS spectra acquired from the surface region and the bulk in the Fe-exchanged crystalline and amorphous LaNiO₃ films directly indicate comparable amounts of Fe in the Ni sites at the surfaces: 9.6% in the amorphous LaNiO₃ film and 12.3% in the crystalline LaNiO₃ film.



10 nm

Figure S10. EDS maps visualizing the compositional distribution in $PrNiO_3$ and $NdNiO_3$ films. The (**a**) $PrNiO_3$ and (**b**) $NdNiO_3$ films are deposited on $SrTiO_3$ substrates. Homogeneous distribution of Pr, Nd, and Ni in each of the films is verified in the maps. The initiation of crystallization takes place at the interface between the substrate and the film, as indicated by an arrow in each image.



Figure S11. X-ray diffraction data of $PrNiO_3$ and $NdNiO_3$ thin films. While no substantial 002 Bragg reflections are observed in the amorphous films, the three substantial 00/ Bragg peaks from each of the crystalline films are clearly identified, as indicated by red arrows.



Figure S12. Tafel plots of pristine and Fe-exchanged nickelate films. (**a**) The plots for $PrNiO_3$ and (**b**) NdNiO₃ films are provided. In good agreement with the result for the LaNiO₃ films, much lower Tafel slopes (less than 36 mV/decade) are consistently demonstrated in the Fe-exchanged crystalline $PrNiO_3$ and NdNiO₃ films. Note that the Tafel slopes of the Fe-exchanged amorphous films (49–55 mV/decade) are higher than those of the Fe-exchanged crystalline films (33–36 mV/decade) in both nickelates.

Pristine LaNiO₃



Fe-containing solid solution



Figure S13. Atomic-scale ABF images and their reverse-intensity contour maps. The surface regions of the pristine, 10%-Fe-solid-solution, and Fe-exchanged LaNiO₃ films are images at an atomic level in ABF mode. As atomic columns in the ABF image (left) have black contrast on a white background, its reverse-contrast image (middle) is necessary to acquire an intensity contour of each column (right).



Figure S14. Additional structure observation and catalytic durability test. (**a**) To examine the surface structure variation, additional STEM observation and EDS analysis were carried out for the crystalline Fe-exchanged LaNiO₃ thin film after 20 cycles in 0.1 M KOH with 0.1 mM Fe(NO₃)₃·9H₂O. As demonstrated in this set of chemical maps and atomic-column-resolved images, it is noted that Fe exchange at the film surface is confirmed and no surface reconstruction is observed, revealing preservation of the perovskite framework. In particular, highly distorted lattices were frequently identified, as shown in the following STEM image. (**b**) Chronoamperometry as a function of time under a constant potential (1.63 V *vs*. RHE) was also performed for the Fe-exchanged LaNiO₃ film in the same electrolyte. The high current density is preserved for a fairly long period of time. As the sample was a thin film, O₂ bubbles on the film were removed by rotating the samples attached on the disc at a high speed.



Figure S15. Structures of the LaNiO₃ supercells used for DFT calculations. (a) Typical geometric optimization was carried out to acquire a thermodynamically stable structure. (b) AIMD simulation together with a MQ method was used to construct a supercell with lattice distortion consistent with the STEM observation. Each red circles indicates the allowed radial displacement, 0.8 Å, of atoms from their initial positions. This displacement (0.8 Å) was set to be ~20% of the cubic lattice parameter of LaNiO₃ so that the perovskite framework is preserved in spite of the lattice distortion. (c) To construct the supercell for the amorphous phase, a MQ method was utilized as well. A sufficient number of MD steps was performed at 3500 K until the lattice energy was stabilized. As denoted by a white square in the lower illustration, a short-range order of [NiO_{6-x}] units is observable in the overall random configuration of atoms.



Figure S16. Electrochemical impedance spectroscopy (EIS) analysis. EIS was carried out to examine the electrical charge transfer behavior between the films and electrolyte solutions. (a) Two *RC* elements in series are represented for the uncompensated component between the working electrode and the reference electrode (R_uC_u) in the high-frequency range and the charge transfer at the interface between the film and the electrolyte $(R_{CT}C_{CT})$ in the low-frequency range. (b) The charge-transfer resistance is remarkably low in the crystalline LaNiO₃ film by Fe exchange. As magnified in the right-hand plot, a small second semicircle is identified, indicating considerably reduced R_{CT} in the Fe-exchanged film. (c) The Nyquist plots for the Fe-exchanged crystalline PrNiO₃ and NdNiO₃ films are provided. The low R_{CT} values by Fe exchange are consistently verified in both cases.



Nondegenerate electronic states

Elongated distortion

Compressed distortion

Figure S17. Two typical Jahn–Teller distortion. (a) Simple ligand-field splitting of the five degenerate 3*d* orbitals as the t_{2g} and e_g levels under the octahedral symmetry of oxygen anions should be perturbed when this high-degree symmetry is broken. (b) If the oxygen octahedron is elongated along the z axis, another energy-level splitting of the 3*d* orbitals is achieved, resulting in strong nondegenerate dx^2-y^2 and dz^2 orbitals of the e_g level in addition to dxy, dyz, and dzx, of the t_{2g} level. (c) When the oxygen octahedron contracts, splitting of the t_{2g} and e_g levels is achieved in a different way. Note that the dz^2 level is higher than that of the dx^2-y^2 level. Therefore, any structural distortion deviating from the octahedral symmetry is anticipated to induce a substantial number of electronic states in a wider range of energy even beneath the Fermi level.



Figure S18. Enhancement of the OER current density by Fe exchange in LaNiO₃ films. The films were annealed at (a) 450°C, (b) 500°C, (c) 750°C, and (d) 800°C. Although it appears that the improved OER activity is attainable within a few anodic cycles, all the films samples were cycled ten times for sufficient ion exchange at the surface.