

Electronic Supplementary Information

Experimental Details

Preparation of Dense Samples

$\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0.2, 0.36,$ and 0.4 were synthesized by solid-state reaction from La_2O_3 (99.99%, Shin-Etsu Chemical), NiO (99.9%, Wako Pure Chemical Industries), and Fe_2O_3 (95%, Wako Pure Chemical Industries). La_2O_3 was dried at $800\text{ }^\circ\text{C}$ in air for over 24 h before use. First, La_2O_3 , NiO , and Fe_2O_3 were mixed and ball milled for 5 h in isopropanol. The mixtures were pressed into pellets under a uniaxial pressure of 10 MPa. These pellets were calcined at $1100\text{--}1200\text{ }^\circ\text{C}$ for 5–32 h in air, sometimes with an intermittent grinding.

The calcined powders were ball milled for 50 h, and subsequently mixed with an organic binder (DIC Corporation, NCB166) with a mass ratio of 10:1. The mixed powders were passed through a sieve ($150\text{ }\mu\text{m}$ mesh) and pressed into bar-like tablets ($37 \times 5 \times (1\text{--}5)$ mm) under a uniaxial pressure of 200 MPa. These tablets were slowly heated to $600\text{ }^\circ\text{C}$ at a rate of $1\text{ }^\circ\text{C min}^{-1}$ in air, and held at $600\text{ }^\circ\text{C}$ for 5 h to remove the binder. After that, the tablets were sintered at $1300\text{ }^\circ\text{C}$ for 10 h in air or oxygen gas.

After sintering, the tablets of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0.2$ contained impurity phases $\text{La}_4\text{Ni}_3\text{O}_{10}$ and NiO , which are more stable than the perovskite phase if oxygen partial pressure is not sufficiently high. (Fe may partially occupy the Ni-sites in $\text{La}_4\text{Ni}_3\text{O}_{10}$ and NiO .¹) These tablets were oxidized to single-phase perovskite under $p_{\text{O}_2} = 392$ bar at $1250\text{ }^\circ\text{C}$ for 5 h using capsule-free HIP (Kobelco $\text{O}_2\text{-Dr. HIP}$) whose sample chamber was filled with compressed Ar-20\%O_2 gas. (We skipped the removal procedure of high-pressure oxygen gas enclosed in the closed pores in the samples, which is described in ref. ².)

Unlike $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0.2$, the dense samples of single-phase LaNiO_3 ($x = 0$) could not be prepared even by solid-state reaction and subsequent oxidation using HIP due to kinetic reasons². Therefore, the nitrate freeze-drying technique was employed instead of solid-state reaction to produce fine powder of mixed oxide. The powder was pressed into bar-like tablets and sintered at $1225\text{ }^\circ\text{C}$ for 20 h in vacuum to obtain dense tablets consisting of fine grains of La_2NiO_4 and NiO . Then they were transformed into single-phase LaNiO_3 by oxidizing the tablets at $1250\text{ }^\circ\text{C}$ under $p_{\text{O}_2} = 300\text{--}392$ bar for 3 h. The detailed procedures are given in ref. ².

Phase Identification, Density Measurements, and Morphology Observation

Powder X-ray diffraction analysis was carried out at room temperature for phase identification using an X'Pert-Pro Alpha-1 (PANalytical, Netherlands) with $\text{Cu-K}\alpha$ radiation and a Johansson monochromator. From X-ray diffraction data, the lattice parameters were calculated by the Rietveld method using X'Pert HighScore Plus software (Version 2.2c).

For evaluating the relative densities (R.D.) of the samples, the theoretical densities of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ were derived from the lattice parameters calculated by the Rietveld method. The volumes of the samples were measured by the Archimedes method using isopropanol as an immersion medium. As infiltration of the immersion medium may lead to underestimation of the volumes, the volumes of the samples were cross-checked by measuring the external dimensions of the bar-like tablets using a micrometer. The relative densities estimated by the external dimensions were well consistent with those by the Archimedes method.

The microstructures of the tablets were observed using scanning electron microscopes (SEM, KEYENCE VE-7800 and JEOL JXA-8530F).

Electrical Conductivity Measurements

Electrical conductivity was measured by the four-probe technique at between room temperature and $800\text{ }^\circ\text{C}$ in air or a mixture of O_2 and Ar gases. Silver wires (Nilaco corporation, $\phi 0.20$ mm) were attached to the bar-like tablets with silver paste (Fujikura Kasei, Dotite 550) as electrodes. Direct current (DC) of 25–1500 mA was applied by either potentio/galvanostat Solartron 1285 or 1287, or VersaSTAT3F. The sample resistance was determined from the slope of the current-voltage plots. Figure 2 in the main text shows a schematic and a photograph of a sample used for the electrical conductivity measurements.

Oxygen Partial Pressure Dependence of the Electrical Conductivity of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$

Figure S1 shows the p_{O_2} dependence of the electrical conductivity of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0, 0.2, \text{ and } 0.4$ at 800°C . The electrical conductivities of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ increased with p_{O_2} , but the variations of the electrical conductivities were less than 12 % in the p_{O_2} range of $10^{-3} - 1$ bar at 800°C . The trend of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0.4$ is consistent with past studies.^{3,4,5} According to Sereda *et al.*,⁵ the increase in the conductivity of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0.4$ is considered due to the increase in the hole concentration as a result of oxygen incorporation.

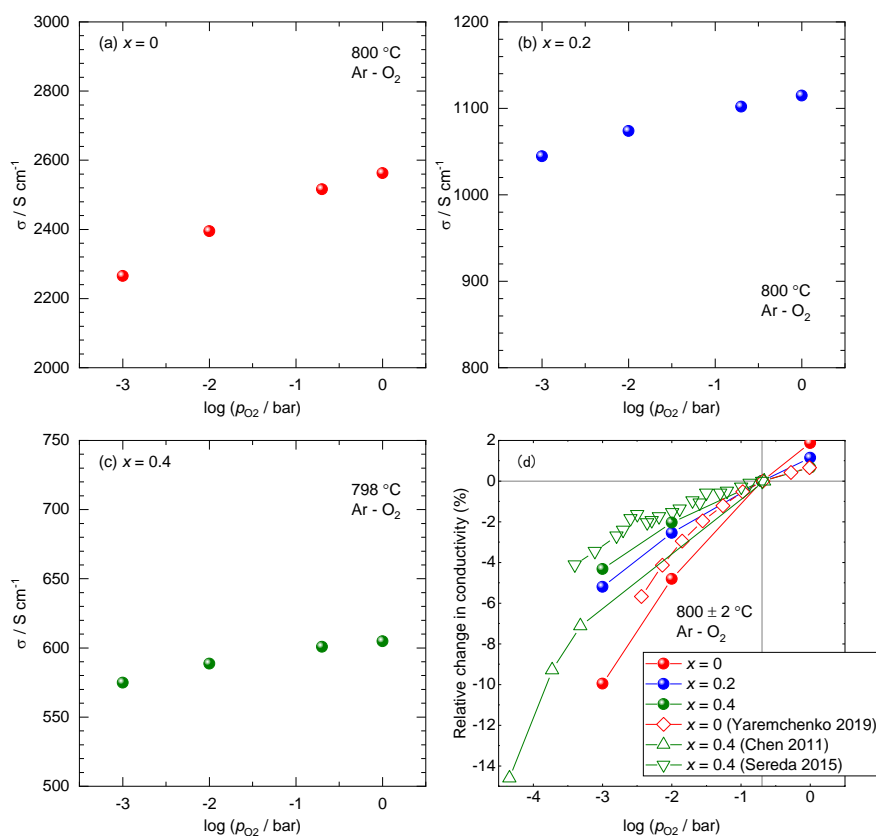


Figure S1. Oxygen partial pressure (p_{O_2}) dependence of the electrical conductivity (σ) of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ measured using dense polycrystalline samples at $800 \pm 2^\circ\text{C}$. (a) $x = 0$; (b) $x = 0.2$; (c) $x = 0.4$; (d) Relative electrical conductivity to those under $p_{\text{O}_2} = 0.2$ bar. Each conductivity value was collected after the sample was kept under a constant p_{O_2} for at least 5 h.

Thermodynamic Stability of Lanthanum Nickelates

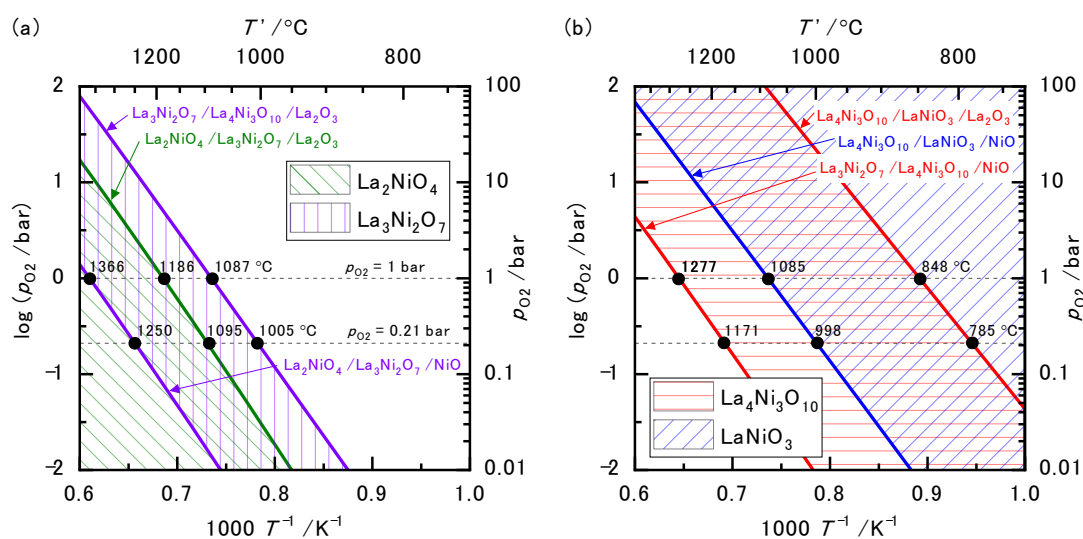


Figure S2. Stable oxygen partial pressure (p_{O_2}) ranges of lanthanum nickelates v.s. inverse temperature. (a) La_2NiO_4 and $La_3Ni_2O_7$; (b) $La_4Ni_3O_{10}$ and $LaNiO_3$. The figure is taken from Ref. ² and a label in (b) has been corrected. Thermodynamic data of NiO and La_2O_3 are taken from Ref. ⁶. and Ref. ⁷, respectively, and those of $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$, and La_2NiO_4 are taken from Ref. ⁸.

References

- 1 E. A. Kiselev and V. A. Cherepanov, *J. Solid State Chem.*, 2010, **183**, 1992-1997.
- 2 Y. Adachi, N. Hatada, K. Hirota, M. Kato and T. Uda, *J. Am. Ceram. Soc.*, 2019, **102**, 7077-7088.
- 3 A. A. Yaremchenko, B. I. Arias-Serrano, K. Zakharchuk and J. R. Frade, *ECS Trans.*, 2019, **91**, 2399-2408.
- 4 J.Y. Chen, J. Rebello, V. Vashook, D. M. Trots, S.R. Wang, T.L. Wenet et al., *Solid State Ion.*, 2011, **192**, 424-430.
- 5 V. V. Sereda, D. S. Tsvetkov, I. L. Ivanov and A. Y. Zuev, *J. Mater. Chem. A*, 2015, **3**, 6028-6037.
- 6 I. Barin, *Thermochemical Data of Pure Substances*, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1995.
- 7 M. Zinkevich, *Prog. Mater. Sci.*, 2007, **52**, 597-647.
- 8 M. Zinkevich, N. Solak, H. Nitsche, M. Ahrens and F. Aldinger, *J. Alloys Compd.*, 2007, **438**, 92-99.