Supporting Information

A new family of perovskite catalysts for oxygen-evolution reaction in alkaline media: BaNiO_3 and $\text{BaNi}_{0.83}\text{O}_{2.5}$

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EXPERIMENTAL SECTION

Materials synthesis: BaNiO₃ was synthesized by flux-mediated crystal growth (1). BaCO₃ (0.986 g, Sigma Aldrich) and NiO (0.373 g, J. T. Baker) were mixed thoroughly and placed in an alumina crucible. The mixed powders were sintered at 1000 °C for 12 h in air, and cooled to room temperature. 0.4 g powders were then placed in an alumina crucible with KOH (50 g, 99.99 %, Sigma Aldrich) and Ba(OH)₂·8H₂O (0.4 g, Sigma Aldrich). The filled crucible was heated at 700 °C for 12 h, and cooled at room temperature. The KOH was slowly dissolved by adding DI water. The unresolved powders were manually filtered 10 times, and the BaNiO₃ crystals were obtained. The extra Ba(OH)₂·8H₂O was required to avoid the formation of NiO as a second phase.

Surface Normalization: Specific surface area was determined for the ground BaNiO₃ through Brunauer-Emmet-Teller (BET) analysis. The BET was measured using BELSORP-mini II (BEL. Japan Inc.), flowing N₂ gas. The specific surface area was about 0.301 m² g⁻¹. Electrochemical surface areas (ECSAs) were estimated by measuring the electrochemical capacitance of the electrode-electrolyte interface in the double-layer regime of the voltammograms.

$$i_{DL} = C_{DL} \times v$$

$$ECSA = C_{DL}/C_s$$

where i_{DL} is the capacitive current, C_{DL} is the specific capacitance of the electrode double layer, v is the scan rate, and C_s is the specific capacitance. The cyclic voltammograms were obtained in N₂-saturated 0.1 M KOH from -0.05 V to 0.05 V versus Hg/HgO at different scan rates between 2.5 and 40 mV s⁻¹ (2).

Electrochemical measurements: Electrode was prepared by drop-casting a catalyst ink. The catalyst ink consisted of the BaNiO₃ (2 mg), carbon black (8 mg, VULCAN® XC72R, surface area: ~220 m² g⁻¹), and Nafion (80 µL, 5 wt. %, Sigma Aldrich). The BaNiO₃ powder

was ground in a ceramic mortar. The catalyst ink was sonicated for 3 min, and then stirred for 30 min. The mixing process was repeated more than 3 times. The catalysts ink (6 μL) was drop-cast onto a glassy carbon electrode (0.196 cm^2 , Pine Instruments), yielding a perovskite loading of 0.295 mg cm^{-2} . OER measurements were performed with a rotating disk electrode setup. Pt and Hg/HgO in saturated 1 M NaOH (~ 0.14 V versus reversible hydrogen electrode (RHE) for Pt) were used as a counter and reference electrodes, respectively. A 0.1 M KOH (99.99 %, Sigma Aldrich) electrolyte was prepared with DI water. The potential calibration of the reference electrode was performed in a high-purity hydrogen-saturated 0.1 M KOH solution. The Pt wire was used as the working electrode. Cyclic voltammetry (CV) was measured at a scan rate of 1 mV s^{-1} and the average of the two potentials where the current crossed zero was obtained to be the thermodynamic potential for the hydrogen electrode reaction. With respect to the measurements of the OER activity on the catalysts, oxygen was saturated during OER cycling due to $\text{O}_2/\text{HO}^\cdot$ equilibrium at 1.23 V versus RHE. The potential was measured by using a potentiostat (Biologic VSP model) at a scan rate of 10 mV s^{-1} and a rotation speed of 1600 rpm. The chronopotentiometric responses were obtained at a rotation speed of 1600 rpm and a constant current density of 10 $\text{mA cm}^{-2}_{\text{disk}}$ in O_2 -saturated 0.1 M KOH for 20 h. All potentials represent iR -corrected potentials.

Scanning transmission electron microscope (STEM): The sample was prepared by using focused ion beam (FIB, FEI company, Helios Nanolab model). The sample was examined with Titan Double Cs corrected TEM (FEI company, Titan cubed G2 60-300 model). The operating voltage was 300 kV. Fourier analysis was performed using the Gatan Digital Micrograph software.

X-ray diffraction (XRD): XRD measurements were performed using a D/MAX-2500H (Rigaku) with Cu $K\alpha$ radiation ($\lambda=0.15418$ nm) in the $20\text{-}80^\circ$ window in the 2θ range. The

lattice parameters and space group were determined by a refinement of the XRD patterns using JADE program (Materials Data Inc.).

X-ray absorption spectroscopy (XAS): XAS measurements at the Ni *K*-edge were collected in total electron yield (TEY) mode at Pohang Light Source at the BL-6D beamline of the Pohang Accelerator Laboratory (PAL), Gyeongsangbuk-do, Korea. XAS measurements at Ni *L*-edge and O *K*-edge were collected in total electron yield (TEY) at Pohang Light Source at the BL-10D beamline of the PAL. Analysis of XAS data was performed following standard procedures using Athena and Artemis interfaces to the IFEFFI software (3).

Density functional theory (DFT): All the calculations were performed with generalized gradient approximation (GGA) (4) exchange-correlation function by Perdew-Burke-Ernzerhof (PBE) (5) using Vienna Ab-initio Simulation Package (VASP) (6).

Pseudopotentials of Ba_{sv}(5s²5p⁶6s²), Ni(4s²3d⁸) and O(2s²2p⁴) were treated with the Projector Augmented Wave (PAW) (7) as recommended. Each atom was relaxed with a plane wave cutoff energy of 520 eV until all forces were smaller than 0.02 eV and the electronic energy was converged lower than 10⁻⁵ eV in each ionic iteration. The Brillouin zone was integrated with gamma point scheme of 17x17x17 for bulk and DOS and 5x5x1 for slab calculations. The bulk structure of BaNiO₃, BaNiO₂ and BaNi_{0.83}O_{2.5} was obtained from literature (8,9). The bulk geometry of perovskite was relaxed first, then (001) surface was curved out. The total number of atoms contained in slab model is 60 for BaNiO₃, 52 for Ba₆Ni₅O₁₅ and 48 for BaNiO₂. For perovskite slab model, the bottom 2 atomic layers of the slab were fixed at the optimized bulk lattice parameter while top 4 atomic layers were relaxed. To prevent interaction between neighboring unit cell due to periodic boundary vacuum spacing of 15 Å in the direction perpendicular to the surface was adopted. Each OER intermediates were adsorbed on top of Ni with 50% coverage.

Figure S1. SEM image of the BaNiO₃. It shows hexagonal-rod shapes of the BaNiO₃ with an average thickness of 100 μm.

Figure S2. Elemental mapping images of the BaNiO_3 . The Ba and Ni atoms are well distributed in the BaNiO_3 .

Figure S3. Schematic of the BaNiO_3 . The interatomic distances of the Ni-Ni, Ni-O, and Ba-Ni are 5.718, 1.897, and 3.518 Å, respectively.

Figure S4. Potential calibration of the Hg/HgO reference electrode in 0.1 M KOH. In

0.1 M KOH solution, $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.896 \text{ V}$.

Figure S5. Nitrogen adsorption-desorption isotherm curves of the BaNiO₃ catalyst.

The BET surface area is $0.301\text{ m}^2\text{ g}^{-1}$.

Figure S6. Cyclic voltammograms of the BaNiO₃ and IrO₂. **a**, cyclic voltammograms measured for the BaNiO₃ catalysts in N₂ saturated 0.1 M KOH at different scan rates from 2.5 to 40 mV s⁻¹. **b**, a plot of anodic current (BaNiO₃) measured at 0.04 V as a function of scan rate. **c**, cyclic voltammograms measured for the IrO₂ catalysts in N₂ saturated 0.1 M KOH at different scan rates from 2.5 to 40 mV s⁻¹. **d**, a plot of anodic current (IrO₂) measured at 0.04 V as a function of scan rate.

Figure S7. Specific OER activity of the BaNiO₃ and IrO₂ catalysts. The numbers in parenthesis represents OER cycle number. The specific activities of the both catalysts were normalized by electrochemical surface area calculated from Fig. S6.

Figure S8. OER activity of the IrO_2 and BaNiO_3 during OER cycling. **a**, carbon black, **b**, IrO_2 , **c**, BaNiO_3 . The specific activity refers to the OER activity normalized by specific surface area. The numbers in parenthesis represents OER cycle number. The OER activity of the BaNiO_3 became stable from approximately 150 cycles, and the deactivation rate was 11.1 % from 150 cycles to 1000 cycles.

Figure S9. HRTEM and elemental mapping images of the BaNiO_3 after 3th cycles. The TEM image clearly shows the surface amorphization. From the elemental mapping images, the amorphous phases would be associated with Ni atoms.

Figure S10. HRTEM image of the BaNiO_3 after 250th cycles. The surface amorphous region disappeared, and the crystalline phases appeared after 250th cycles. It can be related to disappearance of the pseudocapacitive behaviors. Additionally, It can assume that the $\text{BaNi}_{0.83}\text{O}_{2.5}$ would be stable against the surface amorphization.

Figure S11. Chronopotentiometric responses of the BaNiO₃ catalysts. The potential was stable for 20 h at a constant current density of 10 mA cm⁻²_{disk} in O₂-saturated 0.1 M KOH.

Figure S12. Schematic of the BaNiO_2 . The interatomic distances of the Ni-Ni, Ni-O, Ba-Ni(1), and Ba-Ni(2) are 5.505, 1.901, 3.449 Å, and 4.845 Å, respectively.

Figure S13. XRD patterns of the BaNiO_3 after 3th cycles. The patterns correspond to $\text{BaNi}_{0.83}\text{O}_{2.5}$.

Figure S14. Ni K-edge XANES spectra of the NiO and BaNiO₃ before and after OER cycling. It shows that Ni oxidation states in the BaNiO₃ are lowered after OER cycling.

Figure S15. Ni *L*-edge XAS spectra of the NiO and BaNiO₃ before and after OER cycling. It shows that Ni oxidation states in the BaNiO₃ are lowered after OER cycling, which implies that the BaNi_{0.83}O_{2.5} has Ni supermixed valence.

Figure S16. O *K*-edge XAS spectra of the NiO and BaNiO₃ before and after OER cycling. It shows that Ni oxidation states in the BaNiO₃ are lowered after OER cycling, and phase distortion is implied due to pre-edge peak at ~520 eV shifted from that of the NiO. It may be due to the Ni local structure change from face-shared to distorted prism.

Table S1. EDS results of the BaNiO₃. The stoichiometric ratio of Ba and Ni atoms is approximately 1:1.

Element	Atomic %
O	59.83
Ni	19.61
Ba	20.56
Total:	100.00

Table S2. Crystal information on the BaNiO₃. The crystal information was obtained from XRD patterns of the BaNiO₃.

Formula	BaNiO ₃
Crystal system	Hexagonal
Space group	P63/mmc (No. 194)
a (Å)	5.6602
b (Å)	5.6602
c (Å)	4.8017
Z	2
Density (g cm ⁻³)	6.139
Diffractometer	D/Max-2500, Rigaku
Radiation	Cu Kα (λ=1.5418 Å)

Table S3. Crystal information on the BaNi_{0.83}O_{2.5}. The crystal information of the BaNi_{0.83}O_{2.5} was obtained after 3th OER cycles..

Formula	BaNi _{0.83} O _{2.5}
Crystal system	Hexagonal
Space group	R32(No. 155)
a (Å)	9.889
b (Å)	9.889
c (Å)	12.867
Z	18
Density (g cm ⁻³)	6.205
Diffractometer	D/Max-2500, Rigaku
Radiation	Cu Kα (λ=1.5418 Å)

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