3D Porous Ni/NiO_x as a bifunctional oxygen electrocatalyst derived from Freeze dried $Ni(OH)_2$

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Calculation of Tafel slope and Turnover Frequency (TOF) for OER. The Tafel plot is calculated by following equation:

$\eta = a + b \times logi$

Where η is the over potential ($\eta = E_{RHE} - 1.23$), a is y-intercept, b is the Tafel slop, and i (mA / cm^2) is the current density.

The TOF:

$TOF = j \times A/(4 \times F \times n)$

Where j is the current density, A is the surface area of the RDE, F is Faraday's constant (96485 C mol^{-1}), and n is the moles of sample on the RDE.

Calculation of the Koutechy-Levich (K-L) plot for OER. The number of electron transfer for ORR can be attributed by the K-L equation:

$$i^{-1} = i_k^{-1} + \left(0.62 \times n \times F \times A \times D_0^{2/3} \times \omega^{1/2} \times \nu^{-1/6} \times C_{O_2}\right)^{-1}$$

$$i^{-1} = i_k^{-1} + B^{-1} \times \omega^{-1/2}$$

$$B = 0.62 \times n \times F \times A \times D_0^{2/3} \times \nu^{-1/6} \times C_{O_2}$$

Where i_k is the kinetic current, and ω is the rotating rate of RRDE. B^{-1}, based on the Levich equation, is attributed to K-L slope. Where n is the number or electron transfer for ORR, F is Faraday's constant (96485 C mol^{-1}), A is Surface area, D_O is the diffusion coefficient of Oxygen (1.9 × 10^{-5} cm^2 s^{-1}), ν is kinematic viscosity (0.01 cm^2 s^{-1}), C_{O_2} is the bulk concentration of O_2 (1.2 × 10^{-6}).

ω

Calculation of the hydrogen peroxide yield on ORR. The hydrogen peroxide yield (%) and the electron transfer number were determined by RRDE and follow equation.

$$H_2O_2\ (\%) = 2 \times 100 \times \frac{I_r / N}{I_d + I_r / N}$$

$$n = \frac{4 \times I_d}{I_d + I_r/N}$$

Where I_r is current density of ring electrode, I_r is current density of disk electrode, N is

current efficiency of the ring electrode (N=0.4).

Cyclic voltammetry is performed with various scan rating (0.1, 0.08, 0.05, 0.01, 0.005 V/s).

For Linear sweep voltammetry (LSV) of OER, electrode is measured

BET Surface area measurement

Surface area measurement according to Brunauer, Emmett and Teller (BET) is equivalent to determining the amount of gas required to form a monomolecular or "monolayer" covering of gas on the solid substrate. Knowing the cross-section and number of gas molecules that make up the monolayer, the surface area of that substrate can easily be calculated.

The relevant mathematical formulation for B.E.T. equation is

$1/(V(P_0/P-1) = 1/(V_m C)+((C-1))/(V_m C) P/P_0$

where V is the total volume of gas adsorbed at the measured pressure P; Vm is the volume required to cover the solid surface by monomolecular gas layer; P_0 is the saturating pressure of the gas at the adsorption temperature and C is a constant. By taking the '$1/(V(P_0/P-1)$' as the ordinate and P/P_0 as the abscissa, a straight line of slope $(C - l)/(V_m C)$ is obtained, with the intercept at the origin being $1/V_m C$.

To calculate these values, the BET equation is plotted as an adsorption isotherm typically at a relative pressure (P/P_0) between 0.05-0.30. In this range it forms a straight line. Sample does not produce a linear adsorption isotherm over the standard BET range (P/P_0 = 0.05-0.3). In particular, non-linearity is often obtained at P/P_0 values below 0.05 and after 0.3.

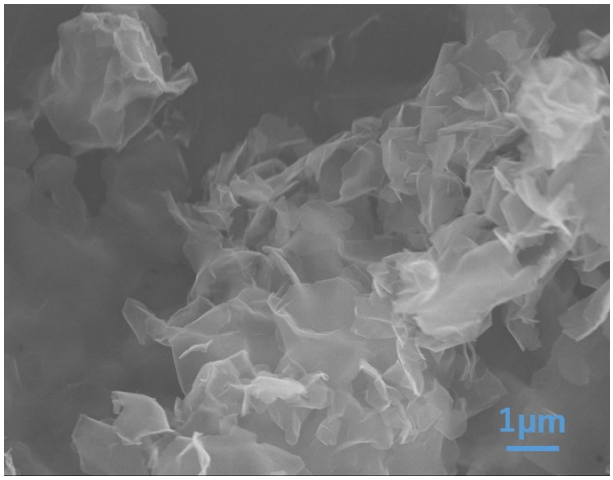

Fig. S1 The SEM image of Freeze-dried $Ni(OH)_2$

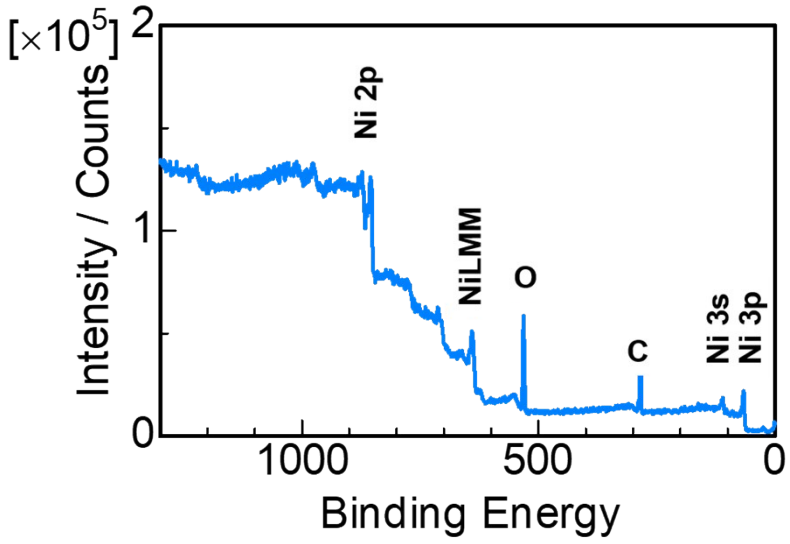

Fig. S2 XPS survey spectrum of freeze-dried Ni/NiO_x. Elemental compositttion of Ni/NiO_x includes Nickel (20.0%) and Oxygen (66.7%).

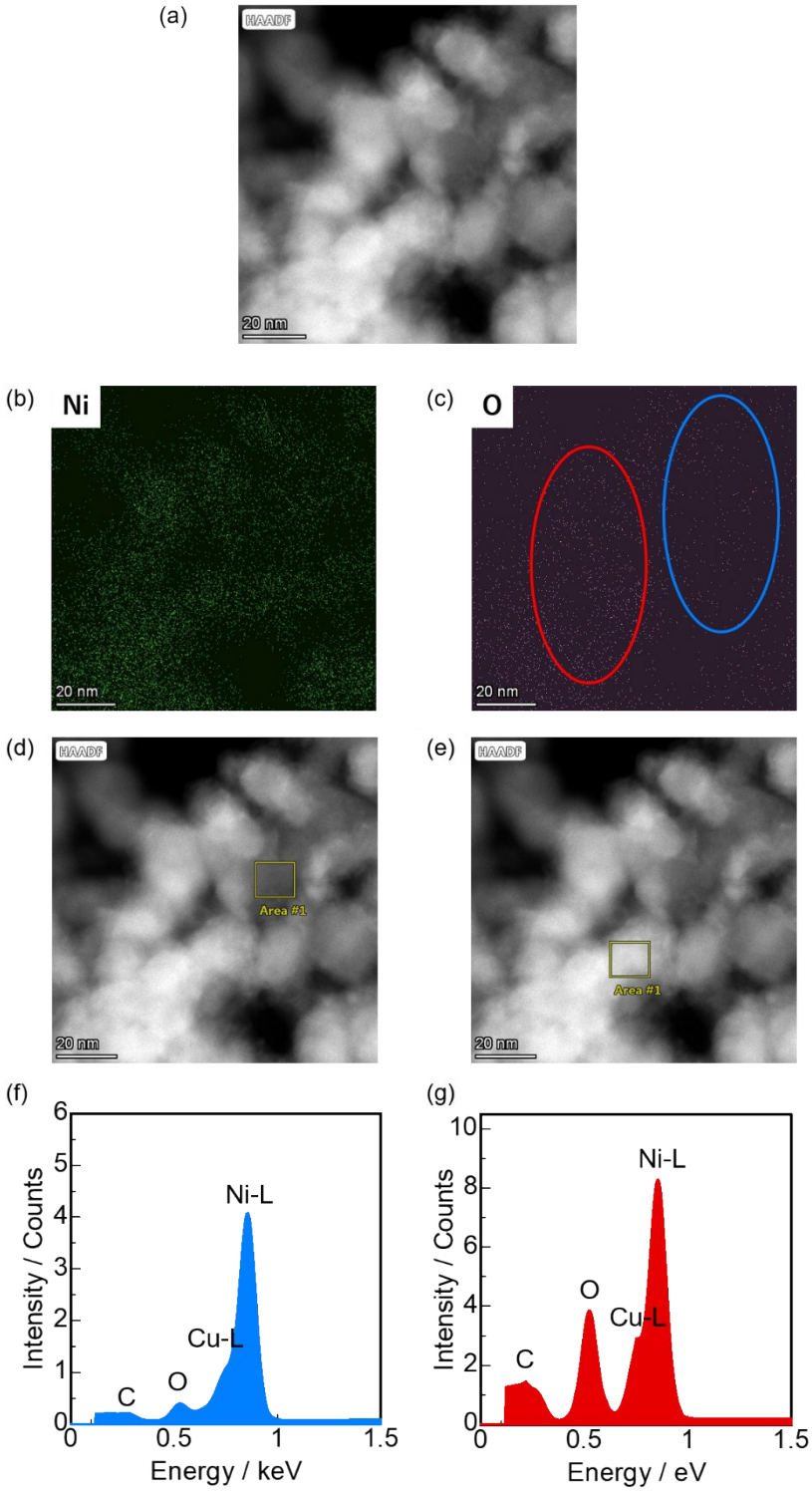

Fig. S3 HAADF-STM EDS spectra of the freeze-dried Ni/NiO_x.

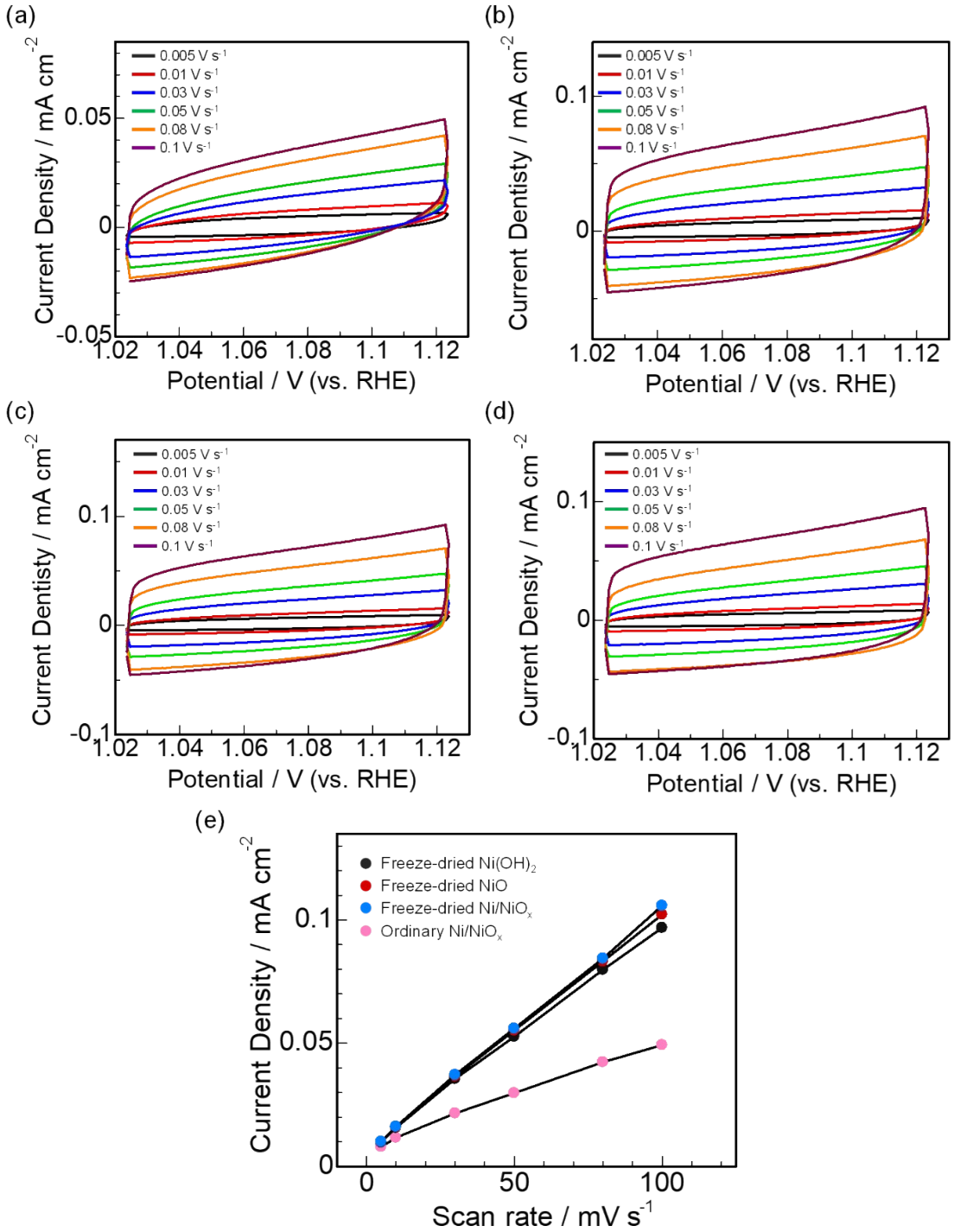

Fig. S4 CV of a) ordinary Ni/NiO_x, b) freeze-dried Ni/NiOx, c) freeze-dried $Ni(OH)_2$ and d) freeze-dried NiO collected at different scan rate in 1.0 M KOH solution; e) Calculated double-layer capacitance (Cdl) of each sample.

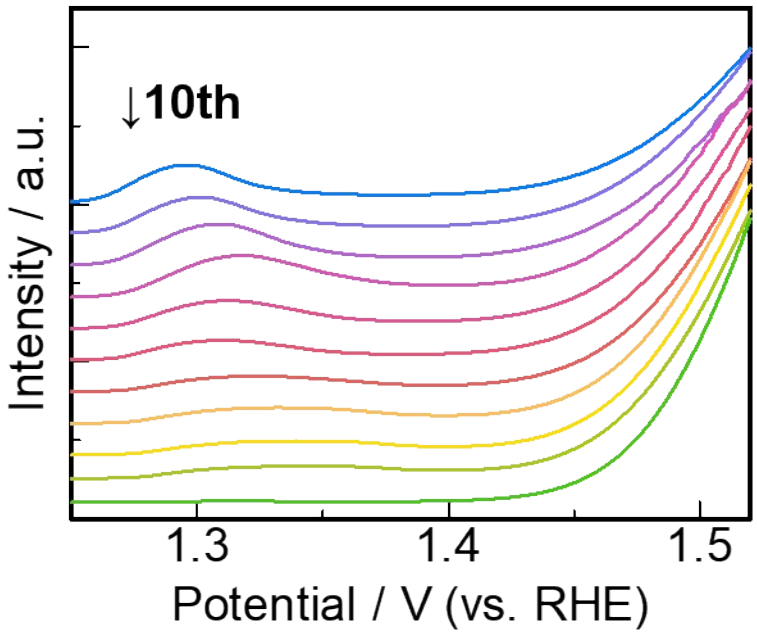

Fig. S5 The OER curves of Freeze-dried Ni/NiO_x between 1st and 100th.

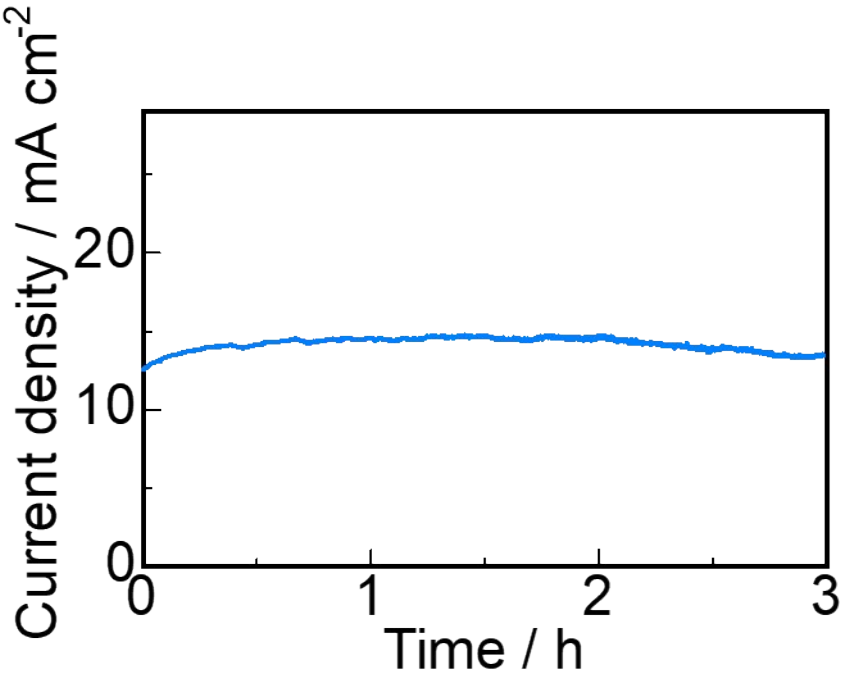

Fig. S6 The chronoamperometric response of freeze-dried Ni/NiO_x at 1.5V

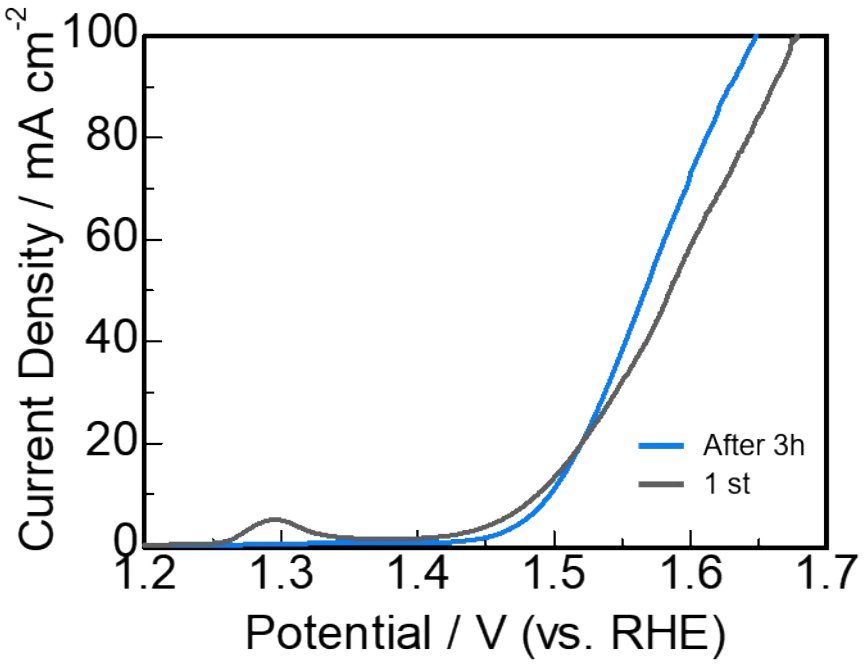

Fig. S7 The OER curves of Freeze-dried Ni/NiO_x after 3h of the chronoamperometric measurement.

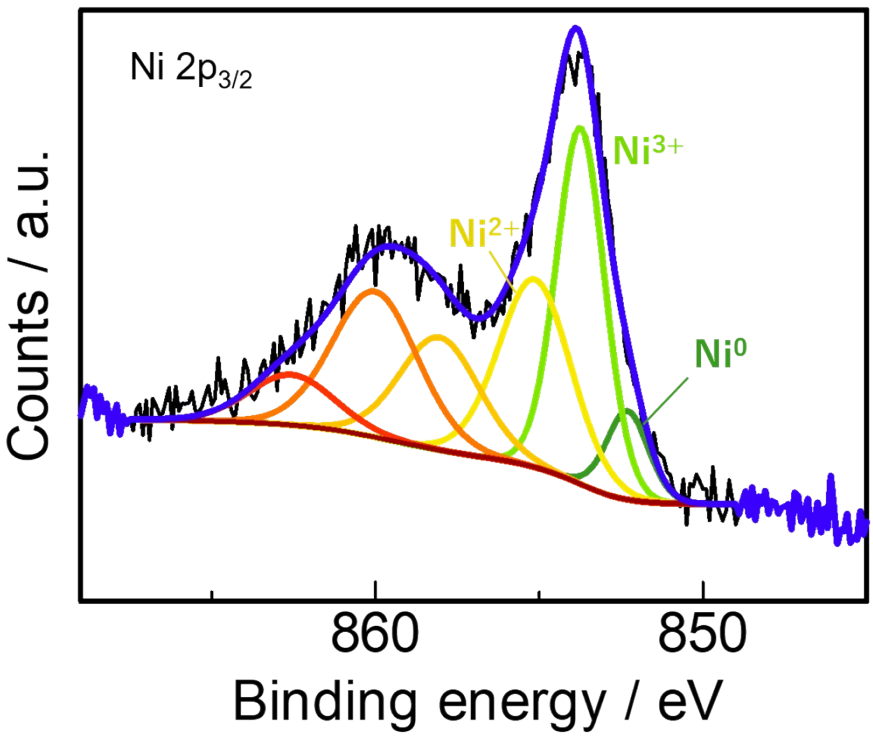

Fig. S8 XPS spectra of Freeze-dried Ni/NiO_x after 100 scans.

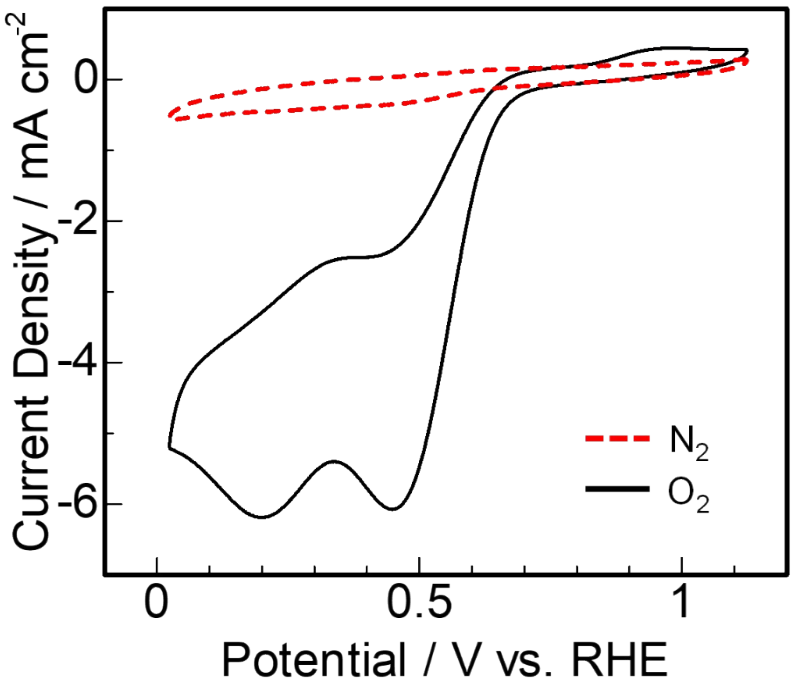

Fig. S9 The CV measurement of freeze-dried Ni/NiO_x under N_2 or O_2.

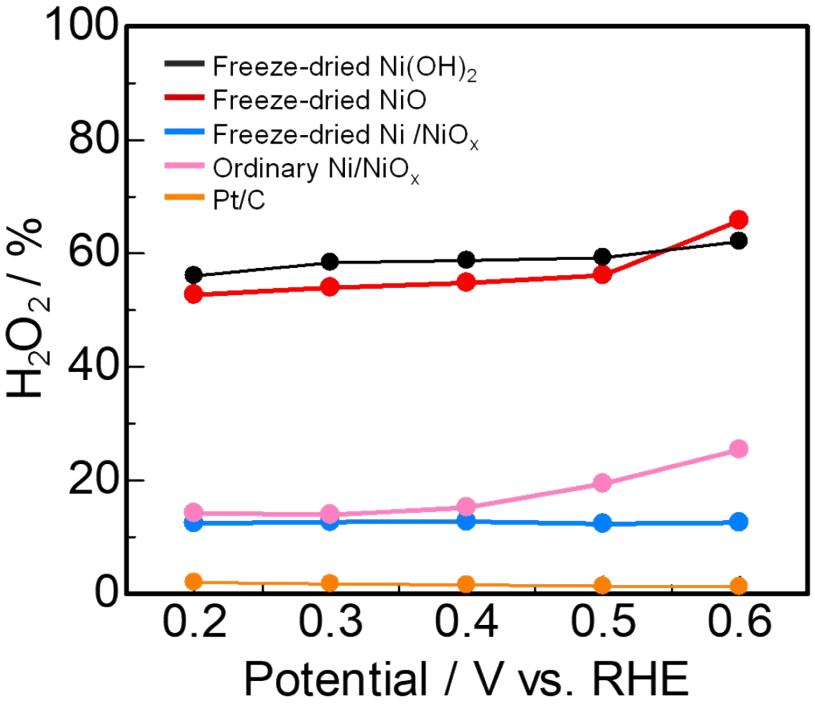

Fig. S10 The yield of hydrogen peroxide.

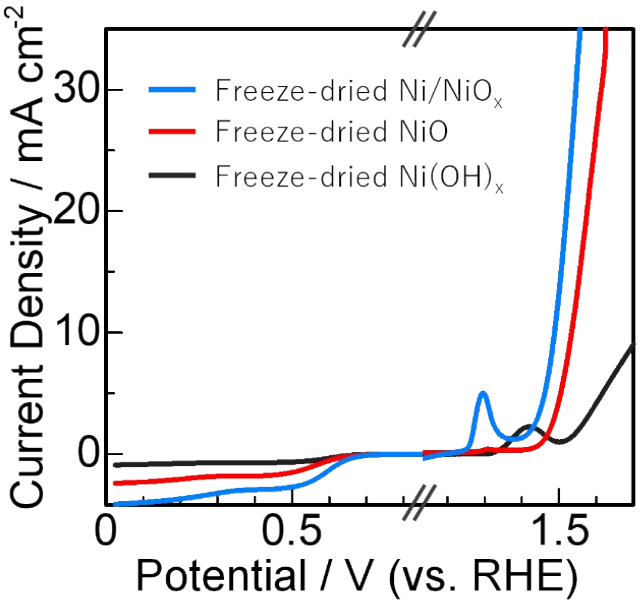

Fig. S11 LSV curves for OER and ORR to evaluate ΔE.

Table S1 Comparison of the OER and ORR activity of freeze-dried Ni/NiO_x with those of Ni based products in reference. Reference numbers belong to the main text.

	Over potential ($E_{i=10}$)	Tafel slope	Harf-wave potential ($E_{1/2}$)	Electron transfer number	Electrolyte	Ref. number
Freeze-dried Ni/NiO_x	240	37	0.62	3.8	1M KOH	This work
Freeze-dried NiO	309	50	0.55	3.0	1M KOH	This work
Freeze-dried $Ni(OH)_2$	370	35	0.56	2.9	1M KOH	This work
NiO/NF-400	310	54	–	–	1M KOH	[15]
Porous Ni/NiO	260	62	0.75	3.8	0.1M KOH	[22]
Ni/NiO nanosheets	300	71	–	3.3	0.1M KOH	[22]
NiO nanosheets	460	178	–	3.0	0.1M KOH	[22]
NiO_x/Ni	390	80	–	–	1M KOH	[32]
AC-NiO	320	49	–	–	1M KOH	[37]
NiO	360	76	–	–	1M KOH	[37]
Ni/NGr	390	98	0.62	3.7-3.9	0.1M KOH	[38]
Ni/Gr	550	–	–	–	0.1M KOH	[38]
Ni@NiO/N-C NW	390	100	–	–	1M KOH	[39]
Ni-NiO@3DHPG	310	55	–	–	1M KOH	[40]

Reference

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