Supporting Information for:

Operando X-ray absorption spectroscopy of hyperfine β-FeOOH nanorods modified with $Ni(OH)_2$ under electrocatalytic water oxidation condition

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-Syntheses of materials

-Ni-Modified β-FeOOH Colloidal Solutions

All starting materials were used as-received. $FeCl_3 \cdot 6H_2O$ (99%), $Ni(NO_3)_2 \cdot 6H_2O$ (99.9%), ethylenediamine and a 1 M aqueous KOH solution were purchased from Wako Pure Chemical Industries (Japan). Each Ni-doped β-FeOOH colloidal solution was prepared by combining 500mL of an aqueous solution containing $FeCl_3 \cdot 6H_2O$ (0.1 M as Fe^{3+}) and the desired amount of $Ni(NO_3)_2 \cdot 6H_2O$ along with ethylenediamine, followed by pH adjustment to the range of 2.0-2.4 and agitation with a magnetic stirrer at room temperature. After 30 min continuous stirring, the solution was aged overnight at room temperature.

-Preparation of the Ni-Modified β-FeOOH Nanorods on Carbon Paper (CP) [1]

Ni-modified β-FeOOH nanorods on CP were prepared by depositing 1000 μL of a given colloidal solution together with a small amount of ethanol on the CP (TORAY, TGP-H-060, 1.8 x 2.2 cm), followed by drying at room temperature for 6 h and further drying under vacuum at 40 °C. The samples were subsequently washed with water and a 0.1 M aqueous KOH solution and then dried. In this manner, a 1.0 mg quantity of the nanorods was loaded on each 1 cm^2 of the CP.

1. T. M. Suzuki, T. Nonaka, K. Kitazumi, N. Takahashi, S. Kosaka, Y. Matsuoka, K. Sekizawa, A. Suda and T. Morikawa, *Bulletin of the Chemical Society of Japan*, 2018, **91**, 778–786.

-Experimental Methods

-Electrochemical Measurements of Water Oxidation.

The electrochemical characteristics of nanorod samples on CP electrodes were investigated in an aqueous 0.1 M KOH solution (pH 12.8) with a three-electrode configuration using a Ag/AgCl reference electrode and a Pt wire counter electrode. Electrochemical O_2 and H_2 evolution during water splitting by the same electrodes were examined using a Pyrex sealed glass reactor (total volume: 115.5 ml) in an aqueous 0.1 M KOH solution (60 ml). A three-electrode configuration incorporating a Ag/AgCl reference electrode and a Pt wire counter electrode was employed with an applied potential of +1.56V (vs. RHE). The amounts of O_2 and H_2 generated with the above electrodes as the anode and a Pt cathode were determined using a gas chromatograph equipped with a thermal conductivity detector (GC-2014, Shimadzu). Potentials in all graphs are shown without subtraction of iR drop.

-Operando Hard X-ray XAS

Hard X-ray XAS (5−9 keV), X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses were conducted using fluorescence yield detection with a 30 element Ge detector (Canberra). When acquiring in situ/operando XAS data, an H-shaped glass cell with a glass frit between the two compartments (Adams & Chittenden Scientific Glass, USA) was used, as reported previously.[2,3]

The sample compartment of the cell contained a hole with a diameter of approximately 8.0 mm in its upper half and a β-FeOOH:Ni/a-$Ni(OH)_2$ sample on CP was glued on to this hole together with a 13 μm thick Kapton film, which was placed on the outer side of the material facing the X-ray beam. The cell was mounted at an angle of 45° with respect to the X-ray beam and the fluorescence signal was detected orthogonally, as shown in Figure 2.

2. M. Favaro, W. S. Drisdell, M. A. Marcus, J. M. Gregoire, E. J. Crumlin, J. A. Haber and J. Yano, *ACS Catalysis*, 2017, **7**, 1248-1258.
3. F. H. Saadi, A. I. Carim, W. S. Drisdell, S. Gul, J. H. Baricuatro, J. Yano, M. P. Soriaga and N. S. Lewis, *J. Am. Chem. Soc.* 2017, 139, 12927−12930

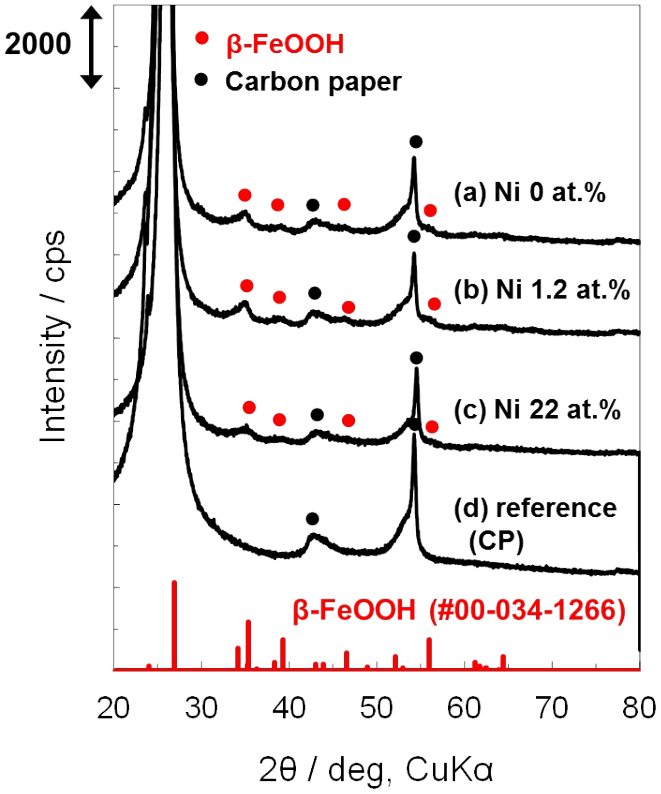

Figure S1. The XRD patterns of β-FeOOH:Ni nanorods synthesized in a one-pot process with different total Ni concentrations, in the form of electrodes deposited on CP.

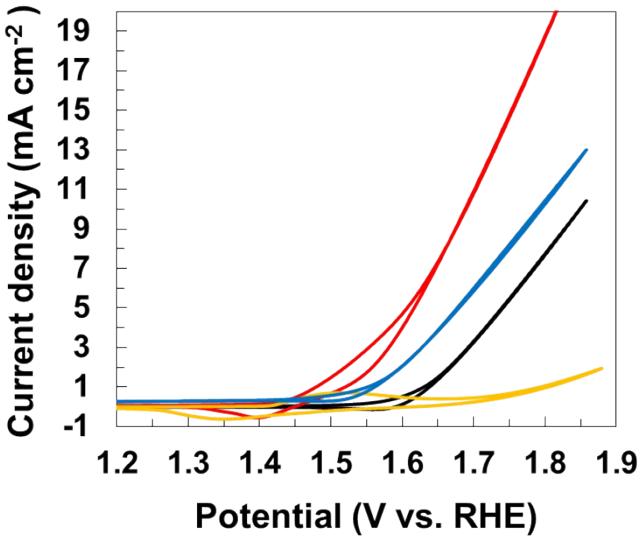

Figure S2 Current-potential curves acquired during OER in 0.1 M KOH over pure β-FeOOH (black), 1%-Ni (β-FeOOH:Ni) (blue), 22%-Ni (β-FeOOH:Ni/a-Ni(OH)$_2$) (red), and amorphous Ni(OH)$_2$ (yellow).

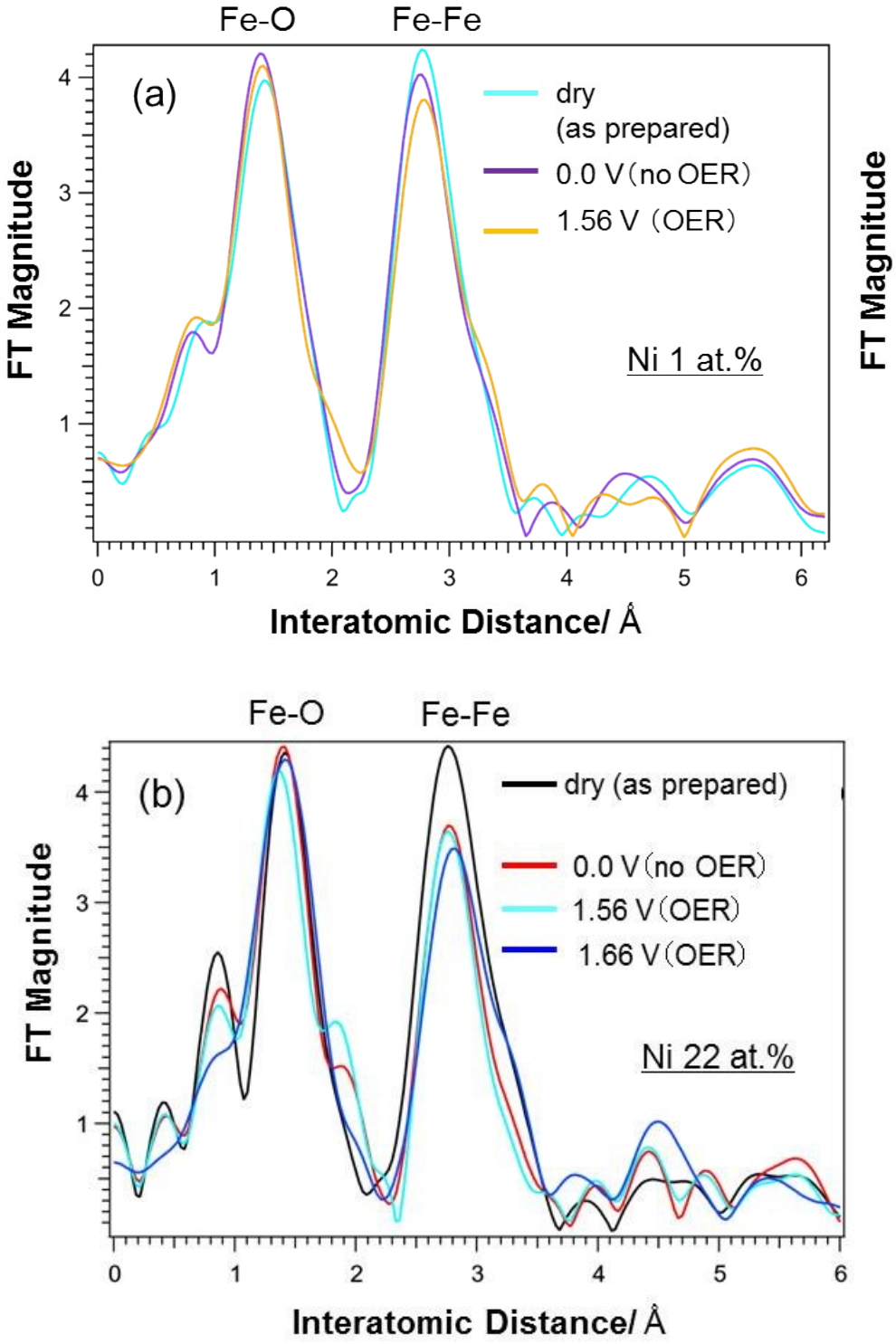

Figure S3 Fe EXAFS spectra acquired from (a) 1% Ni (β-FeOOH:Ni) and (b) 22% Ni (β-FeOOH:Ni surface-decorated with $Ni(OH)_2$) under dry, OC potential and OER potential (+1.56 V) conditions.

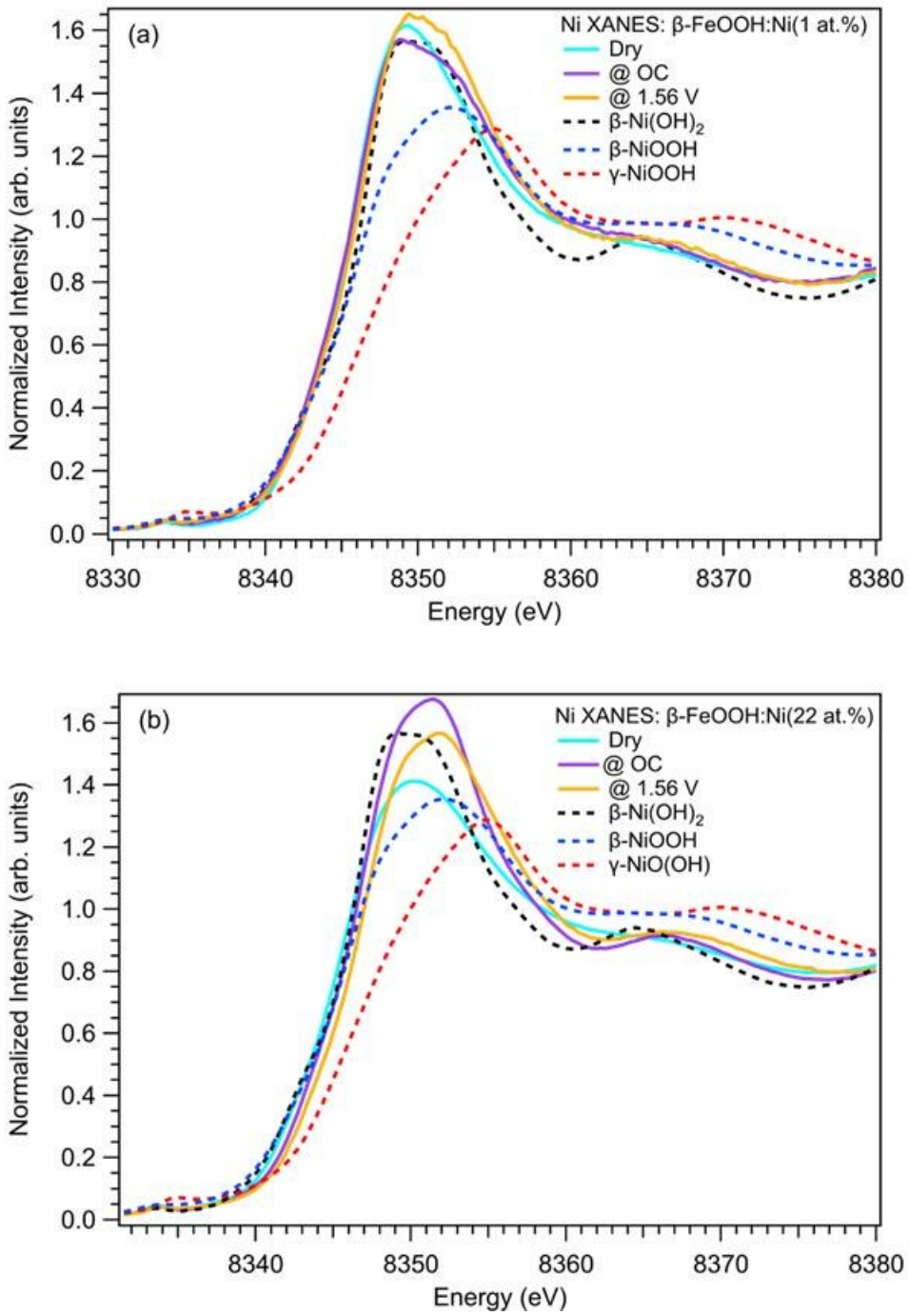

Figure S4 XANES Ni k-edge data acquired from 1 and 22% Ni samples.

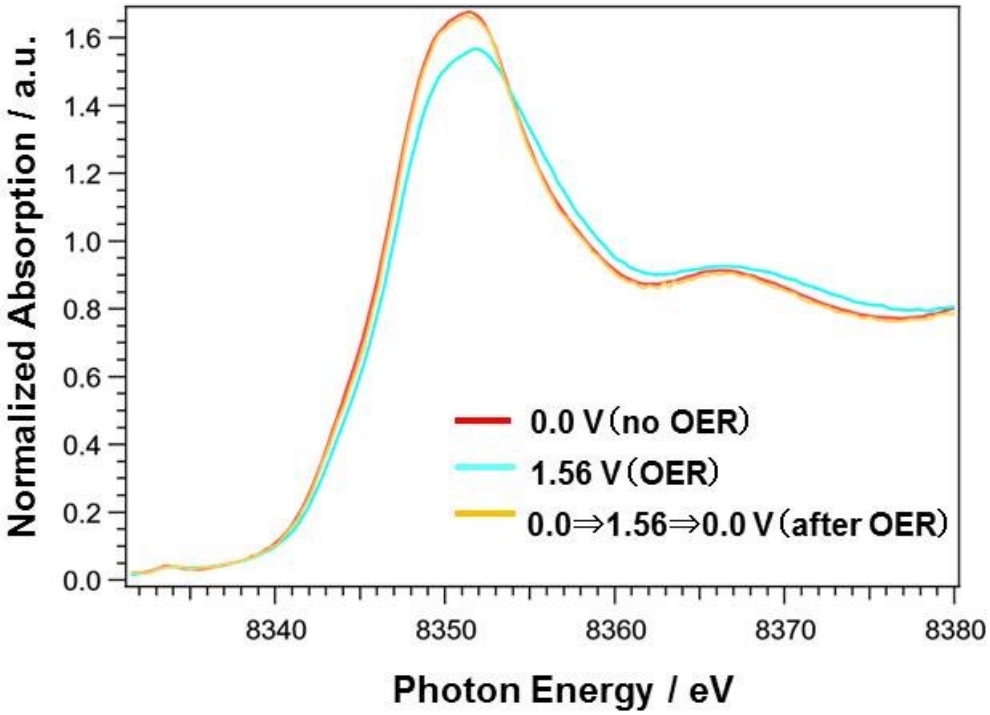

Figure S5 XANES Ni data acquired by cycling from the OC to OER potential and back to the OC potential, indicating reversible changes in the Ni species in a 22% Ni sample.

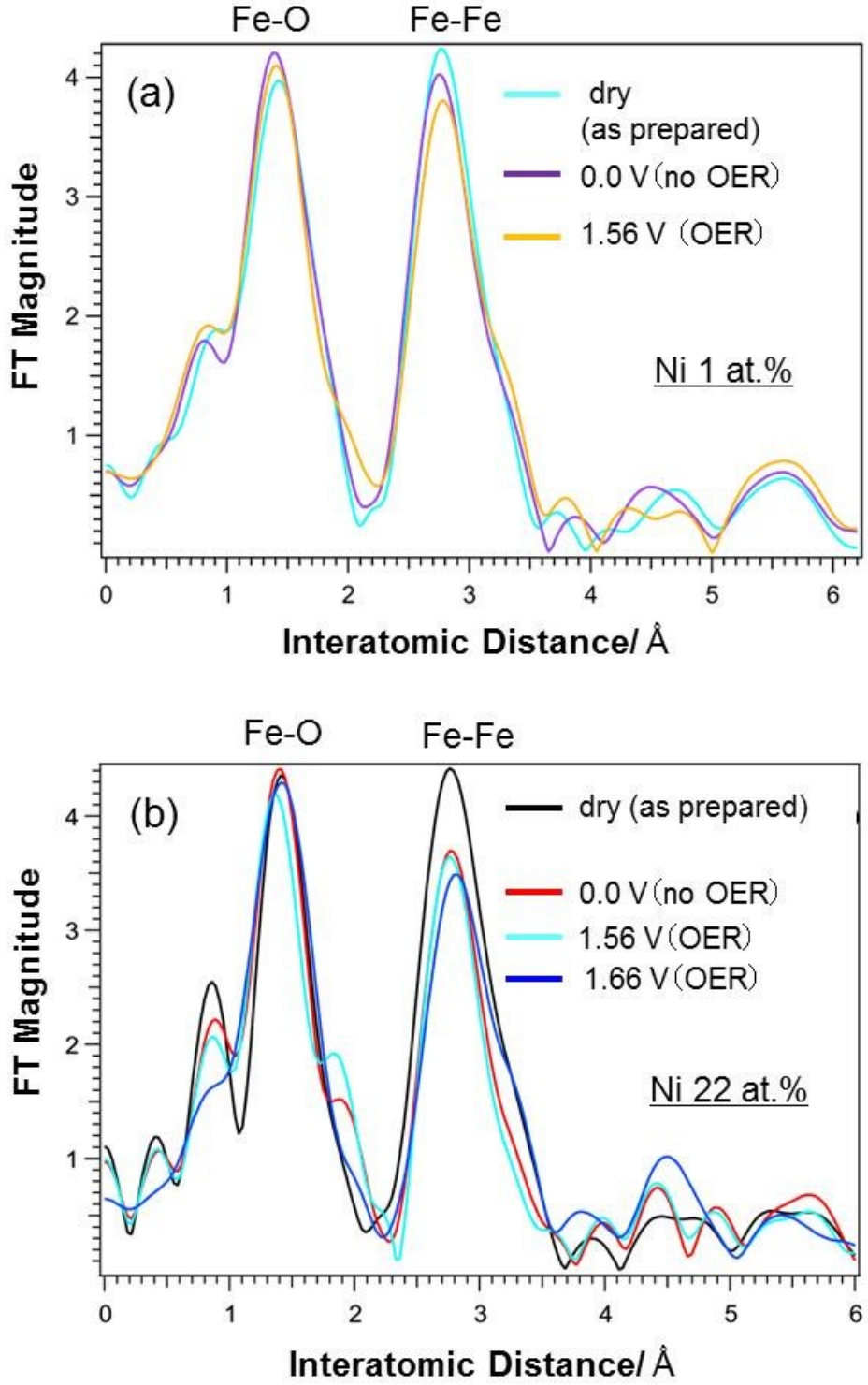

Figure S6 *r*-space EXAFS Fe k-edge data acquired from 1 and 22% Ni samples.

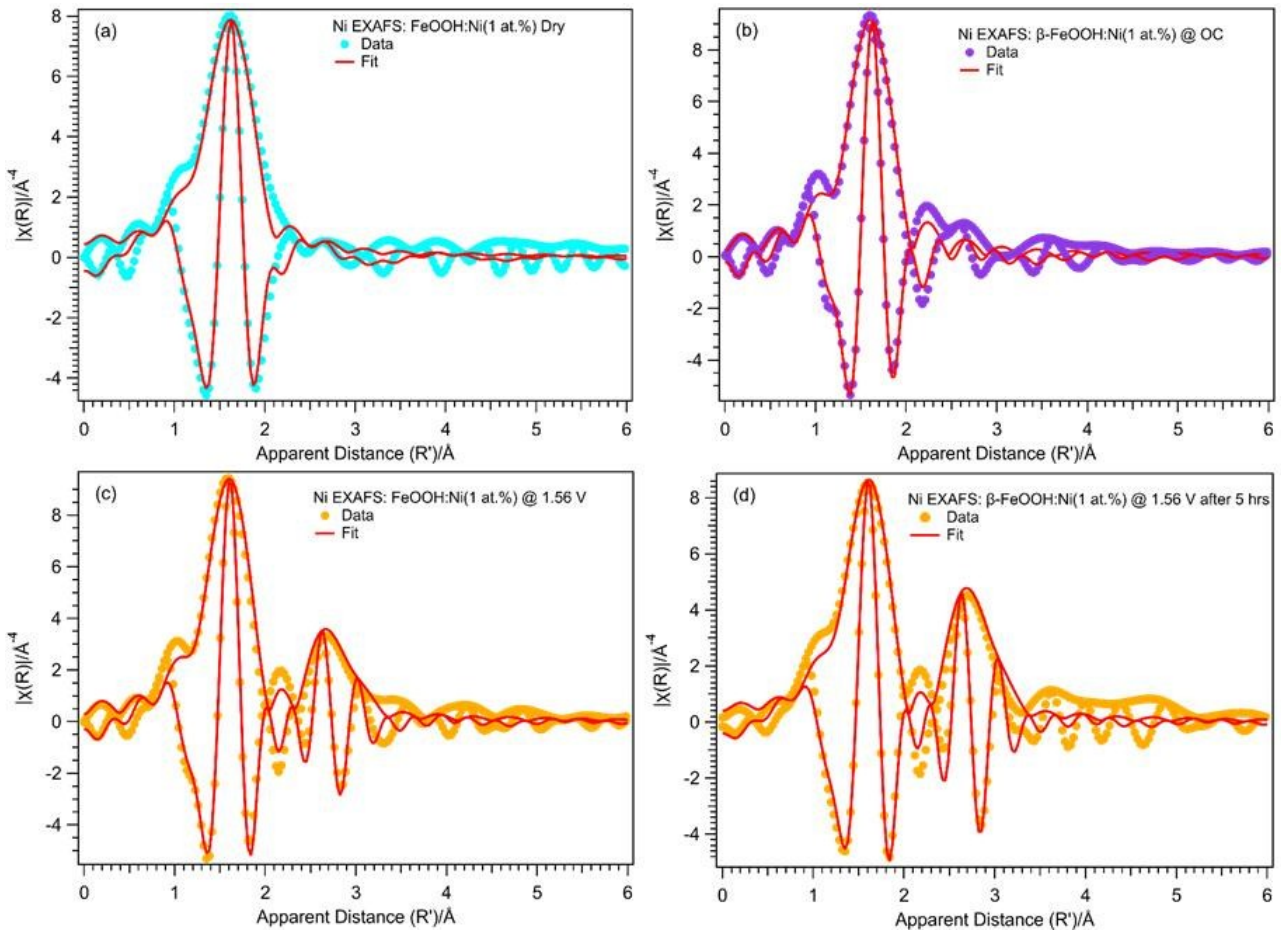

Fig. S7 *r*-space EXAFS data with fits for β-FeOOH:Ni (1 at.%) under (a) dry, (b) OC potential and (c) OER conditions (+1.56 V vs RHE), and (d) after 5 h of catalytic activity. The fast oscillation is the real part of the Fourier transform.

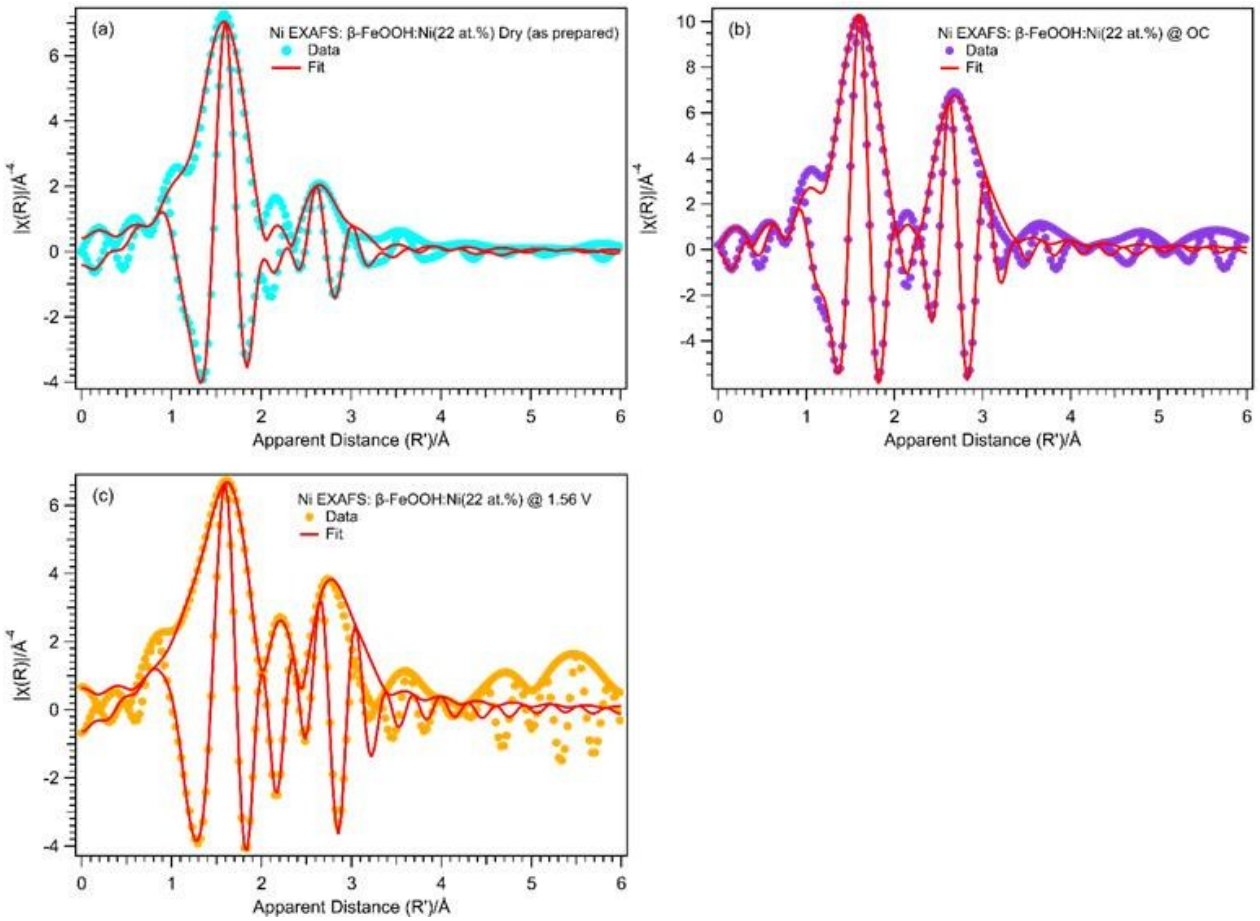

Fig. S8 r-space data with fits for β-FeOOH:Ni/a-$Ni(OH)_2$ (22 at.%) corresponding to dry sample (a) at open circuit potential (b) and under catalytic conditions at +1.56 V vs RHE (c).

Table S1 Best fit parameters.

Sample	Path	R (Å)	N	σ^2 (10^{-3} Å^2)	R-factor (%)	ΔE_0 (eV)
FeOOH:Ni (1 at.%)						
As-syn	Ni-O	2.03±0.02	2.22±0.88	2.84±2.18	1.93	0.70±1.67
	Ni-O	2.16±0.02	3.78±0.88	5.57±2.40		
@ OC	Ni-O	2.08±0.01	6	5.89±0.57	0.14	-1.82±0.73
@ 1.56 V	Ni-O	2.07±0.01	6	5.66±0.89	1.49	-1.77±0.87
	Ni-Ni	3.10±0.02	2.19±0.55	6.72±0.57		
@ 1.56 after 5 hrs	Ni-O	2.07±0.02	6	6.70±1.37	2.56	-1.21±1.26
	Ni-Ni	3.11±0.02	3.67±0.88	8.00±0.05		
FeOOH:Ni (20 at. %)						
As-syn	Ni-O	2.07±0.01	6	9.79±0.96	1.84	-1.42±0.78
	Ni-Ni	3.09±0.02	1.56±0.40	9.57±1.21		
@ OC	Ni-O	2.06±0.01	6	4.70±0.93	1.23	-1.42±0.89
	Ni-Ni	3.10±0.01	5.5±0.65	8.00±0.91		
@ 1.56 V	Ni-O	1.90±0.05	4.92±0.64	6.10±3.69	1.30	-2.03±1.11
	Ni-O	2.06±0.01	1.08±0.64	6.10±3.69		
	Ni-Ni	2.86±0.02	3.88±0.57	5.37±4.73	3.66	
	Ni-Ni	3.10±0.01	1.62±0.57	7.00±1.01		