Supplementary Information (SI) for Journal of Materials Chemistry A.

Supplementary information for

Redox-Mediated Origin of Fe–Ni Synergy in Oxygen Evolution Catalysis

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This PDF file includes:

Electrochemical Analysis and Calculations

Figures. S1-S6

Table S1

Electrochemical Analysis and Calculations

(1) The potentials measured against the Hg/HgO reference electrode were converted to the reversible hydrogen electrode (RHE) scale using the Nernst equation:

$E_{\mathrm{RHE}} = E_{\mathrm{Hg/HgO}} + 0.098 + 0.059\mathrm{pH}_{\mathrm{electrolyte}}$

$E_{\mathrm{RHE}} = E_{\mathrm{Hg/HgO}} + 0.926$ (for 1.0 M KOH (pH 14)

(2) The TOF of OER electrocatalysts was calculated according to the following equation,

$\mathrm{TOF} = \frac{jA}{4Fm}$

where j is the current density at a given overpotential, e.g. η = 300 mV, A is the surface area of the electrode, F is the Faraday constant, and m is the number of moles of the metal on the electrodes. In this study, we assumed that all the metal sites were actively involved in the OER.

(3) Coulometric titration was performed by integrating the $\mathrm{Ni}^{3+} \rightarrow \mathrm{Ni}^{2+}$ reduction current following an anodic hold at 1.45 V vs RHE. The integrated charge (Q) was used to calculate the number of electrons transferred per Ni atom, enabling determination of the average Ni oxidation state.

Figure S1

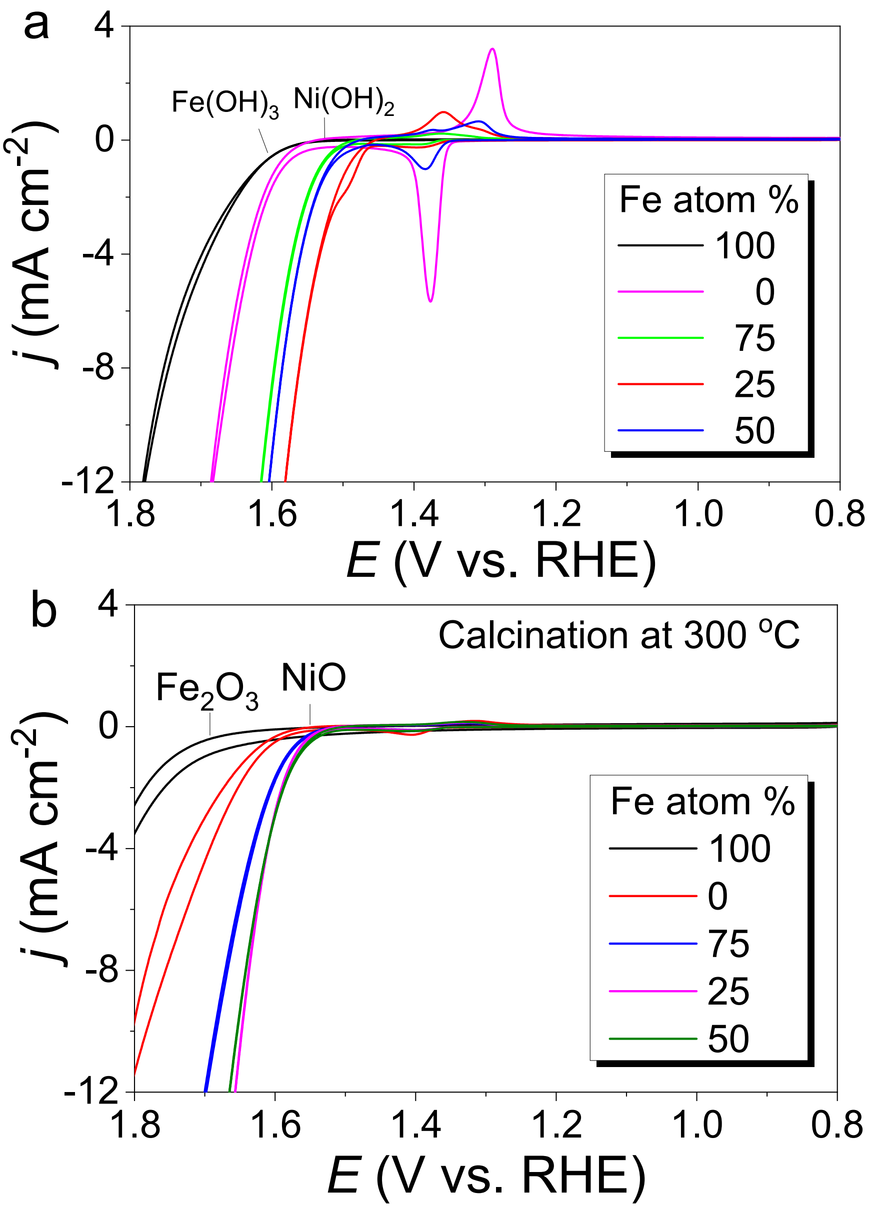

Fig. S1 OER CVs of FeNi LDHs on a GCE measured in Fe-free 1.0 M KOH_{aq} (scan rate: 50 mV s^{-1}): (a) as-synthesized FeNi LDHs and (b) FeNi LDHs calcined at 300 °C, each with varying Fe at%.

Figure S2

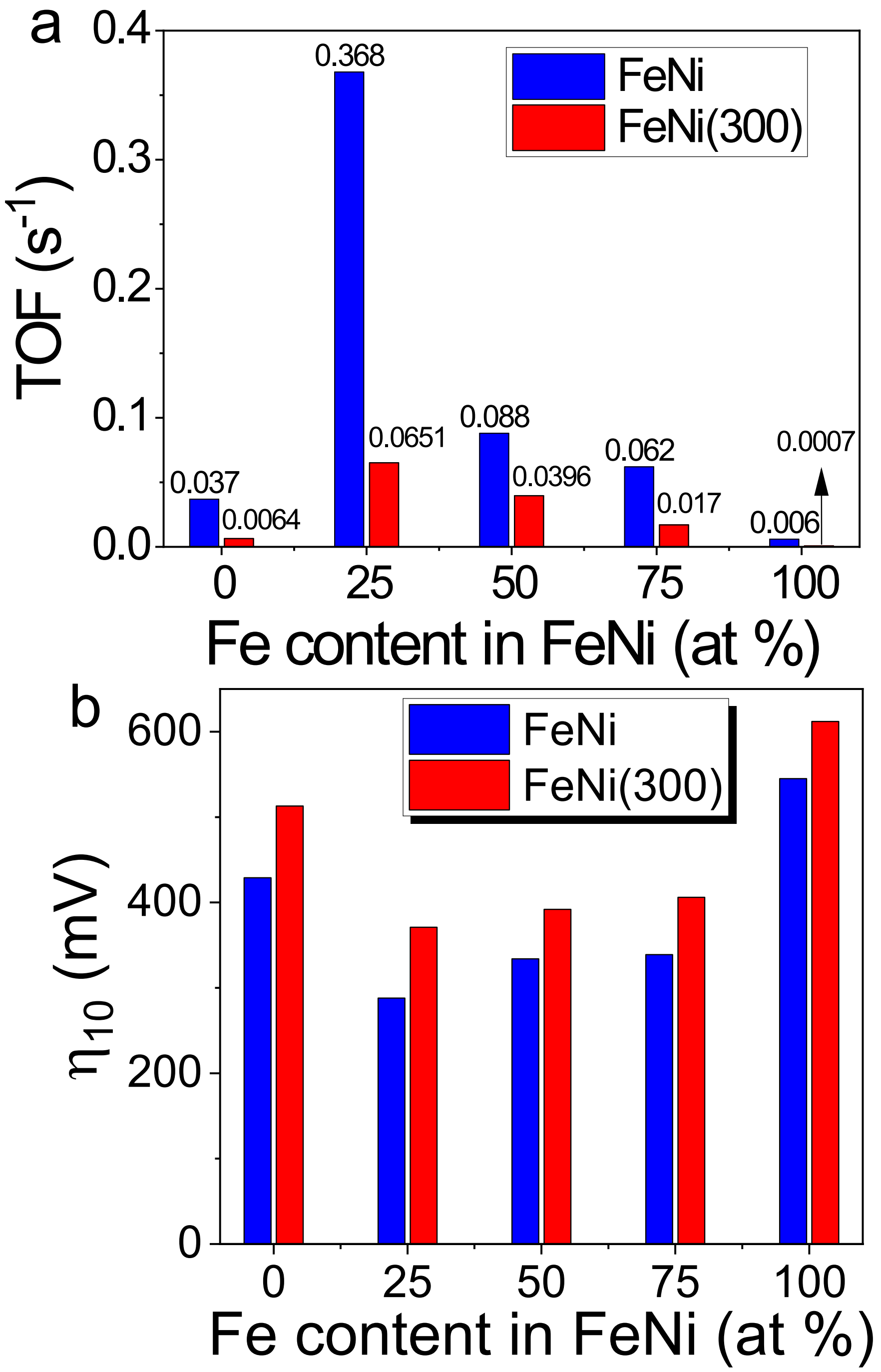

Fig. S2 OER activity of FeNi LDHs: (a) TOF and (b) η_{10}: as-synthesized FeNi LDHs (blue) and FeNi LDHs calcined at 300 °C (red), each with varying Fe at%.

Figure S3

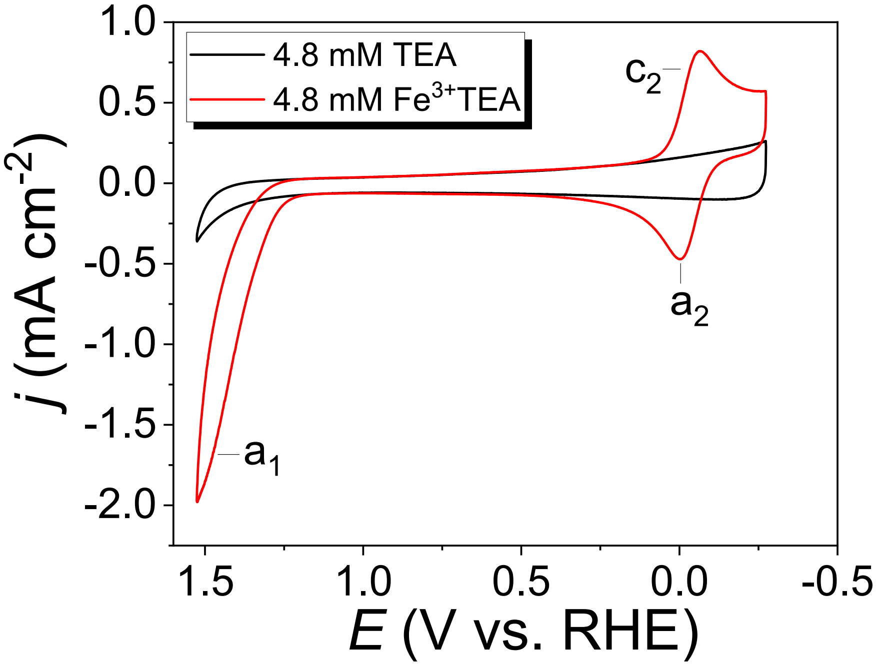

Fig. S3 CVs of 4.8 mM TEA (black line) and 4.8 mM Fe^{3+}TEA (red line) in 1 M KOH$_{aq}$ on a GCE (scan rate: 50 mV s^{-1}).

Figure S4

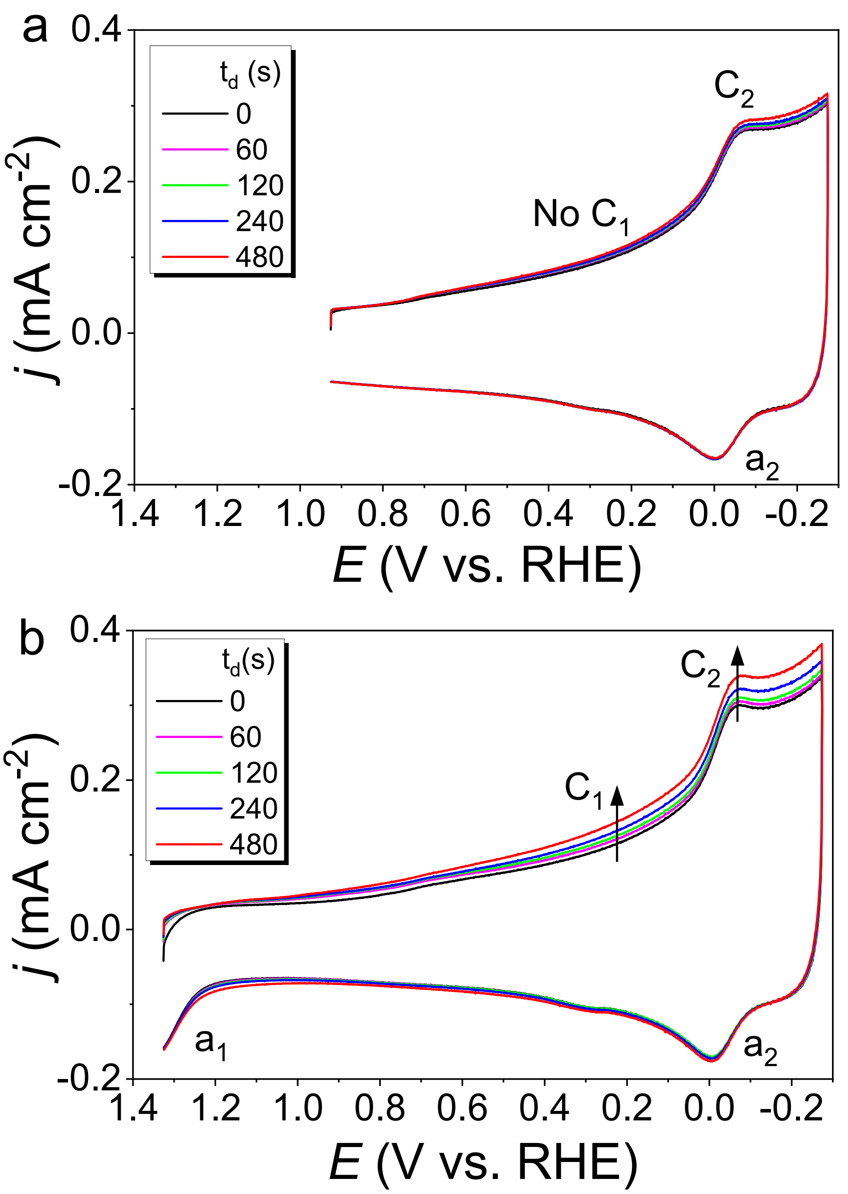

Fig. S4 CVs of 0.6 mM Fe^{3+}TEA in 1 M KOH$_{aq}$ on a GCE (scan rate: 50 mV s^{-1}). Before potential scanning, the electrode was held at (a) 0.93 V (<1.2 V) or (b) 1.33 V (>1.2 V) for varying durations.

Figure S5

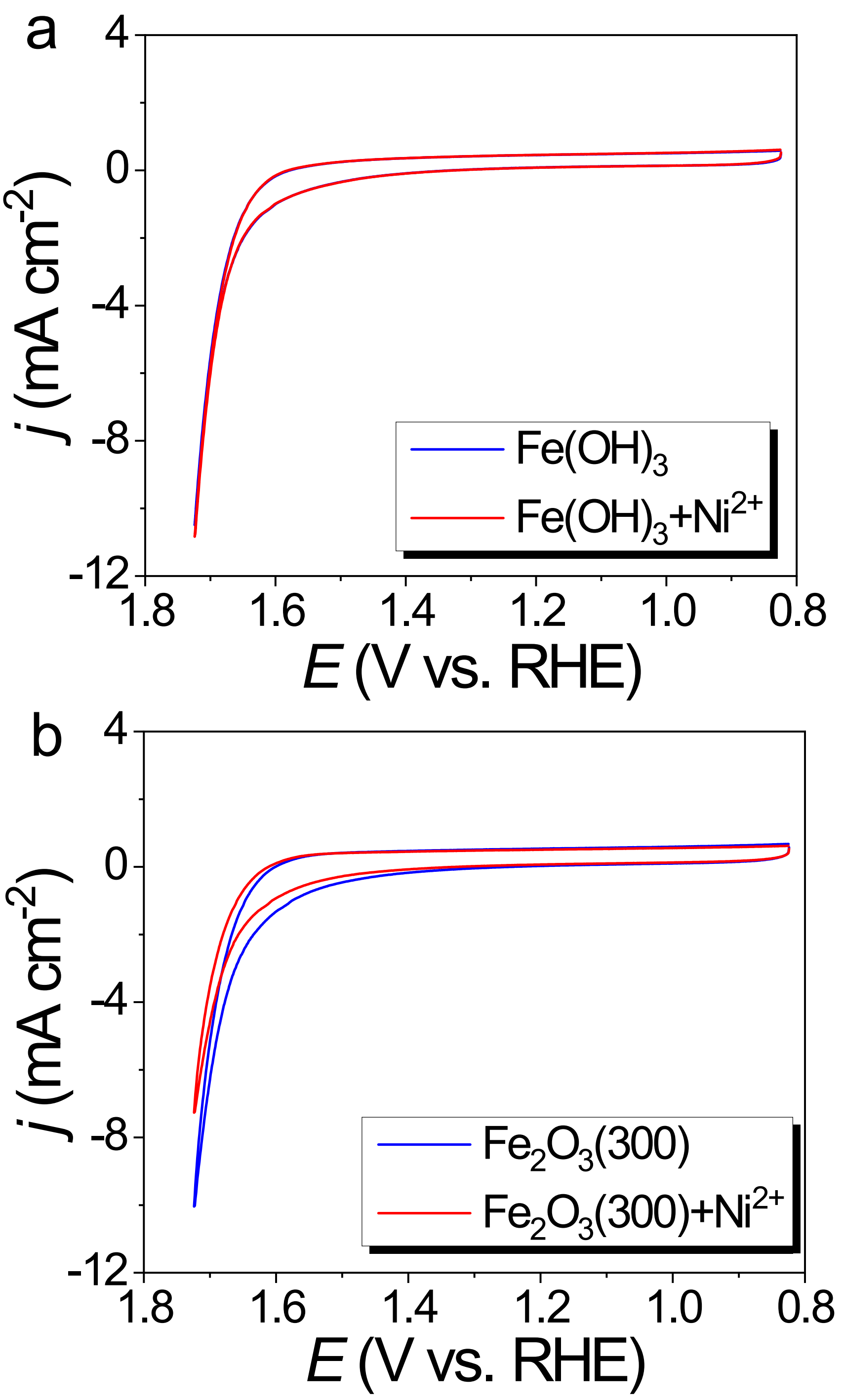

Fig. S5 CVs of (a) $Fe(OH)_3$ and (b) Fe_2O_3(300) in 1 M KOH_{aq} without (blue line) and with (red line) saturated Ni^{2+} (scan rate: 50 mV s^{-1}).

Figure S6

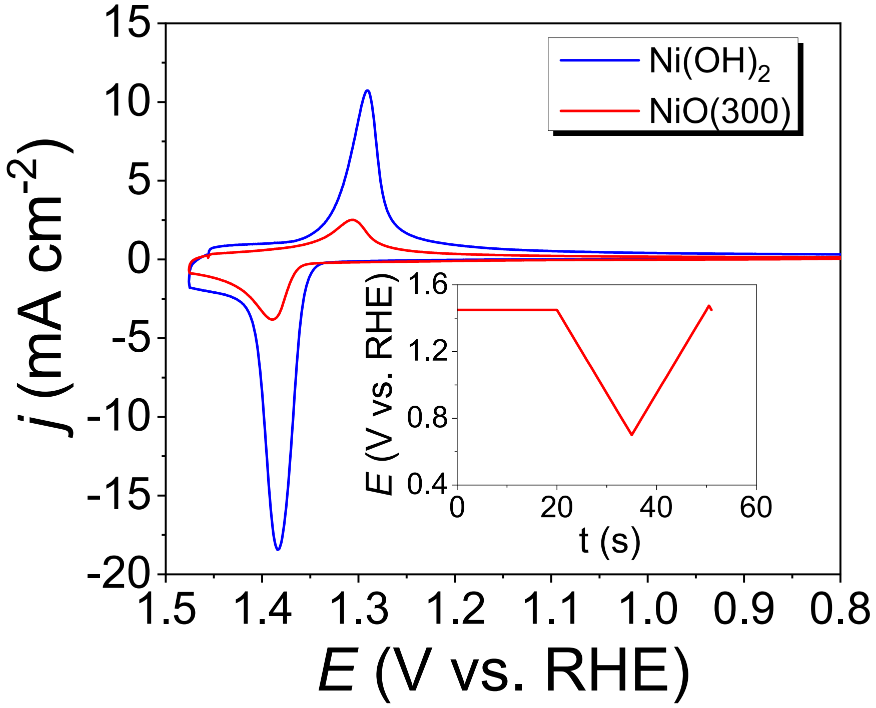

Fig. S6 CVs of Ni(OH)$_2$ (blue) and NiO(300) (red) on the GCE in Fe-free 1 M KOH$_{aq}$ (scan rate: 50 mV s^{-1}). Before scanning, the electrodes were held at 1.45 V (*vs*. RHE) for 20 s to fully oxidize Ni^{2+} to Ni^{3+}. Insets: Potential sweep profiles *vs*. time.

Table S1. The best-fiting FT-EXAFS parameters of catalysts*

	Scattering Path	N	σ^2 (Å^2)	R(Å)	R_f
Ni foil	Ni-Ni	12	0.006	2.48	0.001
NiO	Ni-O	6	0.007	2.06	0.013
β-Ni(OH)$_2$/*β*-NiOOH	Ni-O	6	0.006	2.08	0.019
At 1.45V without Fe^{3+}TEA	Ni-O	5.9	0.007	1.84	0.01
At 1.45V with Fe^{3+}TEA	Ni-O	5.8	0.004	1.82	0.01

*Where N is coordination number, R is distance between absorber and backscatter atoms, σ^2 is Debye–Waller factor value, R_f is R-factor characterizing the goodness of fit. . S_o^2 was fixed to 0.7 as determined from NiO. Error bounds (accuracies) characterizing the structural parameters obtained by EXAFS data analysis are estimated to be as follows: N, ±20%; R, ±1%; and σ^2, ±20% (with phase correction).