Supporting Information

Influence of iron doping on tetravalent nickel content in catalytic oxygen evolving films

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Experimental Methods

A. Materials. $Ni(NO_3)_2 \cdot 6H_2O$ (99.9985%) and $FeCl_2 \cdot 4H_2O$ (99%) were used as received from Strem. KOH (88%) and H_3BO_3 (99.9%) were reagent grade and used as received from Macron. 65–71% TraceSELECT Ultra nitric acid, TraceSELECT nickel standard for ICP and TraceSELECT iron standard for ICP were used as received from Fluka Analytical. Chelex® 100 Resin was obtained from Bio-Rad. All electrolyte solutions were prepared with type I water (EMD Millipore, 18.2 MΩ cm resistivity). Fluorine-doped tin-oxide coated glass (FTO; TEC-7) was purchased as pre-cut 1 cm × 2.5 cm glass pieces from Hartford Glass. P-doped silicon wafers were purchased from Silicon Quest International as precut 4´´ diameter wafers with 2-3.5 Ω cm resistivity, 500–550 μm thickness, and <100> crystal orientation. Unless stated otherwise, all experiments used FTO with 7 Ω/sq surface resistivity.

B. Electrolyte Scrubbing Using Ni(OH)$_2$. KOH electrolyte solutions were cleaned by scrubbing the electrolyte with $Ni(OH)_2$ according to published protocol.[1] In a 50 mL polypropylene conical tube rinsed with 2% trace nitric acid and type I water, ~2 g of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in ~5 mL of type I water. Approximately 20 mL of reagent grade 1 M KOH was added to precipitate $Ni(OH)_2$. The mixture was then centrifuged at 4400 rpm for 1 min, and the solution was decanted. The $Ni(OH)_2$ was washed with ~20 mL of 0.1 M of reagent grade KOH three times by suspending the solid through agitation and decanting the solution after centrifuging for 1 min at 4400 rpm. The washed $Ni(OH)_2$ solid was then re-suspended in 50 mL of reagent grade 1 M KOH to scrub trace Fe from the solution. The mixture was sonicated for 10 min to ensure even dispersion of nickel hydroxide and incubated at room temperature for 3 h. The scrubbed solution was then decanted and stored after centrifuging the mixture at 4400 rpm for 10 min. All scrubbed solutions were also filtered using Corning polystyrene 0.45 μM filters prior to use to further remove any residual nickel from the scrubbing process.

C. Electrolyte Cleaning Using Chelating Resin. KB$_i$ electrolyte solutions were cleaned by treating the electrolyte with regenerated Chelex® 100 Resin (Bio-Rad, Catalog # 210011676) according to the manufacturer's protocol[2] and published protocol[3] with slight modifications. Approximately 15 g of resin was used to clean ~400 mL of buffer at a time. Chelex resin was first washed in 3 M TraceSELECT HNO_3 and then rinsed with 4 L of type I water. All solutions were stirred in 1 L polystyrene bottles and filtered through clean Corning polystyrene 0.45 μM filters. Chelex resin was then regenerated by stirring the resin for 12 h in 1 M TraceSELECT HCl followed by rinsing with 5 L of type I water. The resin was

1. Trotochaud L, Young SL, Ranney JK, Boettcher SW (2014) Nickel-iron oxyhydroxide oxygen-evolution electrocatalysts: the role of intentional and incidental iron incorporation. *J Am Chem Soc 136*:6744–6753.

2. Chelex® 100 Chelex 20 Chelating Ion Exch. Resin Instr. Man. 2014, http://www.bio–rad.com/.

3. Wuttig A, Surendranath Y (2015) Impurity ion complexation enhances carbon dioxide reduction catalysis. *ACS Catal* 5:4479–4484.

then stirred with 1 M KOH (99.99%, semiconductor grade, Sigma-Aldrich) for 24 h at 60 °C. Chelex resin was then rinsed with type I water until the pH of the filtrate was that of the electrolyte to be cleaned, pH 9.2. The prepared resin was then stirred with the 1 M KB_i pH 9.2 electrolyte to be cleaned for at least 72 h before being filtered and kept in clean polystyrene bottles previously washed with 2% nitric acid. pH measurements of 1M KB_i buffer after resin cleaning confirm no pH changes from pH 9.2.

D. Electrochemical Methods. All electrochemical experiments were conducted using a CH Instruments 760C or 760D bipotentiostat, a BASi Ag/AgCl or a CH Instrument CHI 152 Hg/HgO reference electrode, and a Pt-mesh counter electrode in a three-electrode electrochemical cell configuration with a porous glass frit separating the working and auxiliary compartments. Measurements were performed at room temperature (23 ± 1 °C). Electrode potentials were converted to the NHE scale using E(NHE) = E(Ag/AgCl) + 0.197 V or E(NHE) = E(Hg/HgO) + 0.108 V. Overpotentials were computed using η = E(NHE) – {1.23 V – [0.059 × (pH – 0.25 log(P_{O_2}/P^0))]} = E(NHE) – {1.23 V – [0.059 × (pH – 0.25 log 0.2)]}.

E. Borate Mediated As-Deposited and Anodized NiB_i and $Fe^{tr}{:}NiB_i$ Film Preparation. As-deposited films (entry 1, Table 1, i.e., Entry 1-1) were prepared via controlled-potential electrolysis of 0.1 M KB_i, pH 9.2 electrolyte solutions containing 0.4 mM Ni^{2+}.[4] To minimize precipitation of $Ni(OH)_2$ from these solutions, 25 mL of 0.2 M KB_i was added to 25 mL of 0.8 mM Ni^{2+} solution. Unless otherwise stated, depositions were carried out using either an FTO-coated glass piece as the working electrode. FTO-coated glass electrodes were scrubbed, rinsed in acetone and isopropanol, soaked in 2% TraceSELECT nitric acid overnight and then rinsed with water prior to use in all experiments. A ~0.6 cm wide strip of Scotch tape was applied to the FTO coated side such that a 1 cm^2 area was exposed to solution. Unless stated otherwise, deposition by controlled potential electrolysis was carried out on quiescent solutions at 1.15 V without iR compensation and with passage of 1 mC cm^{-2}. A typical deposition lasted 70 s. Films were then rinsed by dipping briefly in type I water to remove any adventitious Ni^{2+} prior to electrochemical and spectroscopic analysis. Anodized NiB_i films were made by subjecting as-deposited films to 0.75 V in scrubbed 1M KOH electrolyte (Table 1, Entry 1-2) or to 1.15 V in resin cleaned 1 M KB_i pH 9.2 (Table 1, Entry 1-3) without iR compensation with stirring for 3h. At this anodic potential the film undergoes structural changes while performing OER.[5] This OER current can be tracked via amperometric current-time curves to monitor film changes. Once the OER current increases and stabilizes, the film has completed activation (primed to perform OER). To make anodized $Fe^{tr}{:}NiB_i$ films, as-deposited films (Table 1, Entry 1-1) were

4.   Dincă M, Surendranath Y, Nocera DG (2010) Nickel-borate oxygen-evolving catalyst that functions under benign conditions. *Proc Natl Acad Sci USA* 107:10337–10341.

5.   Bediako DK, Lassalle-Kaiser B, Surendranath Y, Yano J, Yachandra VK, Nocera DG (2012) Structure-activity correlations in a nickel-borate oxygen evolution catalyst. *J Am Chem Soc* 134:6801–6809.

incubated in reagent grade 1 M KB_i, pH 9.2 for a specified time at open circuit potential and then anodized in either scrubbed 1 M KOH (Table 1, Entry 1-4) or resin cleaned 1M KB_i pH 9.2 (Table 1, Entry 1-5) as described above. High Fe content Fe^{tr}:NiB_i films were made by anodizing as-deposited films (Table 1, Entry 1-1) in reagent grade 1 M KOH (Table 1, Entry 1-6) or reagent grade 1 M KB_i pH 9.2 (Table 1, Entry 1-7) as described above.

F. Borate Mediated As-Deposited and Anodized Fe^{cod}:NiB_i Film Preparation. As-deposited films (Table 1, Entry 1-8) were prepared similarly to above samples except with 0.04 mM of Fe^{2+} and 0.36 mM Ni^{2+}.[6] To minimize precipitation of $Ni(OH)_2$ and $Fe(OH)_3$ from these solutions, all solutions were degassed with Ar gas for 20 min during preparation. In addition, 25 mL of 0.2 M KB_i was added to 25 mL of 0.72 mM Ni^{2+} solution followed by addition of 180 µL of a 11.2 mM stock of Fe^{2+} made from $FeCl_2 \bullet 4H_2O$. Depositions were carried out on FTO-coated glass that were scrubbed, rinsed in acetone and isopropanol, soaked in 2% trace nitric acid overnight and then rinsed with type I water prior to use in all experiments. A ~0.6 cm wide strip of Scotch tape was applied to the FTO coated side such that a 1 cm^2 area was exposed to solution. Unless stated otherwise, deposition by controlled-potential electrolysis was carried out in quiescent solutions at 1.15 V without iR compensation and with passage of 1 mC cm^{-2}. A typical deposition lasted 110 s. Following deposition, films were rinsed by dipping briefly in type I water to remove any adventitious Ni^{2+} and Fe^{2+} prior to electrochemical and spectroscopic studies. Anodized films (Table 1, Entry 1-9) were subjected to 0.75 V in scrubbed Fe-free 1 M KOH electrolyte without iR compensation with stirring for 3 h unless stated otherwise.

G. Cyclic Voltammetry and Coulometric Titrations. Catalyst films were prepared as described above and left at open circuit for 1 min in Fe-free 1 M KOH to equilibrate and then at 0.6 V for anodized films or 0.7 V for as-deposited films for 30 s, immediately after which CV scans were initiated from 0.6 V or 0.7 V sweeping negatively to −0.2 V at which point the direction of scan was reversed, and CVs were terminated at 0.8 V. As-deposited films display the $Ni^{3+/2+}$ reduction peak at higher potentials than anodized films and are consequently held at a higher initial potential (0.7 V vs 0.6 V) prior to CV sweep. These initial equilibrium potentials were chosen because they are above the $Ni^{3+/2+}$ redox feature, thus capturing all charge associated with converting oxidized Ni in the film to Ni^{2+}, but below a potential where OER dominates (i.e., where the current baseline is flat in Figure 1a). Initial potentials were chosen to be exclusive of the OER because charge integration becomes more complicated due to (i) deciphering the contribution of OER current and (ii) preventing O_2 bubble formation on the films (which prohibits electrolyte contact to the film and thus hindering complete film reduction to the Ni^{2+} state). All CV scans and pre-

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6. Smith AM, Trotochaud L, Burke MS, Boettcher SW (2015) Contributions to activity enhancement via Fe incorporation in Ni-(oxy)hydroxide/borate catalysts for near-neutral pH oxygen evolution. *Chem Commun* 51:5261–5263.

electrolysis were corrected for ohmic potential losses. Prior to data collection, the solution resistance was measured with a clean FTO working electrode using the *i*R test function. The working FTO electrode and the reference electrode were kept in the same configuration while the electrolysis cell was replaced for deposition, anodization or CV scans.

H. Inductively Coupled Plasma Mass Spectrometry for Elemental Analysis. Trace elemental analysis was carried out with quadrupole ICP-MS (Thermo Electron, X-Series ICP-MS with collision cell technology). All pipettes and polypropylene tubes were soaked in ~5% TraceSELECT nitric acid overnight and rinsed with type I water. All pipette tips were pre-rinsed with 2% double-distilled trace nitric acid prior to use. Films were digested with 4 mL of 2% double distilled trace nitric acid. Film samples along with standards and controls were then scanned twice for 60 s each for ^{56}Fe, and ^{60}Ni. Internal standards and controls dispersed throughout the samples were run to confirm no signal drift.

I. Electron Energy Loss Spectroscopy (EELS) of Nickel Oxides. EELS data were measured using a Zeiss Libra 200 aberration-corrected TEM equipped with a Ω-type in-column energy filter, operated at an accelerating voltage of 80 kV. The energy loss was calibrated post hoc using the established peak energy of the Ni L_3 edge (854 eV) and energy of the first O K edge peak (532 eV) of NiO[7-10] (purchased as powder from Sigma Aldrich). Backgrounds were fit to an exponential function in the pre-edge region and subsequently subtracted from the measured data. Spectra were normalized by the intensity of the edge jump 10–20 eV after the rising edge. In addition to NiO, stoichiometric $Ni(OH)_2$ and $LiNiO_2$ powders (Sigma Aldrich) were also used as models. γ-NiOOH was prepared via the synthesis of $NaNiO_2$ and subsequent treatment with 5 mole equivalents of Br_2 in acetonitrile as described previously.[11] Powders were suspended in isopropanol and dropcast onto Cu TEM grids possessing an amorphous carbon film for TEM analysis.

J. Film Preparation and STEM-EDS Elemental Mapping. As-deposited NiB_i films (Table 1, Entry 1-1) were electrodeposited onto indium tin oxide (ITO)-coated *p*-type silicon substrates. The ITO coating was fabricated by RF sputter deposition using an ITO (Kurt J. Lesker Co.) target in a 3 mTorr Ar environment at 200 °C. ITO-sputtered p-silicon

7. de Groot FMF, Grioni M, Fuggle JC, Ghijsen J, Sawatzky GA, Petersen H (1989) Oxygen 1s x-ray-absorption edges of transition-metal oxides. *Phys Rev B* 40:5715–5723.

8. Kuiper P, Kruizinga G, Ghijsen J, Sawatzky, GA, Verweij H (1989) Character of holes in $Li_xNi_{1-x}O$ and their magnetic behavior. *Phys Rev Lett* 62:221–224.

9. Koyanama Y, Mizoguchi T, Ikeno H, Tanaka I (2005) Electronic structure of lithium nickel oxides by electron energy loss spectroscopy. *J Phys Chem B* 109:10749.

10. Yoon W-S, Chung KY, McBreen J, Fischer DA, Yang X-Q (2006) Changes in electronic structure of the electrochemically Li-ion deintercalated $LiNiO_2$ system investigated by soft X-ray absorption spectroscopy. *J. Power Sources* 163:234–237.

11. Yang X, Takada K, Itose M, Ebina Y, Ma R, Fukuda K, Sasaki T (2008) Highly swollen layered nickel oxide with a trilayer hydrate structure. *Chem Mater* 20:479–485.

electrodes were rinsed in acetone and water prior to use. Stop-off lacquer from Tolber Division Pyramid Plastics Inc was coated onto the ITO electrode such that a 0.25 cm² area was exposed to solution. Catalyst film electrodeposition parameters were identical to those described above, with the exception of the deposition time, which was chosen to be 3 h in order to generate a film that was ~1 micron in thickness. Anodized Fe^{tr}:NiB$_i$ films (Table 1, Entry 1-7) were held at 1.3 V in reagent grade 1 M KB$_i$ pH 9.2 electrolyte for 3.5 h with compensation for ohmic losses (~36 Ω). Scanning transmission electron microscopy (STEM) samples were obtained from the rinsed and air-dried films using a Zeiss NVision 40 focused ion beam (FIB) to excise a portion of the film. Prior to coarse FIB milling, a 500 nm overcoat of amorphous carbon was first deposited with a 3 kV electron beam, after which a second 2 μm carbon layer was deposited using a 30 kV 80 pA ion beam. This carbon overcoat protects the sample from gallium beam damage during milling at 30 kV. Final thinning was performed using a 5 kV 45 pA ion beam. STEM images and high-resolution EDS maps (Figures 3 and S6) were acquired on a JEOL 2010F TEM/STEM operating at 200 kV with EDS detector from EDAX Inc. The probe size setting was 1.0 nm. ANA and EDS parameters included a dwell time of 400 ms and a frame resolution of 512 × 512.

K. Preparation of Fe^{tr}:NiB$_i$ Films for *in situ* XAS Samples. *In situ* Ni K-edge X-ray absorption near-edge spectra (XANES) was performed on films Table 1, Entry 1-3, 1-5 and 1-7 prepared similarly to as-deposited and anodized films as described above with the only difference being the substrate and thickness of the film. Catalyst films were electrodeposited onto an X-ray transparent (at the Ni K-edge, 8.35 keV) indium tin oxide coated poly(ethylene terephthalate) sheet (ITO-PET) with resistance of 60 Ω/sq and ITO coating of 1300 Å thickness (Sigma Aldrich). The ITO-PET sheets were fit to the home-made Teflon cell for XAS experiments. A 3 cm × 5 cm sheet of ITO was covered with tape to expose 1 cm x 1 cm for deposition (total charge of 3 mC/cm² was deposited (~300s)) and 5 mm at the top for connection to the potentiostat.

L. X-ray Absorption Spectroscopy Data Collection and Analysis. Ni K-edge (8.333 keV) X-ray absorption near-edge structure (XANES) spectra were collected at beamline 9BM-B at the Advanced Photon Source at Argonne National Laboratory using a Si(111) X-ray monochromator with a focused beam size of ~0.5 × 0.5 mm. All data were collected in fluorescence mode using a 4-element Vortex SDD detector. Energy calibration was carried out using Ni foil. XAS data were collected at room temperature using a homemade *in situ* XAS cell (see above). No sample damage due to X-ray beam exposure was observed after multiple scans using the same sample/electrode position. Three to five scans were averaged for analysis. Background subtraction and data normalization were carried out using the Athena software package.[12]

12. Ravel B, Newville M (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J Synchrotron Radiat* 12:537-541.
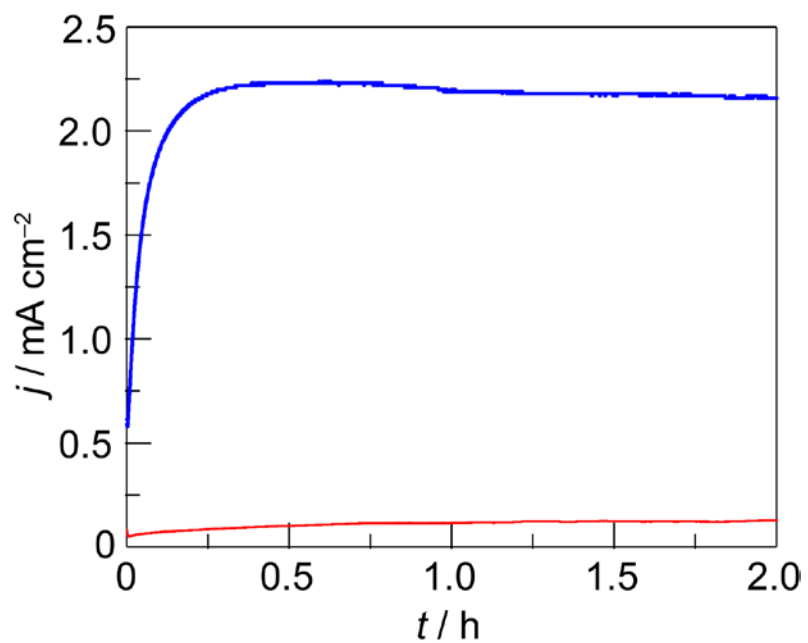
Figure S1. Amperometric current-time curves (E_{appl} = 0.75 V vs NHE) tracking OER current density (j) for a 1.0 mC as-deposited NiB$_i$ catalyst films (Table 1, Entry 1-1) operating in Fe-free 1 M KOH (red, —) and reagent grade 1 M KOH (blue, —).
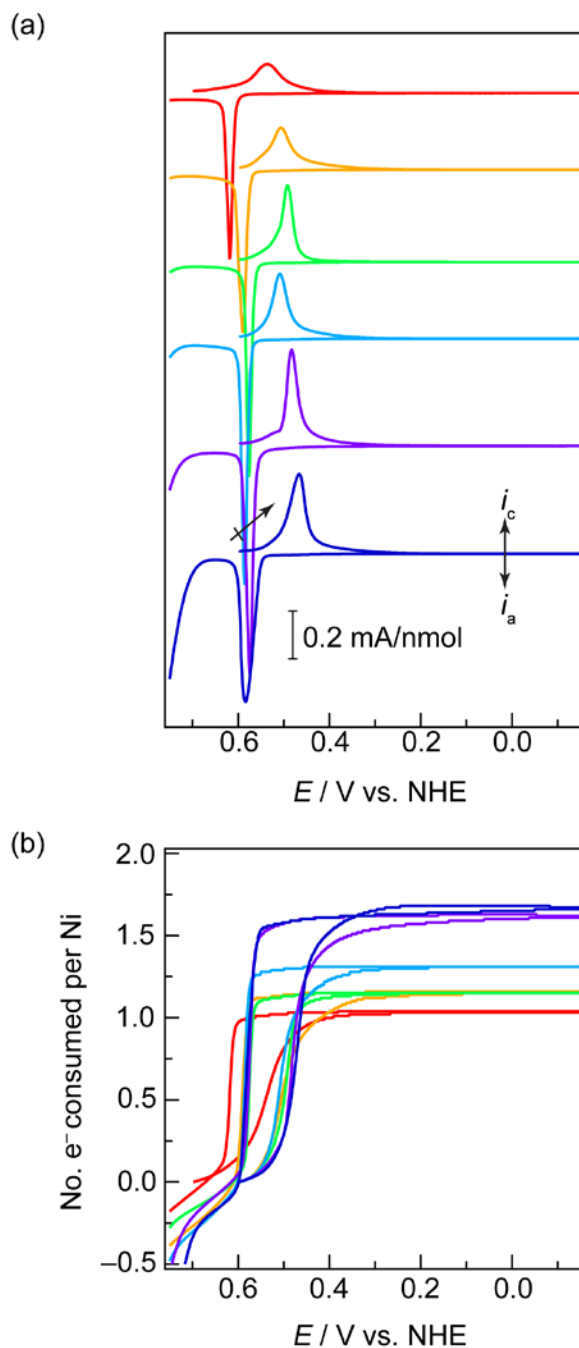
Figure S2. (a) Cyclic voltammograms (CV) taken in Fe-free 1 M KOH for as-deposited NiB$_i$ (—) (Table 1, Entry 1-1) and reagent-grade anodized Fe^{tr}:NiB$_i$ films (—) (Table 1, Entry 1-6), as well as Fe^{tr}:NiB$_i$ films anodized in Fe-free 1M KOH following exposure to reagent grade 1 M KB$_i$ electrolyte for 0 (—), 5 (—), 10 (—) or 30 min (—) (Table 1, Entries 1-2 and 1-4). Data are normalized to Ni loading and offset for clarity. (b) The corresponding number of e$^-$ consumed per Ni throughout the CV scan. The plateaus at low potentials correspond to the data used to calculate Ni resting state valency. The sharp decrease in e$^-$ consumed at high potentials corresponds to charged passed for OER.
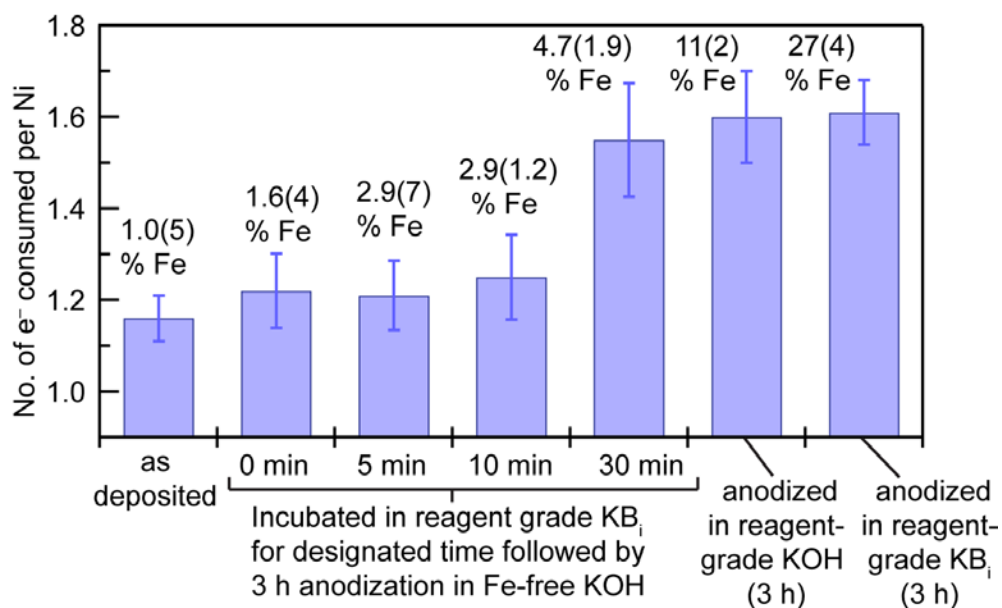
Figure S3. Comparison of coulometric titration results for as-deposited NiB_i film (Table 1, Entry 1-1) and reagent-grade anodized $Fe^{tr}{:}NiB_i$ films (Table 1, Entry 1-6 and 1-7), as well as $Fe^{tr}{:}NiB_i$ films anodized in Fe-free 1 M KOH following exposure to reagent grade 1 M KB_i electrolyte for 0, 5, 10 or 30 min (Table 1, Entries 1-2 and 1-4).
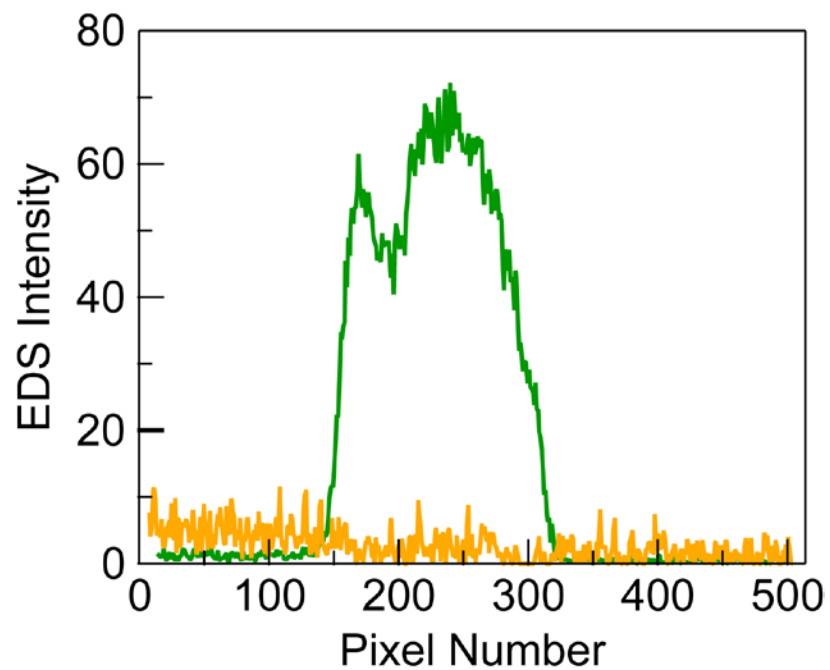
Figure S4. EDS elemental profile (Ni: green, —; Fe: orange, —) across an as-deposited NiB$_i$ film (Table 1, Entry 1-1).
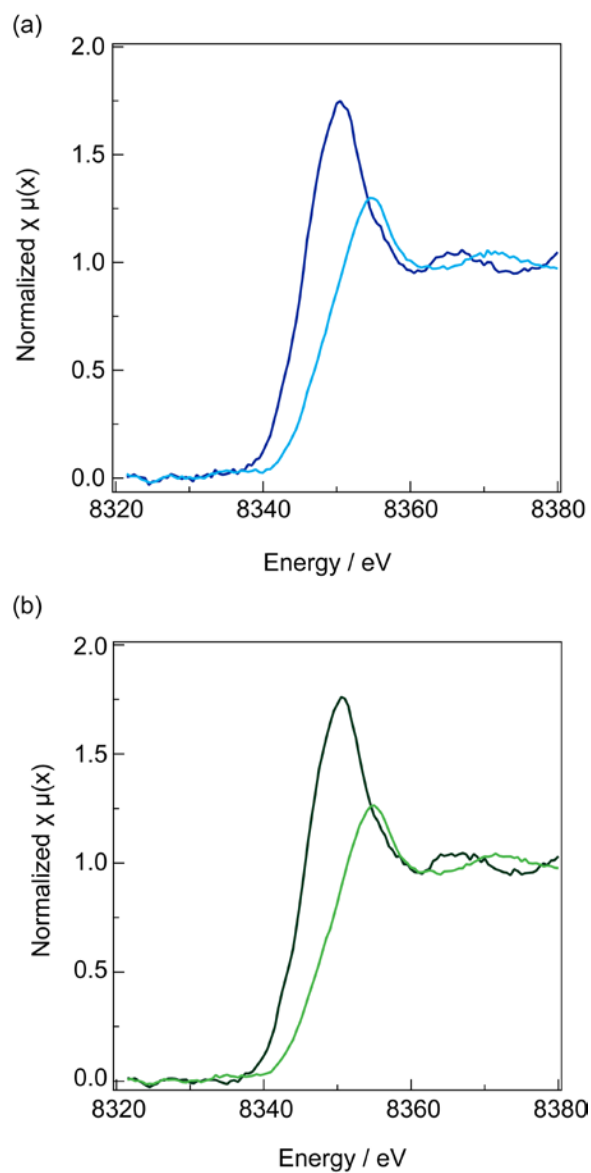
Figure S5. a) Ni K-edge XANES spectra of anodized Fe^{tr}:NiB_i film (Table 1, Entry 1-7) operating in reagent-grade 1 M KB_i pH 9.2 poised at −0.2 V (—) which reduces the Ni in the film to Ni^{2+} and 1.3 V which oxidizes the Ni in the film to higher mixed valency $Ni^{3+/4+}$ (—) and b) Ni K-edge XANES spectra of anodized NiB_i film (Table 1, Entry 1-3) operating in Fe-free 1 M KB_i pH 9.2 poised at −0.2 V (—) and 1.3 V (—).