Electronic Supplementary Information

In-situ anion exchange induced high-performance oxygen evolution reaction catalyst for pH-near-neutral potassium borate electrolyte

Yan Dong[ab], Sridhar Komarneni[b*], Ni Wang[bc], Wencheng Hu[c], Wenyan Huang[bd]

a Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States.
b Department of Ecosystem Science and Management and Materials Research Institute, 204 Energy and the Environment Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802, United States.
c Center for Applied Chemistry, University of Electronic Science and Technology of China, Chengdu 610054, China.
d Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, China.

*Corresponding author.
E-mail address: sxk7@psu.edu

Catalyst/working electrode	***J* (mA cm^{-2})**	**Overpotential η (mV)**	**Electrolyte**	**Reference**
NiFe LDH Seb/FTO	1	376	0.1M K-B_i	This work
Co-B_i film/glassy carbon	1	395	0.1M K-B_i	1
Ni-B_i film/FTO	1	540	0.5M K-B_i	2
Ni-B_i film/ITO	1	425	0.1M B_i	3
Ni-B_i film/FTO	1	390	0.5M K-B_i	4
Ni-B_i film/FTO	1	413	1M K-B_i	5
Ni-B_i film/FTO	0.6	618	0.1M Na-B_i	6
NiO_x-en/FTO	1	510	0.6M Na-B_i	7
NiO_x-B_i/ Au/Ti-coated glass	1	650	0.5M K-B_i	8
CuO/FTO	0.1	430	0.1M K-B_i	9
Cu-B_i/FTO	1	525	0.2M Na-B_i	10

Table S1. Comparison of catalytic performance for NiFe LDH Seb/FTO with other earth-abundant oxygen evolution catalysts in pH-near-neutral borate electrolyte

Sample	R_u(Ω)	R_{ct}(Ω)	α_{dl}	Q_{dl}(mF)	C_{dl}(mF)
NiFe LDH Seb	67.46	39.24	0.7637	0.003016	1.35
NiFe LDH CO	76.23	327.5	0.6174	0.000604	0.0787
NiFe LDH SebCOexc	77.53	416.4	0.6843	0.0001663	0.0206
NiFe LDH SebBOexc0.1	71.6	154.9	0.7258	0.0005283	0.133
NiFe LDH SebBOexc0.5	50.04	124.7	0.6506	0.0005084	0.0590

Table S2 R_u R_{ct}, α_{dl}, Q_{dl} values obtained from simulation of the Nyquist plots using a Randles circuit and the calculated C_{dl} values of each sample.

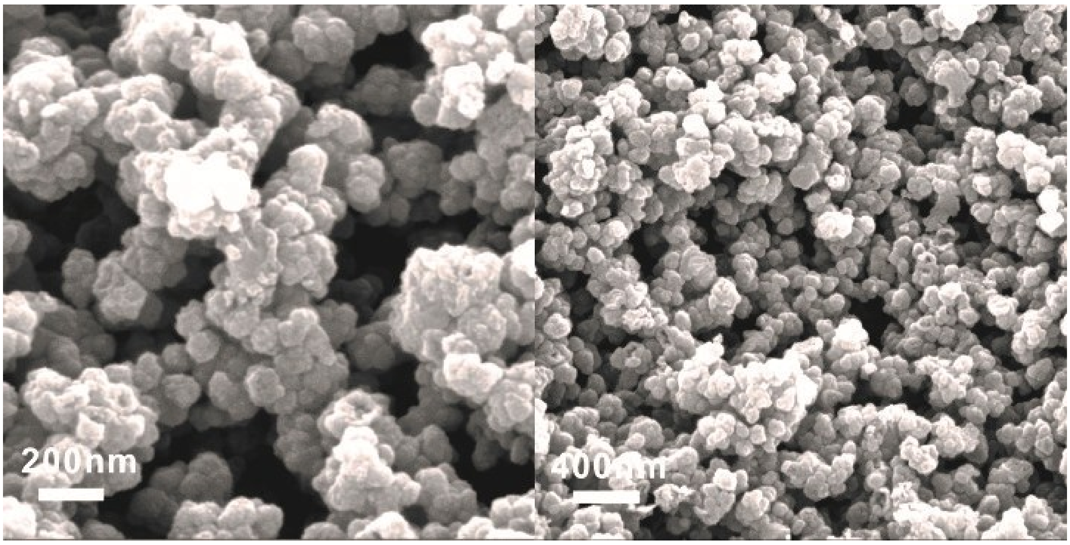

Figure S1. SEM images of NiFe LDH Seb, showing a unique spherical morphology at two different magnifications.

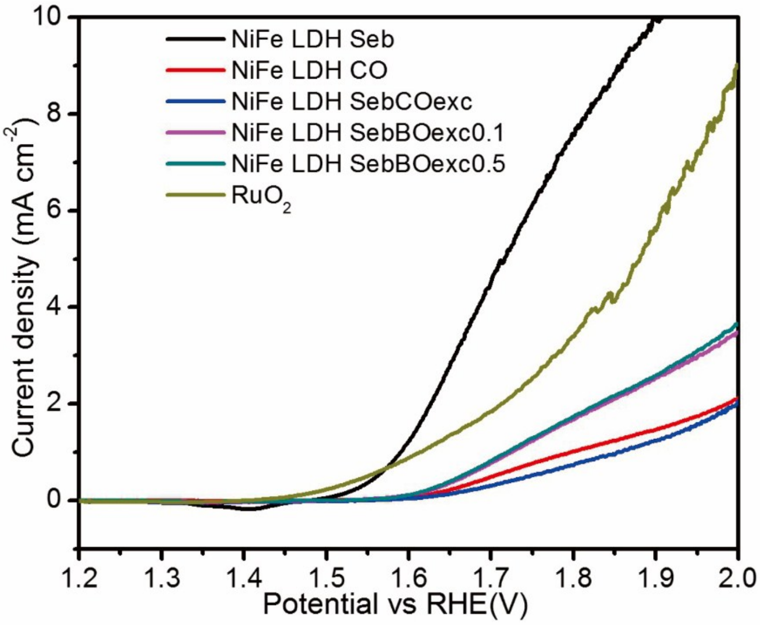

Figure S2. LSVs recorded in the reverse direction

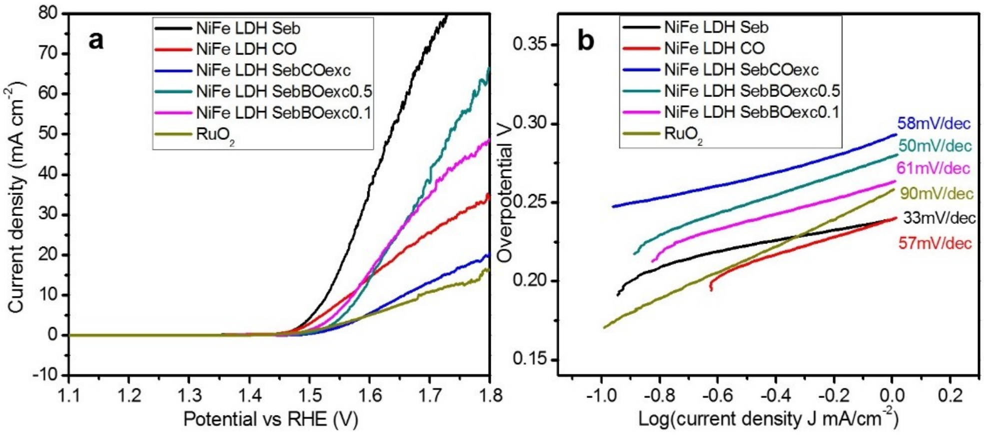

Figure S3. (a) Linear scan voltammograms of the NiFe LDH samples in 0.1M KOH electrolyte on GC working electrode, (b) Corresponding Tafel plots derived from LSVs obtained in 0.1M KOH electrolyte on GC working electrode.

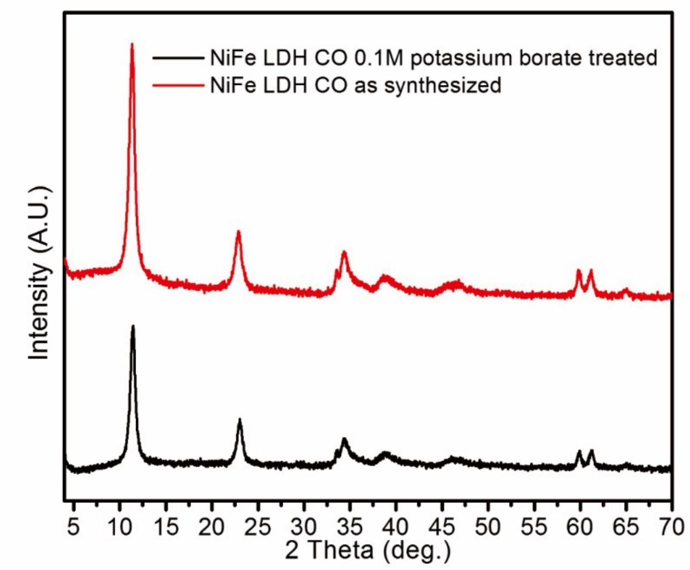

Figure S4. XRD patterns of the as synthesized NiFe LDH CO and 0.1M potassium borate electrolyte treated NiFe LDH CO showing no changes in the positions of the (00*l*) peaks, indicating that borate anions did not exchange with carbonate anions and therefore, did not enter the interlayers of NiFe LDH CO.

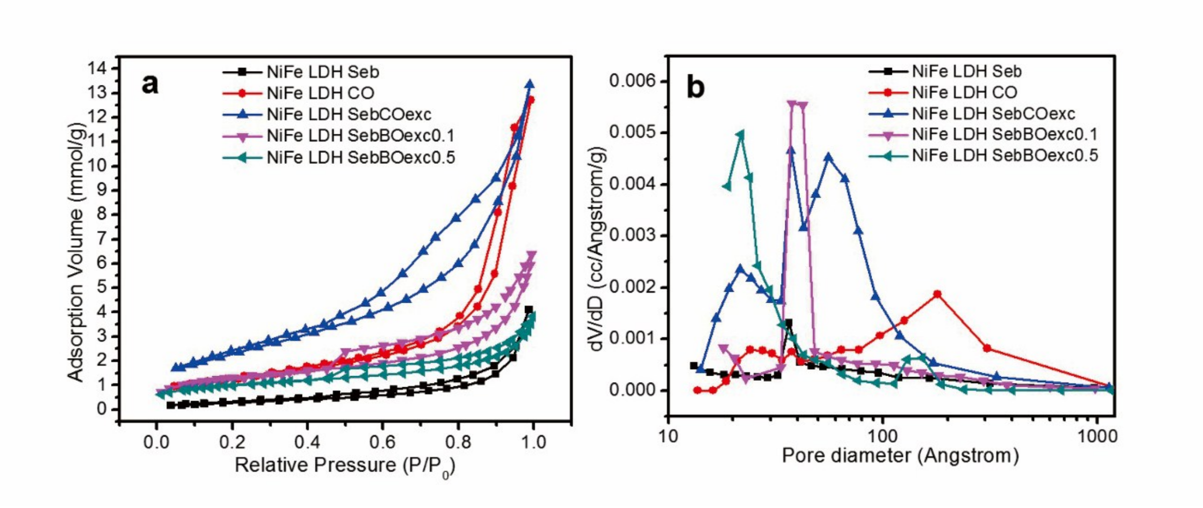

Figure S5 (a) N_2 adsorption/desorption isotherms (b)BJH pore size distribution of each sample

Sample	NiFe LDH Seb	NiFe LDH CO	NiFe LDH SebCOexc	NiFe LDH SebBOexc0.1	NiFe LDH SebBOexc0.5
BET surface area (m^2/g)	26.5	100.2	190.7	103	77.6

Table S3. BET surface area of each sample

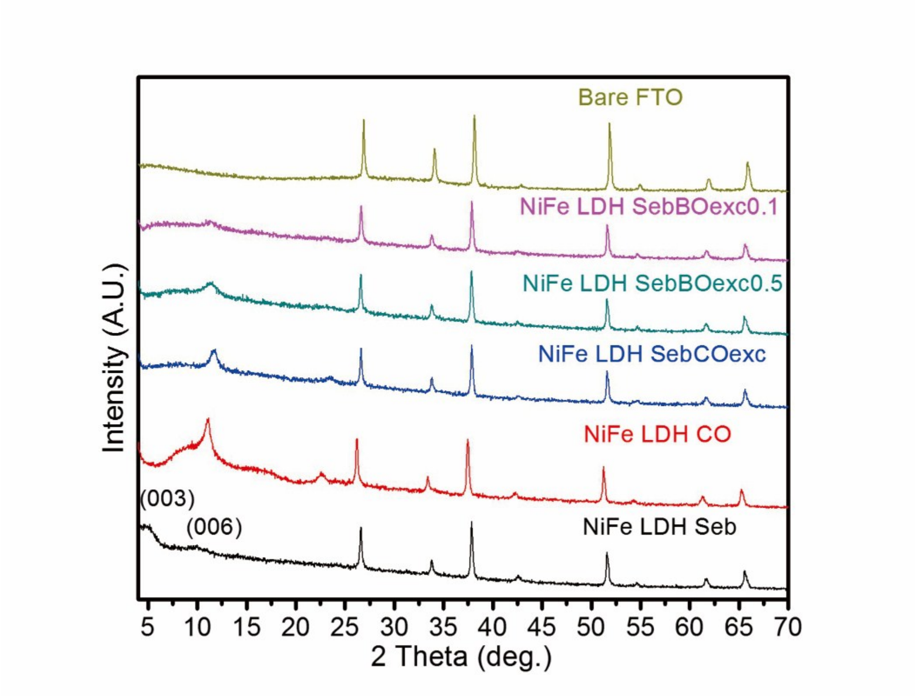

Figure S6 XRD patterns of different LDH samples drop casted on the FTO electrode after ultrasonication, the (003) diffraction peaks of NiFe LDH Seb can still be clearly observed.

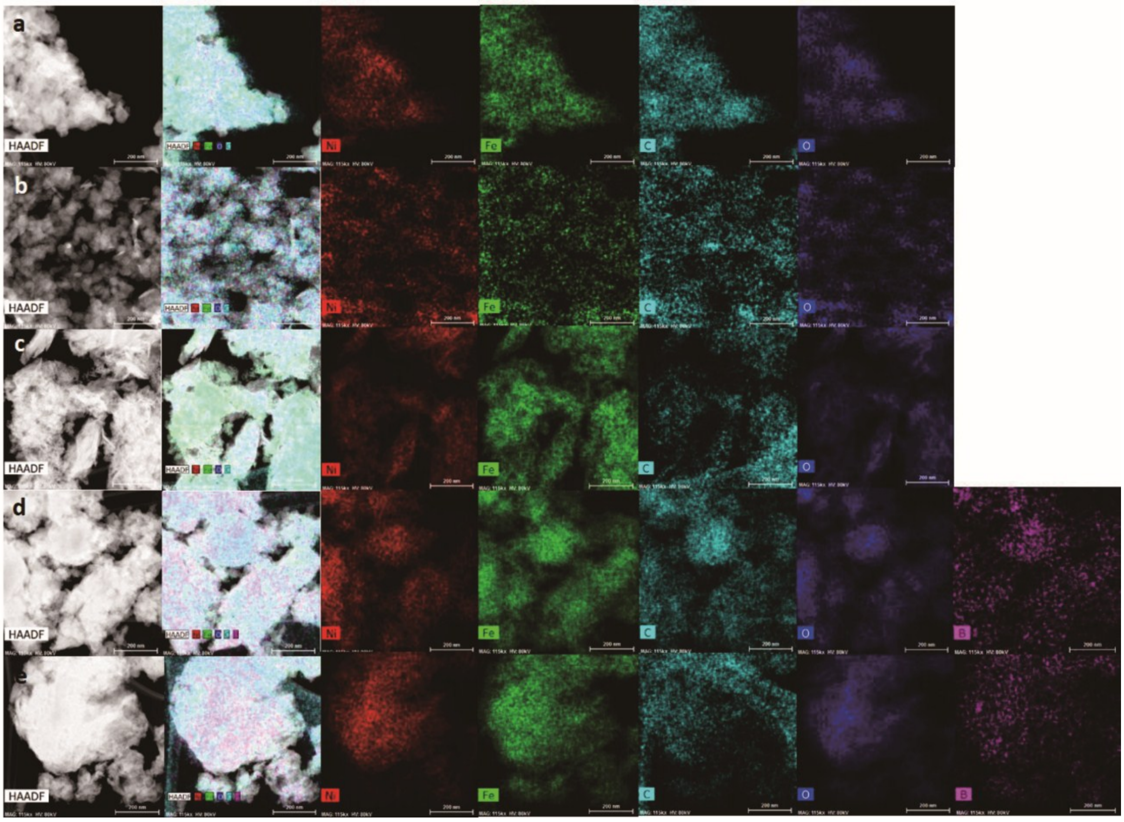

Figure S7 EDS elemental mapping of each sample obtained in HAADF-STEM mode on Talos F200X TEM, (a) NiFe LDH Seb, (b) NiFe LDH CO, (c) NiFe LDH SebCOexc, (d) NiFe LDH SebBOexc0.1, (e) NiFe LDH SebBOexc0.5. Please note that EDS is not an accurate method to determine the concentration of boron since boron is too light to be accurately and effectively detected by using this technique.

Sample	Ni	Fe	C	O	B
NiFe LDH Seb	8.38%	8.78%	47.90%	34.94%	0
NiFe LDH CO	10.74%	3.45%	45.64%	40.17%	0
NiFe LDH SebCOexc	12.25%	14.37%	14.49%	58.89%	0
NiFe LDH SebBOexc0.1	7.81%	11.86%	34.69%	38.02%	7.62%
NiFe LDH SebBOexc0.5	9.49%	9.74%	17.02%	51.15%	12.6%

Table S4. EDS elemental composition of each sample

The EDS elemental mapping of each sample was obtained on Talos F200X TEM in HAADF-STEM mode and the elemental composition of each sample is shown in Table S4. The ratio of Ni/Fe is slightly different for each sample. The different Ni/Fe ratios of NiFe LDH Seb and NiFe LDH CO could be attributed to the different pHs under which the sample was synthesized (pH=7 for NiFe LDH Seb and pH=9 for NiFe LDH CO). Since the K_{sp} value of $Ni(OH)_2$ ($2.0x10^{-15}$)and $Fe(OH)_3$ ($4x10^{-38}$) is different, under different pHs, Ni and Fe were coprecipitated with different Ni/Fe ratios and NiFe LDH with different Ni/Fe ratios were formed. NiFe LDH SebCOexc and NiFe LDH SebBOexc0.1 were both derived from NiFe LDH Seb by treating NiFe LDH Seb in solutions with different pHs (pH=13 for NiFe LDH SebCOexc and pH=9.2 for NiFe LDH SebBOexc0.1). The Ni/Fe ratio of NiFe LDH SebCOexc and NiFe LDH SebBOexc0.1 are both lower than that of NiFe LDH Seb, indicating that some of the Ni ions were dissolved when NiFe LDH Seb was treated in these solutions. According to the pourbaix diagram of Ni, under alkaline condition, Ni could form $Ni(OH)_3^-$ which will be dissolved and this could be the reason for the lower Ni/Fe ratio in NiFe LDH SebCOexc and NiFe LDH SebBOexc0.1. For NiFe LDH SebBOexc0.5, the Ni/Fi ratio is almost the same with that of NiFe LDH Seb, even though it was also derived from NiFe LDH Seb by treating NiFe LDH Seb in the K-B_i solution (pH=9.2) like NiFe LDH SebBOexc0.1. The high concentration of borate anions (0.5M) used for NiFe LDH SebBOexc0.5 could help to precipitate the dissolved Ni, which could be the reason for its relatively higher Ni/Fe ratio compared to NiFe LDH SebBOexc0.1.

References

1 Y. Surendranath, M. Dincă and D. G. Nocera, *J. Am. Chem. Soc.*, 2009, **131**, 2615–2620.

2 I. Roger and M. D. Symes, *J. Am. Chem. Soc.*, 2015, **137**, 13980–13988.

3 M. Dincă, Y. Surendranath and D. G. Nocera, *Proc. Natl. Acad. Sci.*, 2010, **107**, 10337 LP-10341.

4 D. K. Bediako, Y. Surendranath and D. G. Nocera, *J. Am. Chem. Soc.*, 2013, **135**, 3662–3674.

5 D. K. Bediako, B. Lassalle-Kaiser, Y. Surendranath, J. Yano, V. K. Yachandra and D. G. Nocera, *J. Am. Chem. Soc.*, 2012, **134**, 6801–6809.

6 C. He, X. Wu and Z. He, *J. Phys. Chem. C*, 2014, **118**, 4578–4584.

7 A. Singh, S. L. Y. Chang, R. K. Hocking, U. Bach and L. Spiccia, *Energy Environ. Sci.*, 2013, **6**, 579–586.

8 A. M. Smith, L. Trotochaud, M. S. Burke and S. W. Boettcher, *Chem. Commun.*, 2015, **51**, 5261–5263.

9 X. Liu, S. Cui, Z. Sun and P. Du, *Electrochim. Acta*, 2015, **160**, 202–208.

10 F. Yu, F. Li, B. Zhang, H. Li and L. Sun, *ACS Catal.*, 2015, **5**, 627–630.