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## COMMUNICATION

## Contributions to Activity Enhancement via Fe Incorporation in Ni-(oxy)hydroxide/borate Catalysts for Near-Neutral pH Oxygen Evolution

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

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DOI: 10.1039/x0xx00000x

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**Ni-borate materials are oxygen evolution catalysts that operate at near-neutral pH and have been found previously to improve due to structural changes induced via anodic conditioning. We find that this increased activity after conditioning at 0.856 V vs. SCE, as measured on a turn-over frequency basis (TOF) at 400 mV overpotential (TOF = 0.38 s<sup>-1</sup>), accompanies significant Fe incorporation (14%). Films conditioned in Fe-free electrolyte exhibit ~10 times lower activity (TOF = 0.03 s<sup>-1</sup>). By co-depositing Fe/Ni we demonstrate high activity without conditioning (TOF = 0.24 s<sup>-1</sup>) which improves further with shortened (~30 min) conditioning (TOF = 1.4 s<sup>-1</sup>).**

The need for solar energy storage has been thoroughly reported.<sup>1-3</sup> Electrolytic and photoelectrochemical water splitting to produce hydrogen fuel and oxygen are two routes to scalable energy storage. Both methods could benefit from improvements in oxygen evolution reaction (OER) catalysts, as the OER suffers from substantial overpotential losses (300-400 mV) compared to the hydrogen evolution reaction (<50 mV).<sup>3-5</sup> Despite the considerable number of reported OER catalysts, identifying the catalytically relevant species/active-sites and increasing activity through rational design remain challenges/opportunities.<sup>6-11</sup>

Ni-based catalysts have been shown to be among the most active in basic conditions.<sup>7, 12-16</sup> Although Ni-based catalysts have been investigated for some time, Trotochaud et. al. recently showed that the incidental incorporation of Fe impurities from electrolytes are in-fact completely responsible for the high catalytic performance of NiOOH in base, with Fe-free NiOOH having very poor electrocatalytic activity.<sup>13, 17</sup> Incidental Fe incorporation and subsequent increase in OER activity was observed by Corrigan in the 1980s for the Ni(OH)<sub>2</sub>/NiOOH system.<sup>18, 19</sup> Louie et. al. also studied mixed Ni/Fe (oxy)hydroxide films and found that the activity was maximized and relatively constant for 10-60 % Fe.<sup>20</sup> Of potential interest for OER catalysts integrated with

semiconductors in photochemical water-splitting devices are those that function in near-neutral conditions, as they may offer more flexibility in the semiconductor materials used which must also be stable in the electrolyte.<sup>21</sup> Ni-(oxy)hydroxide/borate (NiO<sub>x</sub>-B<sub>i</sub>) catalysts were reported and studied by Nocera and coworkers which function in near-neutral pH of ~9 and have reasonably high activity. These films were locally comprised of NiOOH structural fragments and the catalytic activity was observed to increase after anodic conditioning. The improvement was attributed to changes in Ni oxidation state and film structure.<sup>22-24</sup>

Here we study the effect of incidental and intentional Fe incorporation on NiO<sub>x</sub>-B<sub>i</sub> catalyst film activity in near-neutral borate buffers. We show that both incidental Fe incorporation via anodic conditioning in a borate buffer and intentional Fe co-deposition result in increases in OER activity compared to as-prepared catalyst films. Additionally, when NiO<sub>x</sub>-B<sub>i</sub> films are conditioned under rigorously Fe-free conditions, no increase in catalytic activity is observed implying that Fe is a critical component of the film activation process.

NiO<sub>x</sub>-B<sub>i</sub> films were synthesized via anodic electrodeposition as reported previously.<sup>22,23</sup> Briefly, a gold-coated glass-slide electrode was immersed in a 0.4 mM Ni(NO<sub>3</sub>)<sub>2</sub> solution buffered to pH 9.2 and held at 0.909 V vs. SCE until 10 mC of charge was passed (Fig. S1). As-deposited films exhibited relatively low OER activity as illustrated by cyclic voltammetry (Fig. 1A, red). Additionally, no Fe was detectable via X-ray photoelectron spectroscopy (XPS) in the as-deposited NiO<sub>x</sub>-B<sub>i</sub> films (Fig. 1A, insert). As previously reported, significant increases in water-oxidation current were observed after anodic polarization in borate electrolyte (Fig. 1A). NiO<sub>x</sub>-B<sub>i</sub> films were conditioned at 0.856 V vs. SCE for 2, 5, 15, 30 and 120 min in 0.5 M potassium borate buffer solutions at pH 9.2 and subsequently characterized via voltammetry after each conditioning interval in the conditioning cell. It is important to

note that the hysteresis between forward and reverse scans is an artifact of the non-stirred conditions necessary for comparison with Fe-free experiments (see below). After conditioning for 2 h, NiO<sub>x</sub>-B<sub>i</sub> samples were characterized via XPS and found to contain 14% Fe (relative to Ni). This suggests that the increased activity corresponds to Fe incorporated incidentally from the

absorbent, however, introduces soluble Ni<sup>2+</sup> into the pH ~9.2 electrolyte. For films conditioned/tested in the purified Fe-free electrolyte, background deposition of NiO<sub>x</sub>-B<sub>i</sub> was observed which increases the amount of catalyst on the electrode with time. To minimize this effect the electrolyte was, in all cases, not stirred during conditioning at 0.856 V vs. SCE.

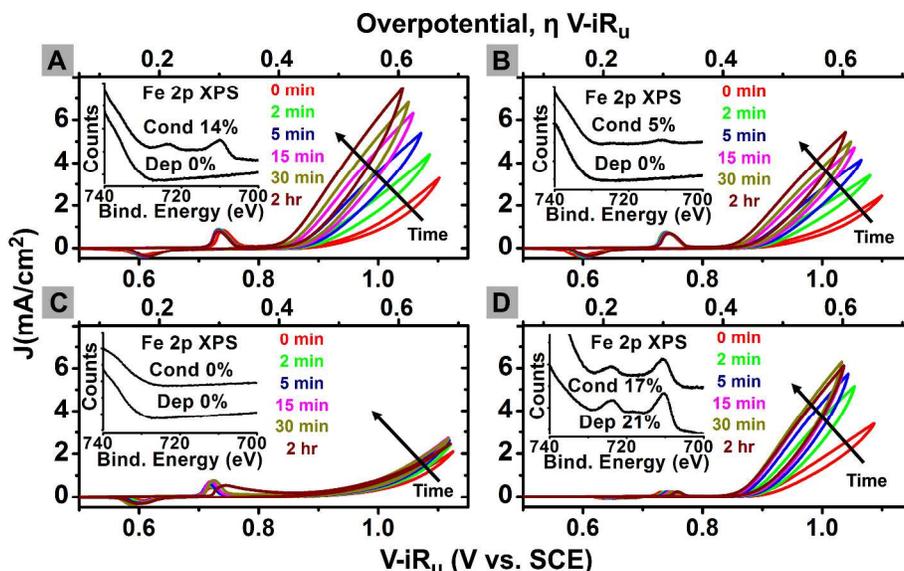


Fig. 1: Electrochemical and XPS characterization of Ni-(oxy)hydroxide/borate films. (A) Catalyst anodically conditioned in ~1 ppm Fe containing borate electrolyte, (B) catalyst conditioned in ~0.1 ppm Fe containing electrolyte, (C) catalyst film conditioned in Fe-free borate electrolyte and (D) co-deposited Ni-Fe-(oxy)hydroxide/borate film conditioned in ~1 ppm Fe electrolyte.

borate electrolyte during conditioning, which was found to contain trace Fe impurities at ~1 ppm via the supplier lot analysis and diluted to 0.5 M. The enhancement in catalytic activity may be due to a combination of both the observed compositional changes and the structural changes previously reported.<sup>23</sup>

The increase in OER activity due to conditioning is also dependent on the concentration of trace Fe species in the conditioning electrolyte. NiO<sub>x</sub>-B<sub>i</sub> samples were similarly synthesized and conditioned in a borate buffer electrolyte solution containing ~0.1 ppm trace Fe prepared from precursors obtained from a different supplier. Again, an increase in OER current is observed in cyclic voltammograms (Fig. 1B). Additionally, no Fe is detected via XPS in as-prepared films and after 2 h of conditioning in the higher-purity electrolyte, catalyst films are found to contain 5% Fe (Fig. 1B and insert).

To further illustrate the role of Fe impurities in the observed increase in OER activity, NiO<sub>x</sub>-B<sub>i</sub> films were conditioned in rigorously Fe-free borate electrolyte solutions. Fe-free borate buffer solutions were produced from further purifying high-purity borate buffer solutions with a high-purity Ni(OH)<sub>2</sub> powder absorbent following the method of Trotochaud et al., who showed that Fe has a strong affinity for Ni(OH)<sub>2</sub>.<sup>17</sup> By agitating a slurry of high-purity Ni(OH)<sub>2</sub> powder in an electrolyte, trace Fe is removed. The use of Ni(OH)<sub>2</sub> as an

Cyclic voltammograms show significantly lower OER activity with the absence of Fe impurities in the conditioning electrolyte (Fig. 1C). The activity of the film is essentially unchanged during the course of the 2 h conditioning experiment in the purified electrolyte, and Fe is not found via XPS analysis in those films (Fig. 1C insert). The increase in OER current after conditioning is due to additional Ni deposition from the purified electrolyte, increasing the total catalyst loading. This data further support the hypothesis that the observed OER activity is correlated to Fe content in the catalyst films in near-neutral pH, as it is in basic pH. Catalyst films were found to be stable at OER potentials via microgravity measurements (Fig. S11). Films partially degraded at cathodic potentials present during voltammetry. Material was subsequently partially re-deposited when the electrode was held at anodic potentials.

To directly increase catalyst performance, Fe was intentionally incorporated into catalyst films via anodic co-deposition from a mixed solution of Ni(NO<sub>3</sub>)<sub>2</sub>/FeCl<sub>2</sub> (Fig. S2). From a solution with a Ni:Fe ratio of 9:1, as-deposited films had a ratio of 3.8:1, i.e. 21% Fe (Fig. 1D insert). Although Ni-Fe-(oxy)hydroxide/borate (NiFeO<sub>x</sub>-B<sub>i</sub>) films improved after short conditioning, the intentional incorporation of Fe reduced the need for anodic conditioning in electrolyte solutions (Fig. 1D) from > 2 h to less than 30 min.

The data in Figure 1 are normalized only to geometric area and do not take into account the amount of catalyst on the electrode surface. Films deposited from the mixed Ni-Fe solutions show a substantially smaller pre-OER Ni<sup>2+/3+</sup> wave in the voltammetry (Fig. 1) compared to those deposited from the Ni-only precursors. To determine the intrinsic activity of the catalysts we compare the turn over frequencies (TOF), calculated at an overpotential of 400 mV and normalized to the number of Ni atoms in the film (Fig. 2A). To estimate the number of Ni we integrate the pre-OER oxidation wave in the voltammetry and assume 1 e<sup>-</sup> per Ni center, which is in good agreement with the ~1.1 e<sup>-</sup> per Ni determined via microbalance measurements assuming the film was composed entirely of NiOOH (Fig. S7). We note that this simplification thus likely slightly underestimates intrinsic film activities as previous studies have found ~1.6 e<sup>-</sup> per Ni.<sup>23</sup> The TOF of rigorously Fe-free NiO<sub>x</sub>-B<sub>i</sub> films remains constant with conditioning. The TOF for Ni films in electrolyte containing Fe-impurities increases after several minutes at anodic potentials and eventually levels off after several hours. Catalyst films where Fe was intentionally incorporated not only have initially substantially higher TOFs, but also show increases in TOF over the first 30 min. The remaining OER activity dependence for NiFeO<sub>x</sub>-B<sub>i</sub> with conditioning may be attributed to film rearrangement.<sup>23</sup> The absolute TOF for the Ni-Fe films (~1.4 s<sup>-1</sup>) is substantially higher than that for the Ni films, even after anodic conditioning (~0.3 s<sup>-1</sup>).

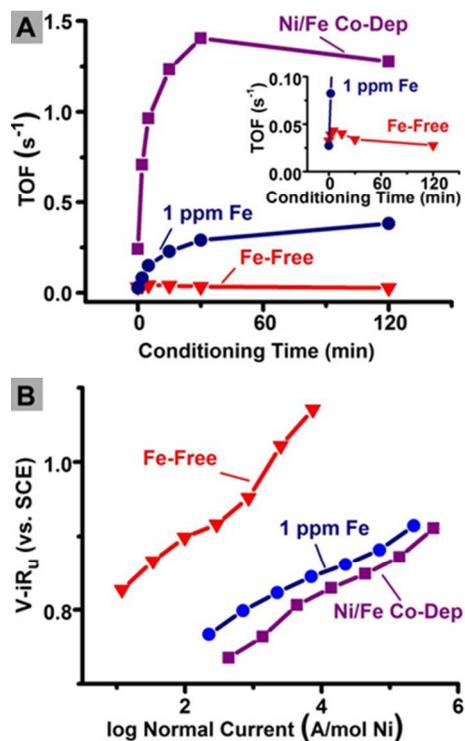


Fig. 2: TOF and Tafel analysis of catalyst films. (A) TOF as a function of time conditioned at 0.856 V vs. SCE in electrolyte with trace Fe impurities (blue), rigorously Fe-free (red) and Ni/Fe co-deposited films (purple), (B) Tafel plot of

catalyst films conditioned for 2 h in regular purity electrolyte (blue), Fe-free electrolyte (red), and unconditioned Ni/Fe co-deposited catalyst films.

Further evidence that the presence of Fe plays a key role in the observed activity of (NiO<sub>x</sub>-B<sub>i</sub>) catalyst films is seen in a Tafel plot comparison (Fig. 2B). Tafel slopes were calculated from points in the linear regime up to a current density of 10<sup>-2.5</sup> A/cm<sup>2</sup>. The Tafel slope of (NiO<sub>x</sub>-B<sub>i</sub>) conditioned for 2 h was 46 mV/decade while for the films conditioned in rigorously Fe-free electrolyte it was 78 mV/decade. Unconditioned Ni/Fe co-deposited films had similar catalytic activity as conditioned (NiO<sub>x</sub>-B<sub>i</sub>) with a Tafel slope of 56 mV/decade, suggesting a similar OER mechanism involving Fe in both. Due to deposition of trace Ni from the electrolyte solution during both conditioning and chronopotentiometric experiments, Tafel data were normalized to the number of electrochemically active Ni centers to provide a comparison across samples (Fig. S5). To minimize deposition during conditioning the solution was not stirred, although the solution was stirred during Tafel measurements to facilitate bubble release from the film surface.

In summary, we have demonstrated that the OER activity in NiO<sub>x</sub>-B<sub>i</sub> catalysts is significantly enhanced through the introduction of Fe. If sufficiently Fe-free conditions are used such that Fe incorporation is not observed via XPS, the OER activity is inhibited. This work is important for the application of NiO<sub>x</sub>-B<sub>i</sub> catalysts, as the higher activity NiFeO<sub>x</sub>-B<sub>i</sub> phases can now be directly targeted, thus reducing reliance on electrolyte Fe impurities and anodic conditioning to form the active phase.

This work was supported by the National Science Foundation through CHE-1301461. Matt Kast and Adam Batchellor are thanked for insightful discussion and Lilia Piper for assistance with electrode fabrication. We acknowledge assistance from Stephen Golledge with interpretation of XPS data in the Center for Advanced Materials Characterization in Oregon (CAMCOR). CAMCOR analytical facilities are supported by grants from the W.M Keck Foundation, the M.J. Murdock Charitable Trust, ONAMI, the Air Force Research Laboratory (under agreement number FA8650-05-1-5041), NSF (grant number 236200), and the University of Oregon. S.W.B. acknowledges support from Research Corporation for Science Advancement as a Cottrell Scholar.

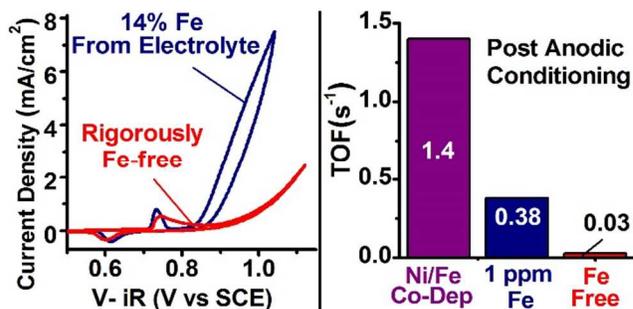
## Notes and references

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Electronic Supplementary Information (ESI) available: Figures S1-S11 and additional synthesis and characterization details. See DOI: 10.1039/c000000x/

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## TOC Figure