Supporting Information

Electrochemical Study of the Promoting Effect of Fe on Oxygen Evolution at Thin 'NiFe-Bi' Films and the Inhibiting Effect of Al in Borate Electrolyte

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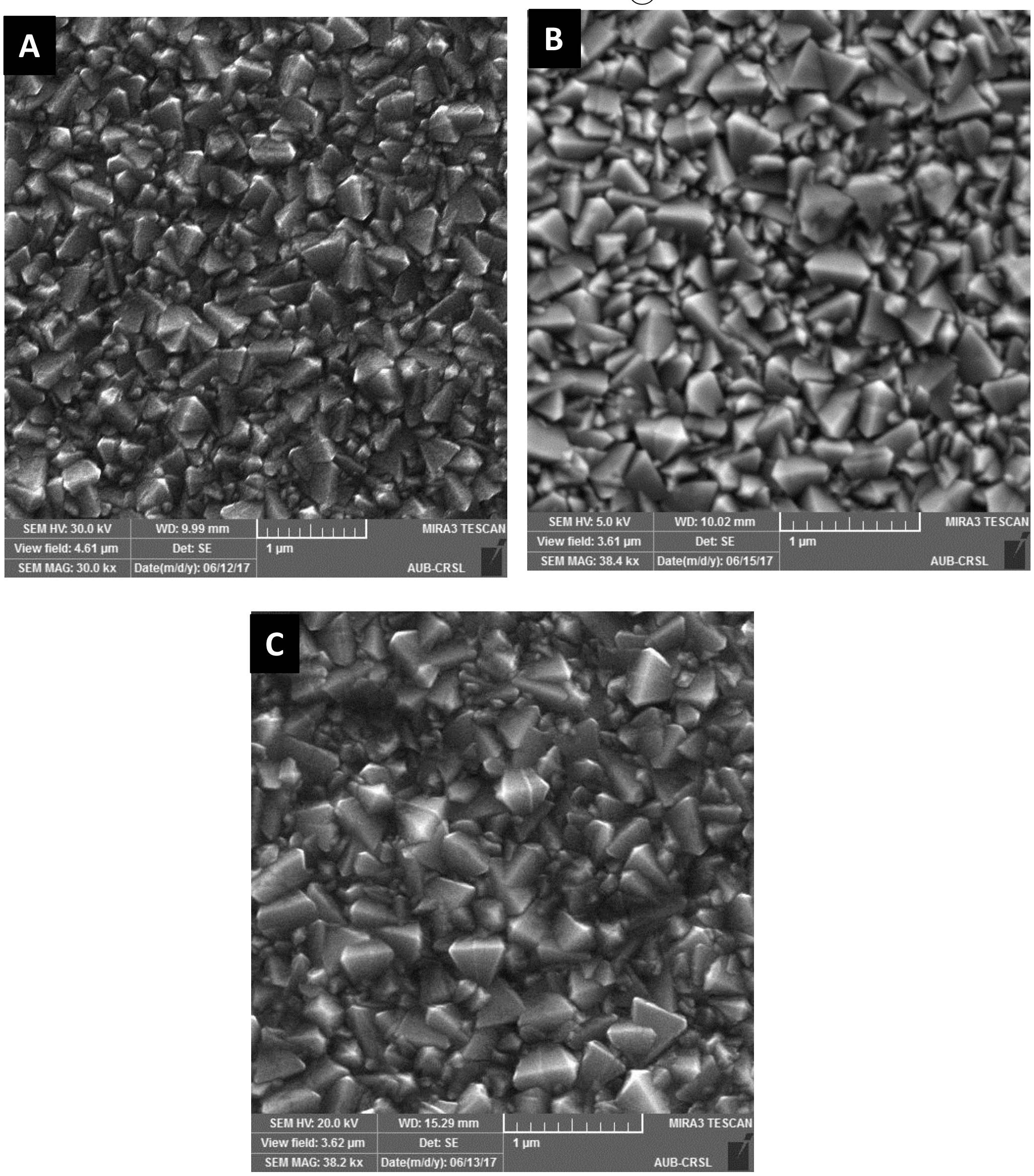

Figure SI.1 SEM image of as-deposited Ni-Bi)$_{1mC}$ (A) and $Ni_{0.6}Fe_{0.4}$-Bi (B) on FTO, and of the FTO surface (C).

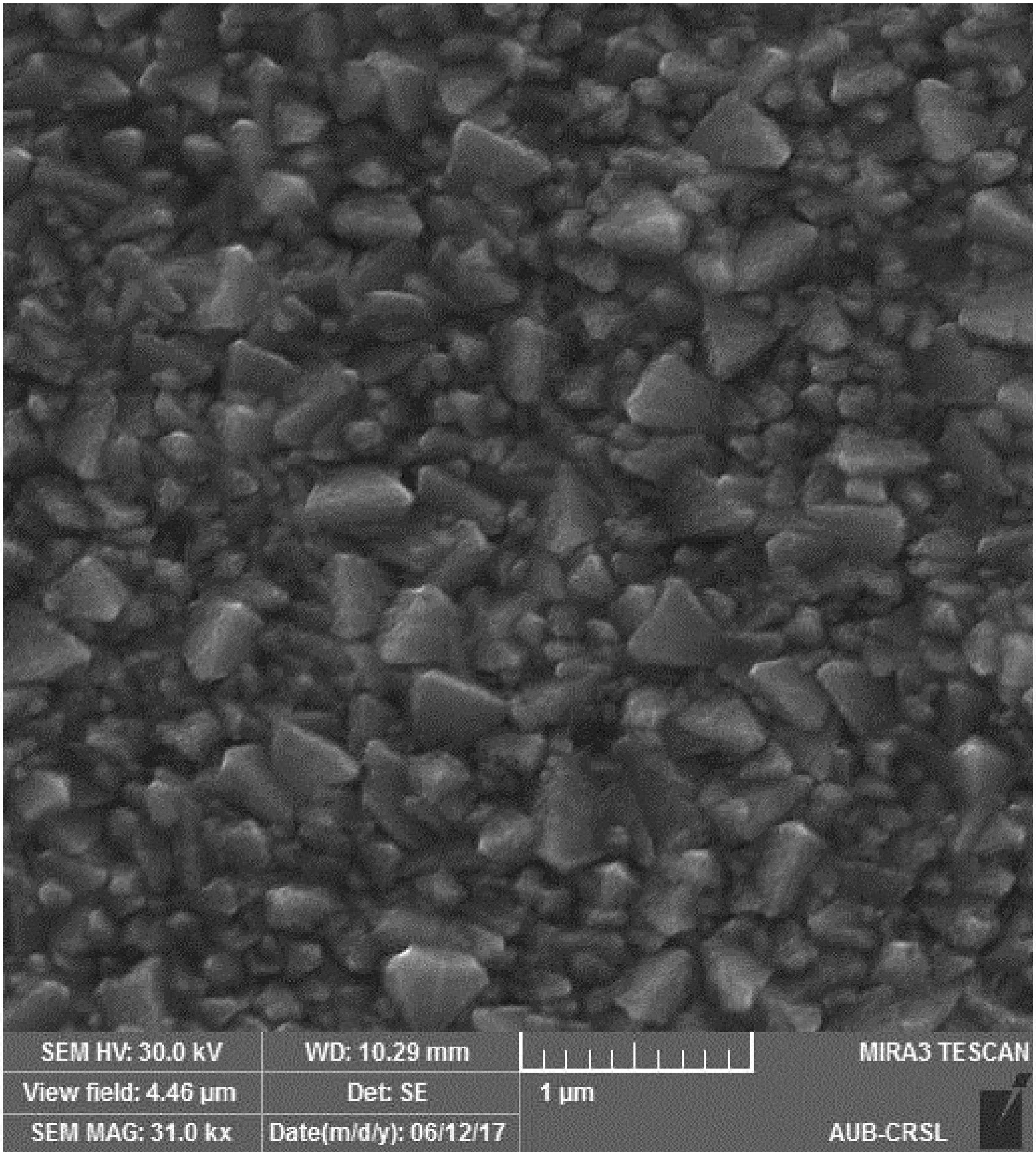

Figure SI.2 SEM image of as-deposited Ni-Bi)$_{10mC}$ (deposited by passing a charge of 10 mC/cm^2) on FTO.

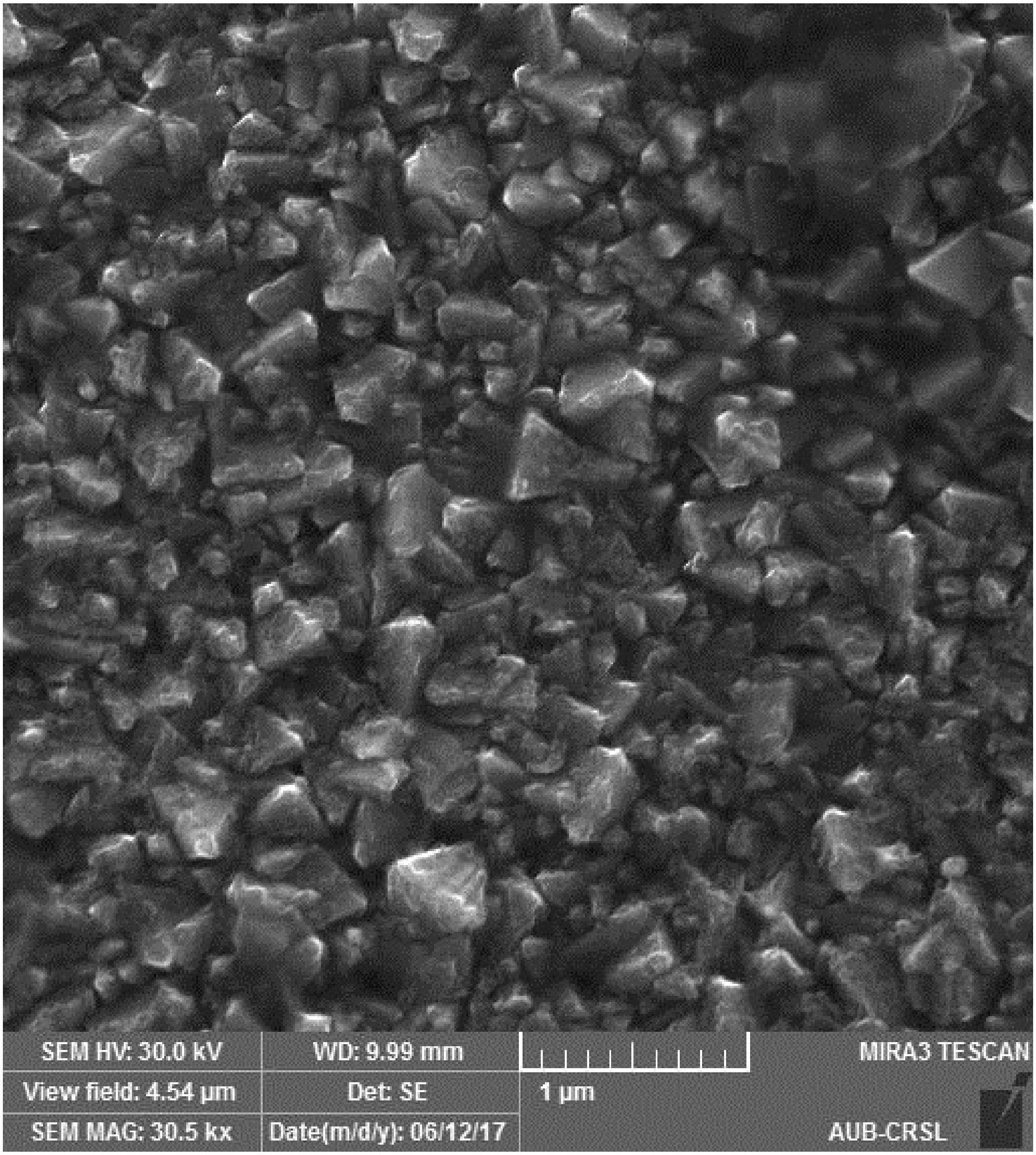

Figure SI.3 SEM image of as-deposited $Ni_{0.4}Fe_{0.6}$-Bi)$_{10mC}$ (deposited by passing a charge of 10 mC/cm^2) on FTO.

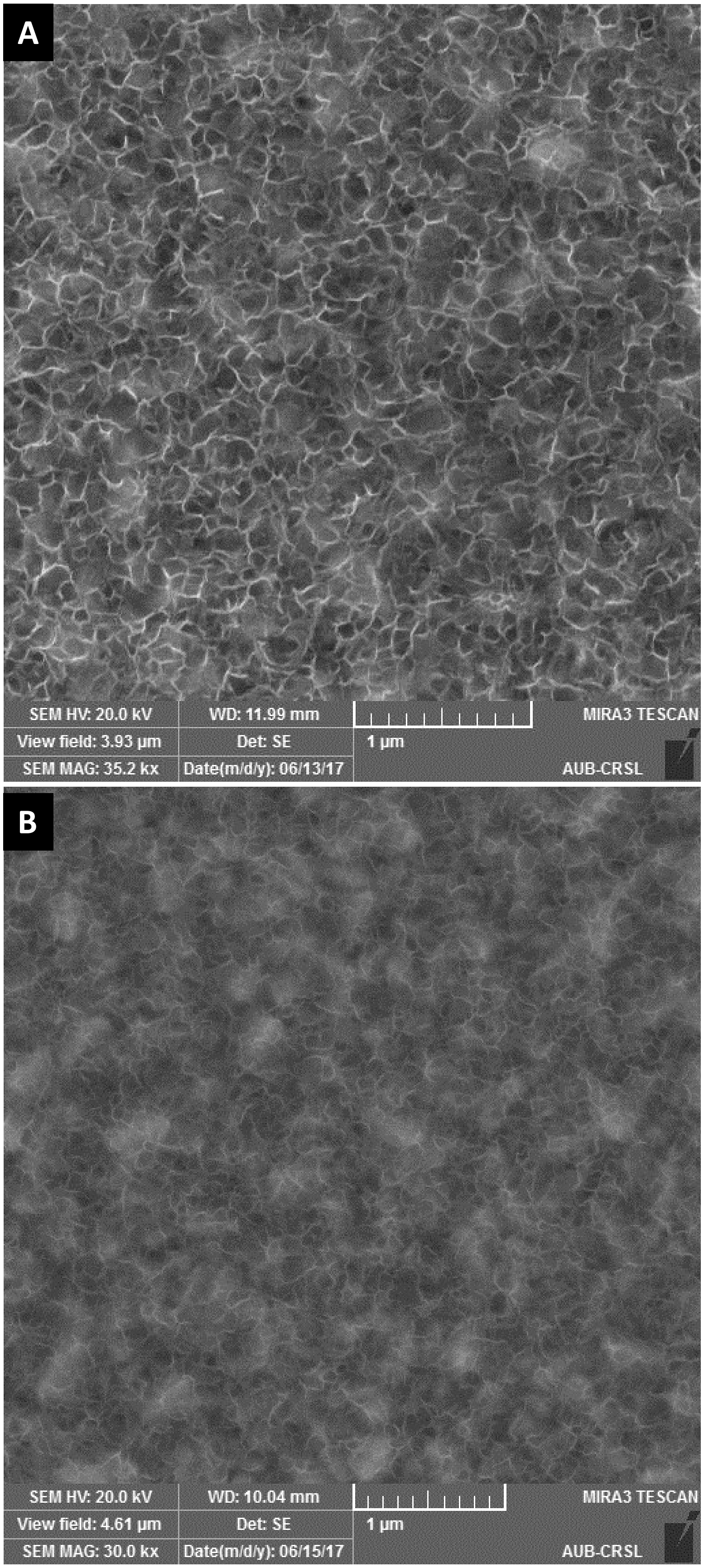

Figure SI.4. SEM images of Ni-Bi)$_{400mC}$ (deposited by passing a charge of 400 mC/cm^2) on FTO: as-deposited (A) and after anodic conditioning (B).

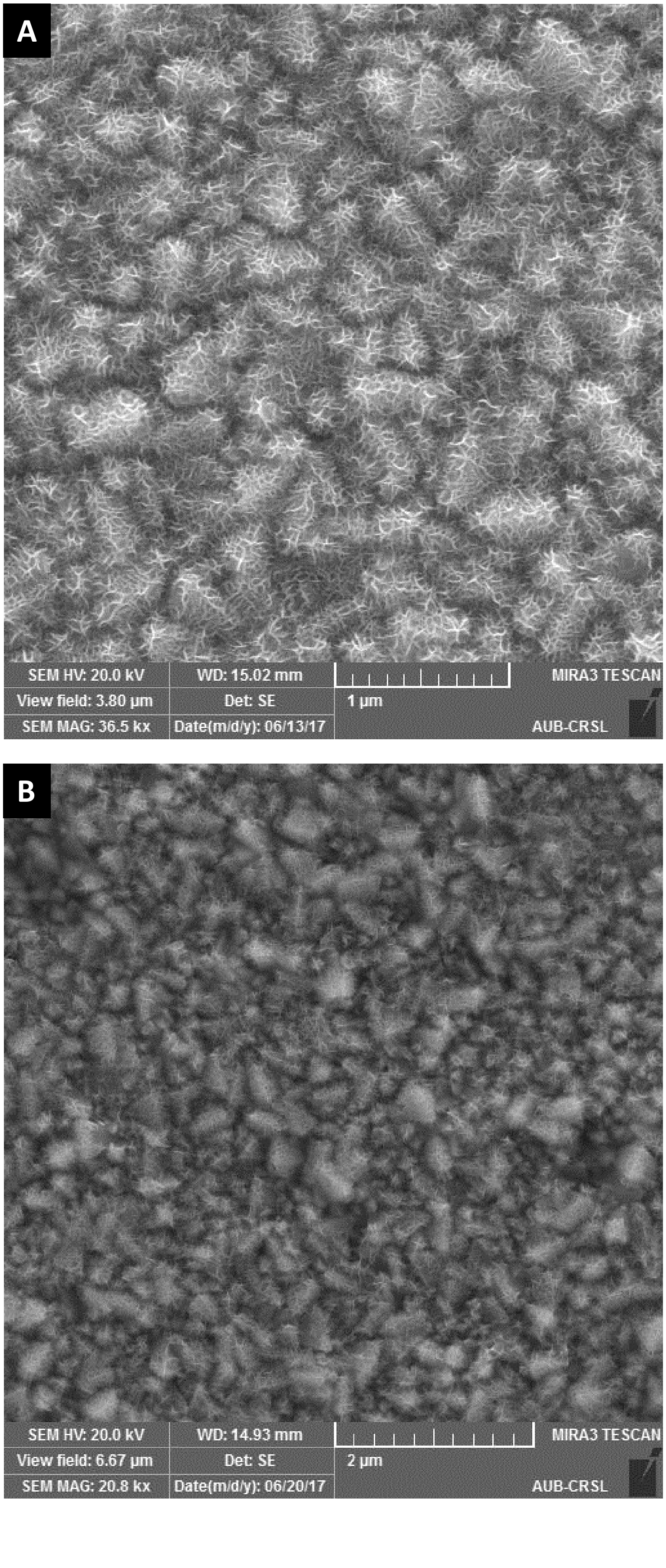

Figure SI.5. SEM images of $Ni_{0.6}Fe_{0.4}$-Bi$)_{400mC}$ (deposited by passing a charge of 400 mC/cm^2) on FTO: as-deposited (A) and after anodic conditioning (B). (Note these images have different scale bars.)

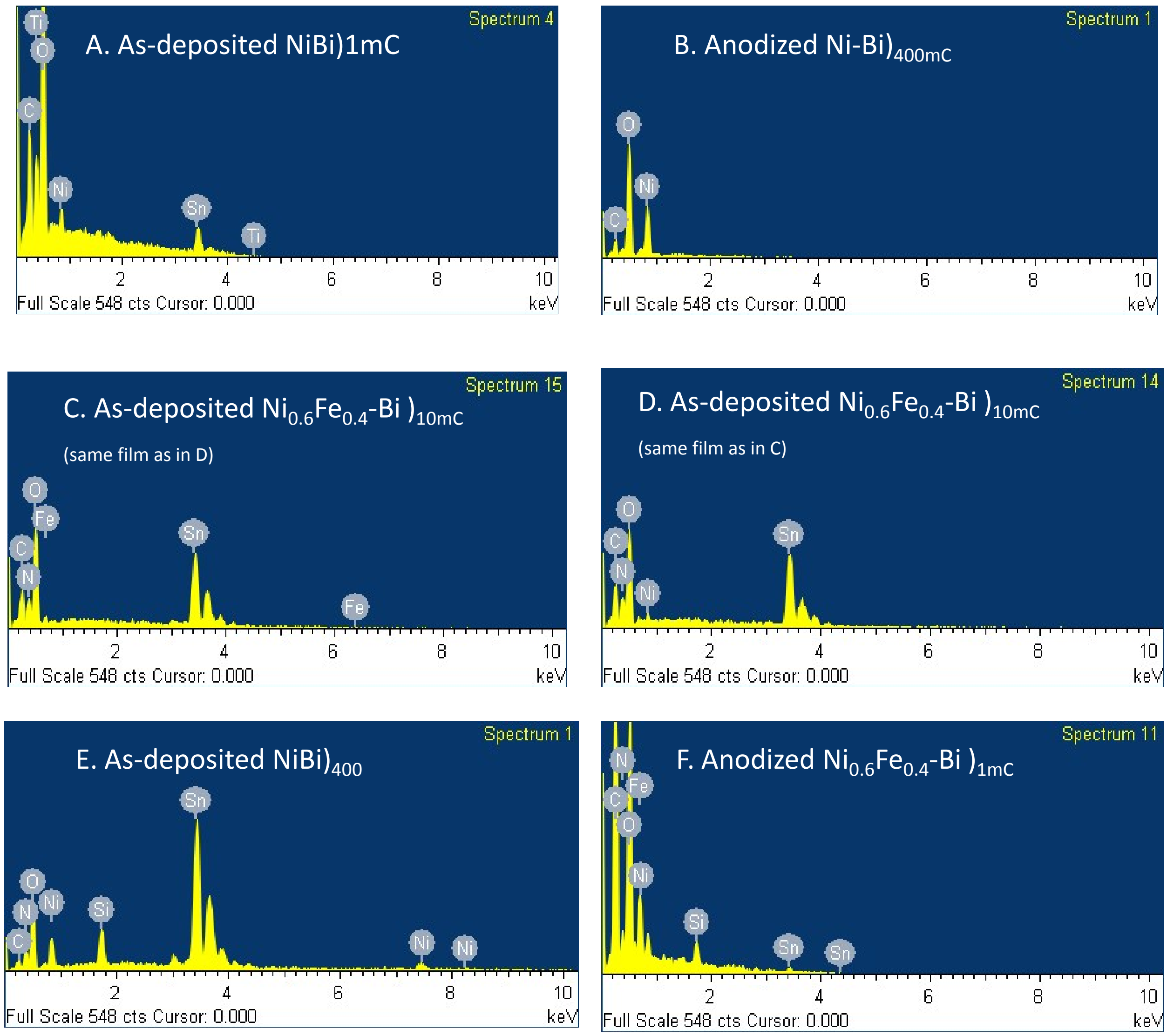

Figure SI.6 EDX spectra of as-deposited Ni-Bi)$_{1mC}$ (A), anodized Ni-Bi)$_{400mC}$ (B), as-deposited $Ni_{0.6}Fe_{0.4}$-Bi)$_{10mC}$ same film one only showing the Fe peaks identified (C) and the second only showing the Ni peak identified (D), as-deposited Ni-Bi)$_{400mC}$ (E), and anodized $Ni_{0.6}Fe_{0.4}$-Bi)$_{1mC}$ (F).

Note on EDX analysis: Note that that the identification of the elements in EDX spectra using the instrument software was different in different spectra of different spots on the same film, for example one spectrum of the thin as-prepared $Ni_{0.6}Fe_{0.4}$-Bi)$_{10mC}$ identified only the Fe peak and a second spectrum showed only the Ni peak. In another example, EDX spectrum of anodized $Ni_{0.6}Fe_{0.4}$-Bi)$_{400mC}$ did not show the Fe peak, but only the Ni peak, while EDX of as-prepared $Ni_{0.6}Fe_{0.4}$-Bi)$_{400mC}$ showed both Ni and Fe peaks, and while Fe was detected in the ultra-thin anodized $Ni_{0.6}Fe_{0.4}$-Bi)$_{1mC}$ film as shown in the spectrum in (F). EDX analysis is used only to show the detection of the elements Ni and Fe, and could not be used to assess inclusion of Fe from traces in the electrolyte in Ni-Bi films prepared without intentional Fe co-deposition, nor for quantitative determination of Ni:Fe ratios even at thicker films deposited at 400 mC/cm^2. Films are denoted relative to ratios of Ni:Fe during co-electrodeposition.

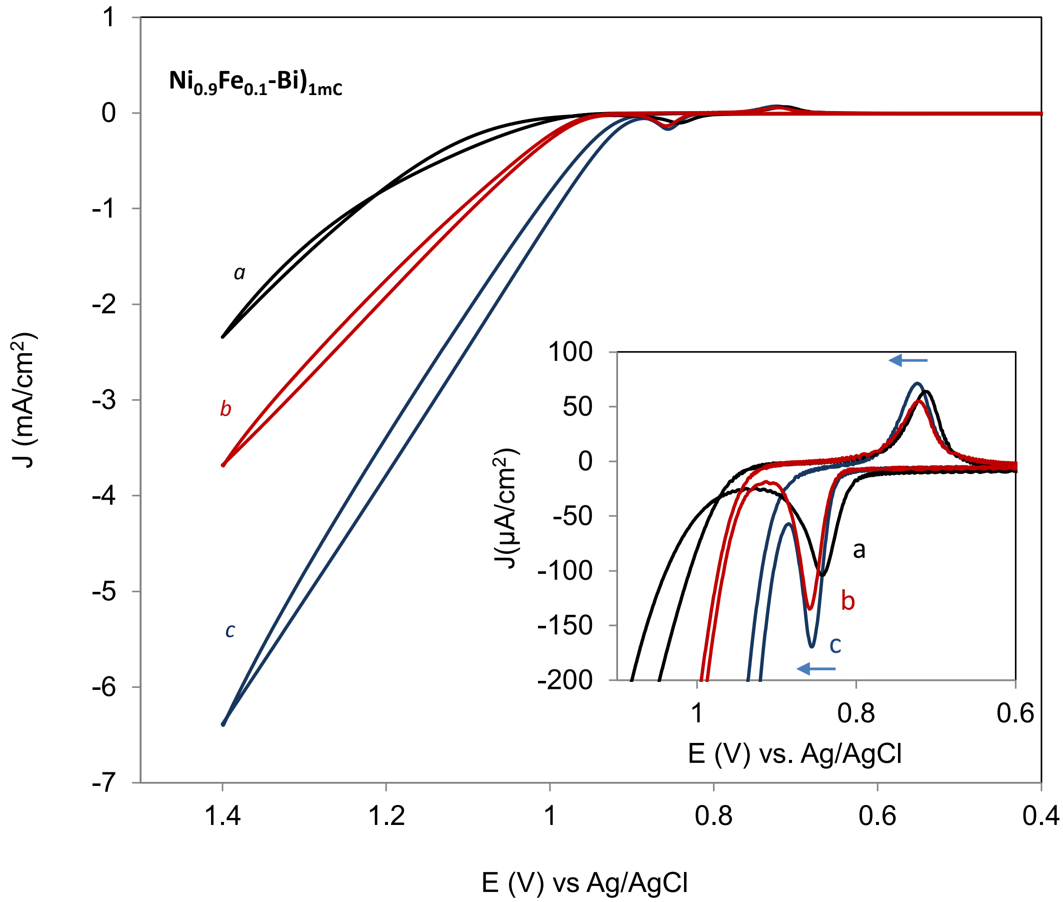

Figure SI.7 First scan CV (a), an intermediate scan CV (b), and a CV after applying an anodic bias of 0.903 V for ~ 3 h (c) acquired of $Ni_{0.9}Fe_{0.1}$-Bi)$_{1mC}$. The inset shows the potential region of the $Ni(OH)_2$/NiOOH redox peaks, showing the anodic shift in the peaks in subsequent potential sweeps. The supporting electrolyte is 1 M KBi pH ~9.2. Scan rate is 10 mV/s.

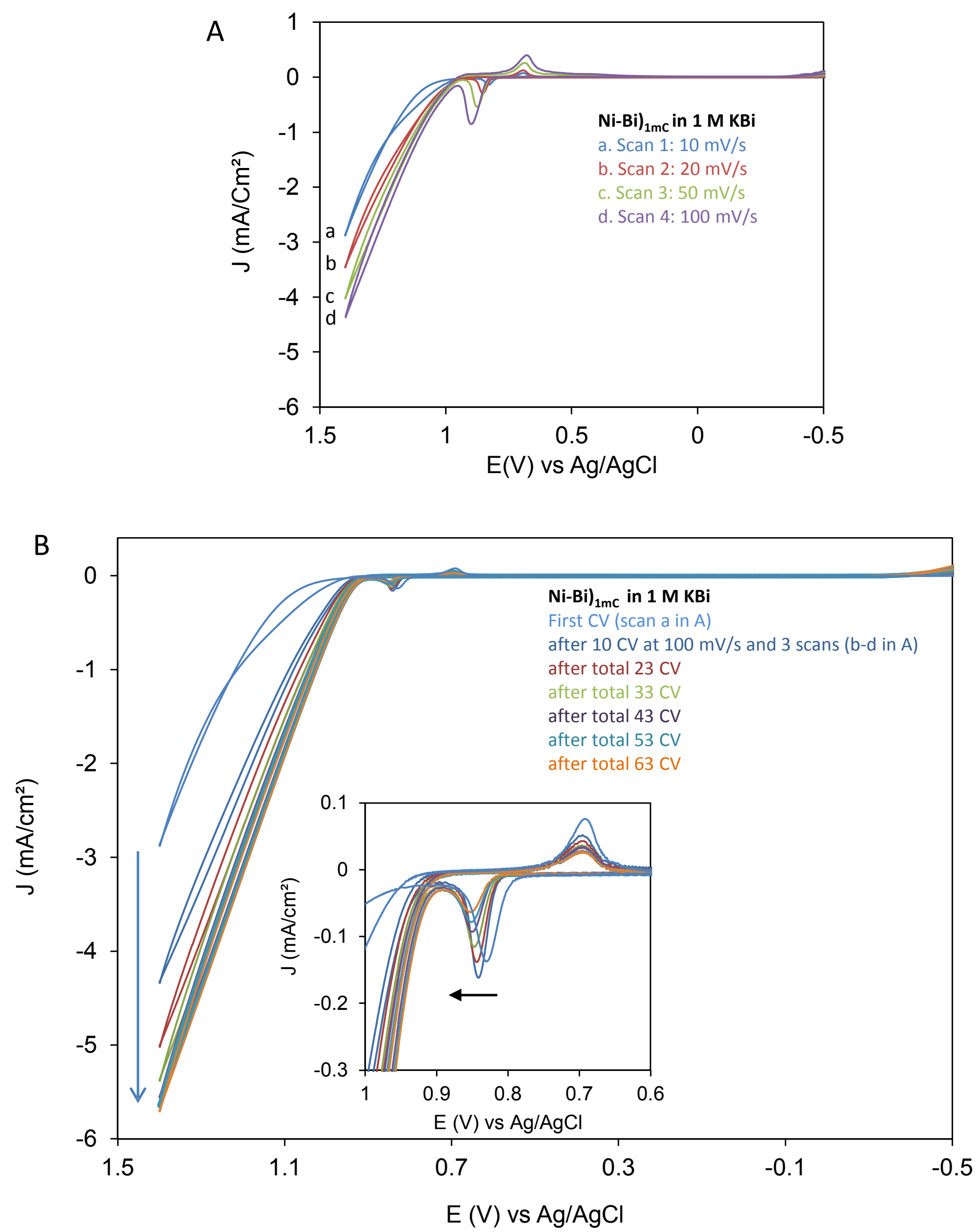

Figure SI.8 Ni-Bi)$_{1mC}$ in 1 M KBi: (A) First CV scan at 10 mV/s (a), second scan at 20 mV/s (b), third scan at 50 mV/s (c), and fourth scan at 100 mV/s (d), showing the increase in OER activity. (B) First CV scan then CV scans at 10 mV/s, after increments of 10 CVs were acquired at 100 mV/s (following the scans b-d). The Figure shows the progressive increase in OER activity and decrease in overpotential with multiple scanning of potential (contrasted to the fast increase in OER activity when 0.16 mM Fe^{3+} was added to the electrolyte, or the absence of this increase in OER activity with multiple scanning when 0.16 mM Al^{3+} was added to the electrolyte). For clarity, the number of CVs (13-63) refers to the CVs acquired at 100 mV/s before each scan at 10 mV/s and the 3 CVs at the scan rates 20, 50, and 100 mV/s. The inset shows the anodic shifts in the $Ni(OH)_2$/NiOOH peaks and the decreases in charges in consecutive scans.

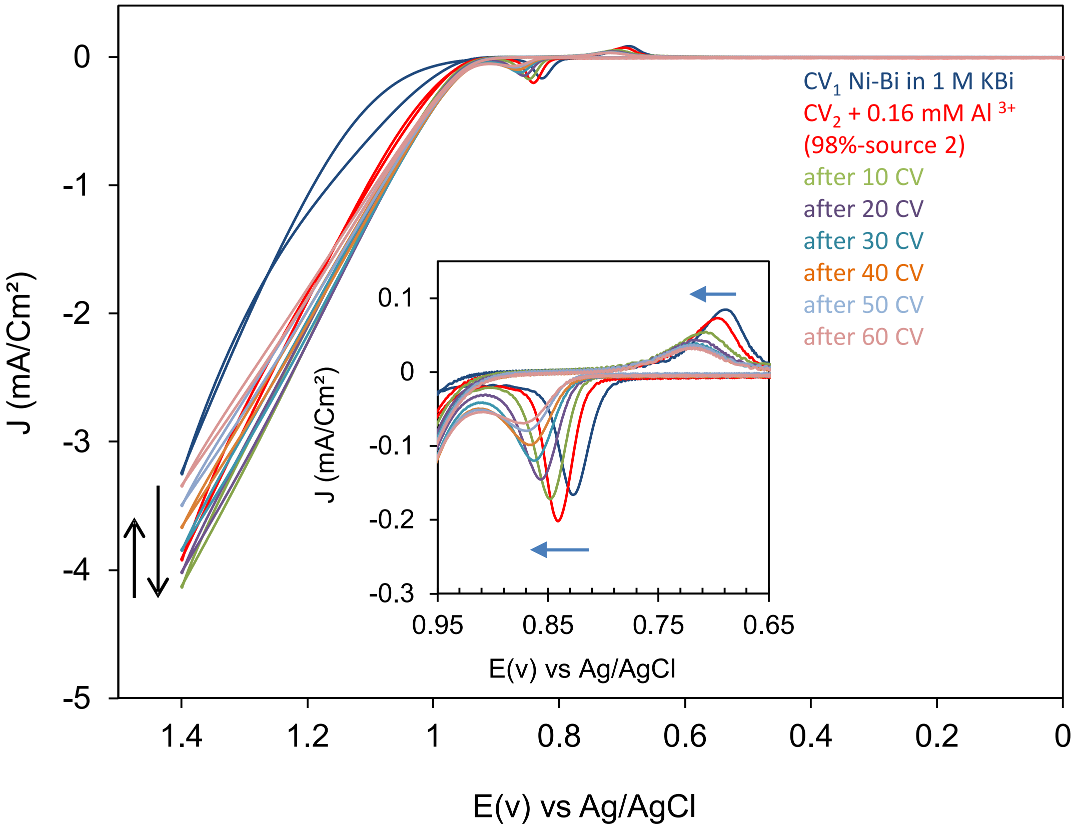

Figure SI.9 Cyclic voltammograms of Ni-Bi)$_{1mC}$ film as first scan in 1 M KBi before and immediately after addition of 0.16 mM Al^{3+} (*source 2: 98%Al, 0.001%Fe*), and then CVs acquired at 10 mVs after 10 CVs were acquired at 100 mV/s repeated 6 times in the same solution. Scan rate is 10 mV/s. The inset shows the anodic shifts in the $Ni(OH)_2$/NiOOH peaks and decreases in charges in consecutive scans in the presence of 0.16 mM Al^{3+}. The number of CVs (10-60) refers to the total number of scans acquired at 100 mV/s.

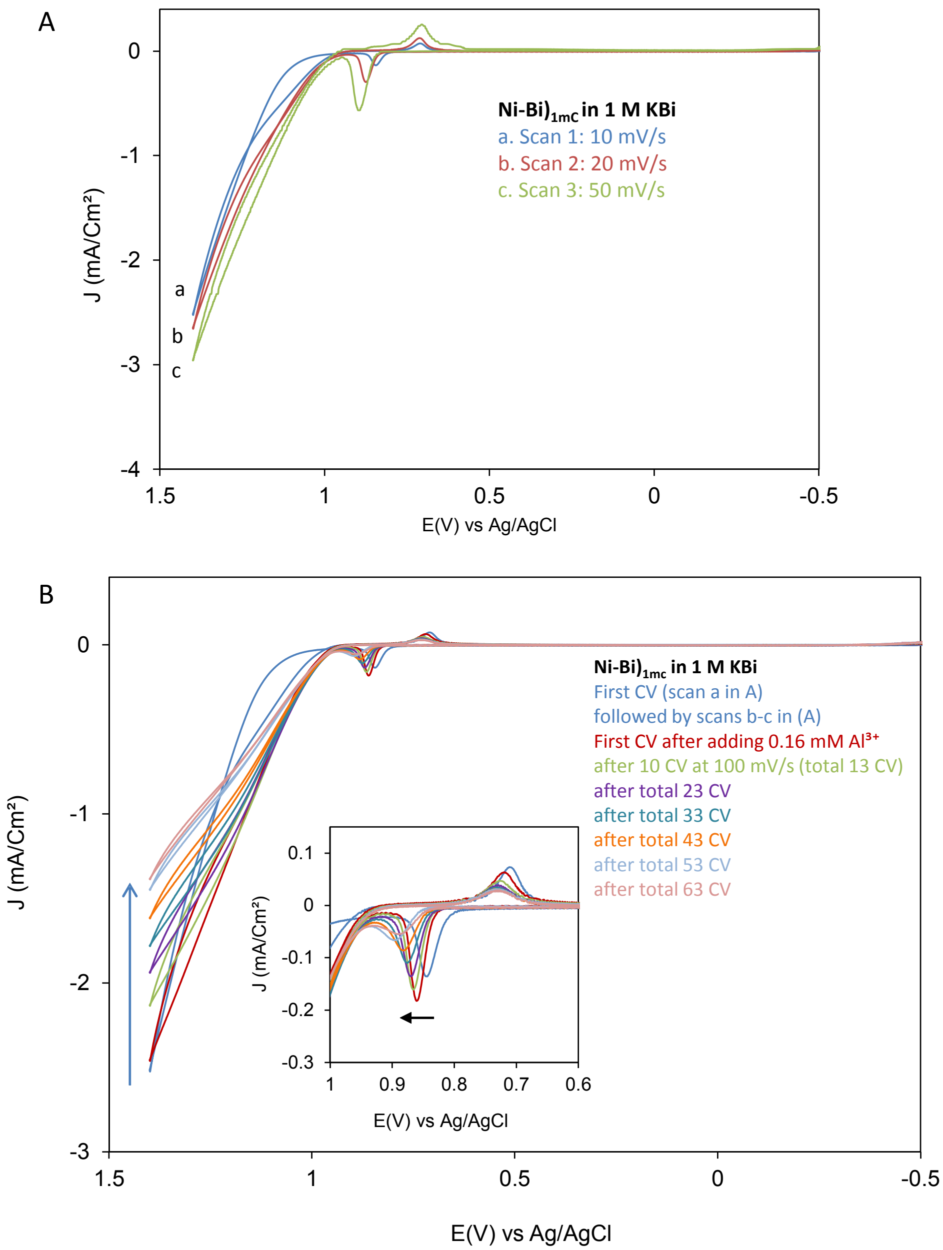

Figure SI.10 (A) First CV scan of Ni-Bi)$_{1mC}$ in 1 M KBi at 10 mV/s (a), followed by a CV at 20 mV/s (b) and 50 mV/s (c) showing the decrease in OER overpotential. (B) First CV scan, then the first scan after addition of 0.16 mM Al^{3+} (*source 1: 99.999%Al*) acquired after the OER activity had increased in 1 M KBi as shown in Panel A, then CVs acquired at 10 mV/s after 10 CVs (repeated 6-times) were acquired at 100 mV/s, showing the decrease in OER activity in the presence of Al^{3+} with subsequent potential scanning. To be compared to the result in Figure SI.8 in the absence of Al^{3+} addition. For clarity, the number of CVs (13-63) refers to the CVs acquired at 100 mV/s before each scan at 10 mV/s and the 2 CVs at 20 and 50 mV/s before adding Al^{3+} and 1 CV at 10 mV/s after adding Al^{3+}. The inset shows the anodic shifts in the $Ni(OH)_2$/NiOOH peaks and the decreases in charges in consecutive scans.

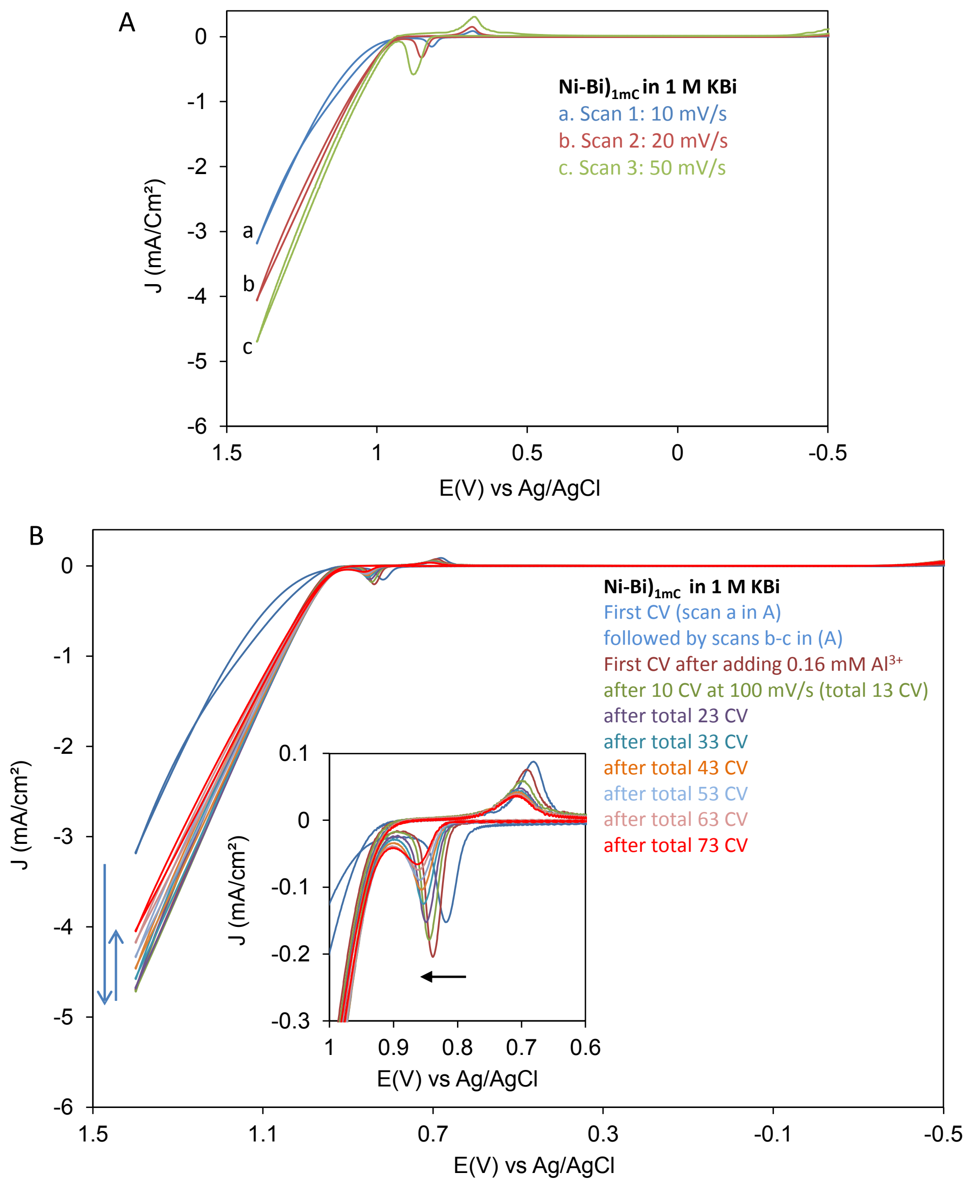

Figure SI.11 (A) First CV scan of Ni-Bi)$_{1mC}$ in 1 M KBi at 10 mV/s (a), followed by a CV at 20 mV/s (b) and 50 mV/s (c) showing the decrease in OER overpotential. (B) First CV scan, then the first scan after addition of 0.16 mM Al^{3+} (*source 2: 98%Al, 0.001%Fe*) acquired after the OER activity had increased in 1 M KBi as shown in Panel A, then CVs acquired at 10 mV/s after 10 CVs (7-times) were acquired at 100 mV/s, showing the decrease in OER activity in the presence of Al^{3+} with subsequent potential scanning. To be compared to the result in Figure SI.8 in the absence of Al^{3+} addition. For clarity, the number of CVs (13-73) refers to the CVs acquired at 100 mV/s before each scan at 10 mV/s and the 2 CVs at 20 and 50 mV/s before adding Al^{3+} and 1 CV at 10 mV/s after adding Al^{3+}. The inset shows the anodic shifts in the $Ni(OH)_2$/NiOOH peaks and the decreases in charges in consecutive scans.

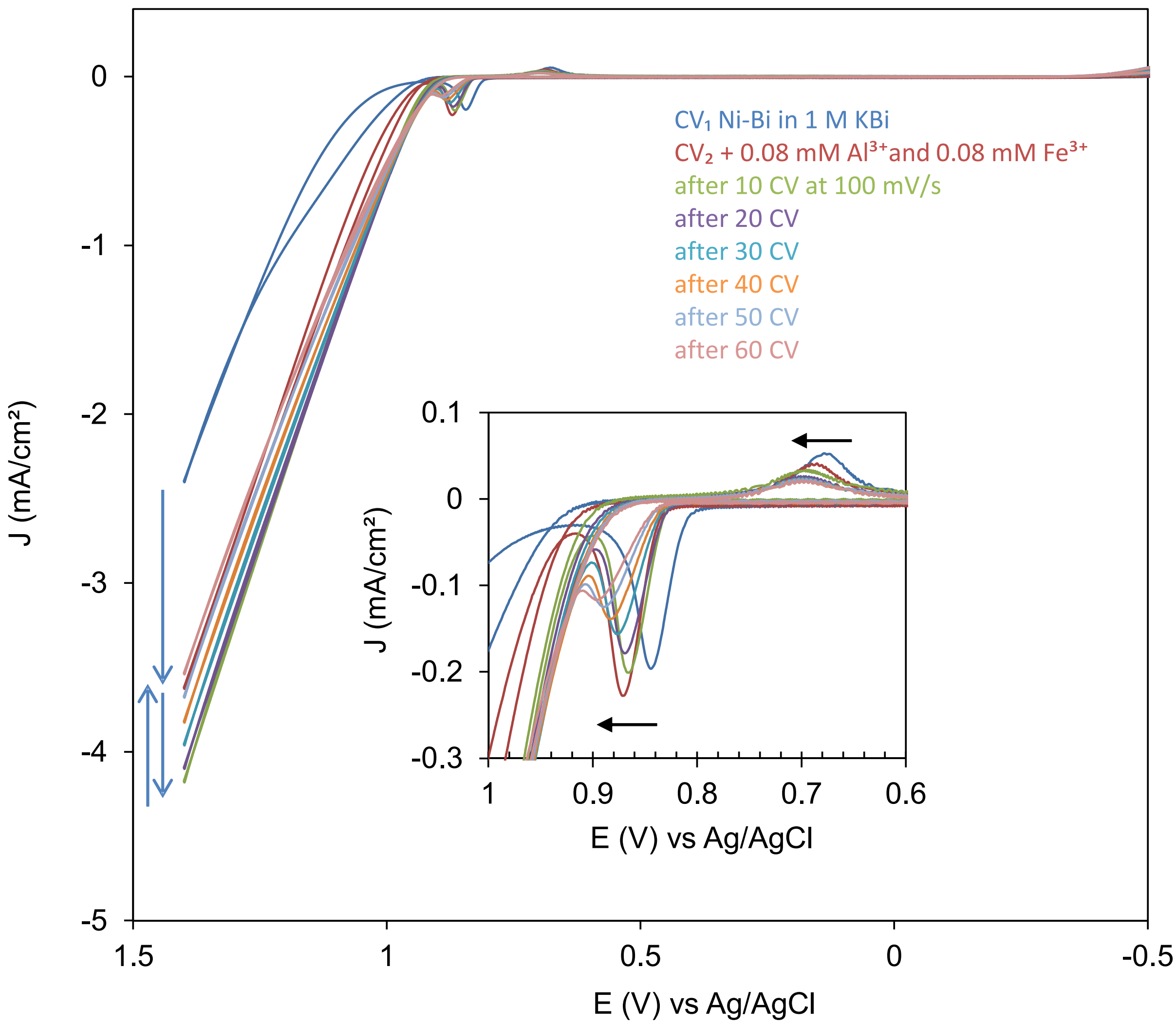

Figure SI.12 Cyclic voltammograms of Ni-Bi)$_{1mC}$ film as first scan in 1 M KBi before and immediately after addition of 0.08 mM Al^{3+} and 0.08 mM Fe^{3+}, and then CVs acquired at 10 mVs after 10 CVs were acquired at 100 mV/s repeated 6 times in the same solution. Scan rate is 10 mV/s. The inset shows the anodic shifts in the $Ni(OH)_2$/NiOOH peaks and the decreases in charges in consecutive scans in the presence of 0.08 mM Al^{3+} and 0.08 mM Fe^{3+}. The number of CVs (10-60) refers to the total number of CV scans acquired at 100 mV/s.

Comparison of OER activity to literature reports and discussion:

The activity of ultra-thin Ni-Bi and NiFe-Bi films was compared to thin Ni-Bi films on planar substrates and to 3-dimensional Ni-Bi films reported in the literature. At ultra-thin films in this study, the Tafel plots onset started at higher overpotential than reported thin Ni-Bi films, but both the onset of the Tafel region and the overpotential that yielded a current density of 1 mA/cm^2 shifted to lower overpotential with increasing Ni coverage. A current of 1 mA/cm^2 was measured at 430-440 mV at Ni-Bi$)_{1mC}$, at ca. 420 mV at Ni-Bi$)_{10mC}$, and at 399-404 mV at Ni-Bi-Bi (N=3) prepared by passing 100 mC/cm^2. By comparison, Dincã et al. reported a current of 1 mA/cm^2 at 425 mV overpotential in 1 M KBi at Ni-Bi deposited at 300 mC/cm^2 with a Tafel plot starting at 300 mV;[34] while Bediako et al. reported 1mA/cm^2 measured at ~400 mV at thin NiBi at 1 mC/cm^2 (from Tafel plots presented), and the Tafel region started at ~320-330 mV.[32] The onset of the linear Tafel region was at ~400 mV at $NiO_x)_{1mC}$ and decreased to ca. 388 mV at Ni-Bi$)_{10mC}$ to 350-370 mV at Ni-Bi$)_{100mC}$. Similarly at NiFe-Bi, 1 mA/cm^2 was measured at ~429-440 mV at $Ni_{0.9}Fe_{0.1}O_x)_{1mC}$ similar to Ni-Bi$)_{1mC}$, at ~447-455 mV at $Ni_{0.6}Fe_{0.4}O_x$, and at ca. 470 mV at $Ni_{0.4}Fe_{0.6}O_x$, therefore also increasing with decreasing Ni content. It is noted that Ni-Bi$)_{1mC}$ films in this study resulted in a deposited charge of 0.4 mC/cm^2 Ni charge compared to 0.9 mC/cm^2 reported by Bediako et al.[32] and therefore contained less Ni. The TOFs are lower at low potential than reported by Bediako et al. in 0.5 M KBi/1.75 M KNO_3 pH 9, which equaled 0.9 s^{-1} at 400 mV at NiBi at 1 mC/cm^2 (5.9 nmol Ni/cm^2) and 0.5 s^{-1} by passing 0.4 mC/cm^2 (3.4 nmol Ni/cm^2).[32] The latter Ni content is closer to Ni-Bi$)_{1mC}$ here (~3 $nmol/cm^2$) but the TOF at 400 mV was ca. 0.1 s^{-1} and was 0.13 s^{-1} at 409 mV in 1 M KBi, and the TOF equaled 0.23 s^{-1} at 411 mV at $Ni_{0.6}Fe_{0.4})_{1mC}$, lower than reported. Boettcher et al. reported at Ni-Bi deposited by passing 10 mC/cm^2 a TOF of 0.38 s^{-1} at 400 mV after conditioning (14% Fe found), but only

0.03 s^{-1} in Fe-free electrolyte at 400 mV; while they reported a TOF of 0.24 s^{-1} before conditioning for films with co-deposited Fe, and 1.4 s^{-1} after conditioning (with 1.1 e per Ni).[35] The CVs show that 1 mA/cm^2 was measured at ~420 mV (estimated from Figure 1 A in ref. 35) after conditioning in 1 ppm Fe containing borate.[35] It is noted that the current delivered at a certain overpotential and the TOF are both functions of the amount of Ni deposited, and other factors such as solution and film resistance, the impurities in the solution and the electrolyte. It is possible that experimental variations in Fe inclusion, or resistance and structure of the substrate, and solution resistance, electrolyte concentration and impurities, could have affected the amount deposited, the distribution on the surface, and therefore the currents and the onset of the Tafel region. Note that high steady-state TOF per Ni center at the ultra-thin Ni-Bi films were measured at high potentials equaling 2.74 ± 1.62 s^{-1} at η = 457 mV ± 3, N=2 at Ni-Bi$)_{1mC}$ and reached 5.08 ± 0.73 s^{-1} at η = 460±0 mV at $Ni_{0.6}Fe_{0.4}$-Bi (N=3).

On the other hand, recently reported 3D nanoarrays for instance of NiBi, Ni-Co-Pi, and NiFe-Bi yielded significantly greater currents at lower overpotential,[49-54] for example, 10 mA/cm^2 was reported at 363 mV at 3D NiFe-LDH@NiFe-Bi in 0.5 M KBi,[50] and a Ni-Bi nanoarray on carbon cloth was reported to drive 10 mA/cm^2 at 470 mV in 0.1 KBi.[54] These films contained significantly greater amounts of Ni (loading in the mg range loading, or $\mu mol/cm^2$), and yielded Tafel slopes of 100-200 mV/dec and lower TOF.[49-54] Detailed results of these recently reported nanostructured films are as follows: 1) Bimetallic Ni-substituted cobalt borate nanowire array on carbon cloth (of 3.8 μm thickness, Ni-Co-Bi loading of 2.1 mg/cm^2) required 388 mV to deliver 10 mA/cm^2, but the TOF was 0.33 s^{-1} at 500 mV, and 0.2 s^{-1} at 450 mV, and the Tafel slope was 142 mV/dec.[49] 2) 3D nanoarray of NiFe-borate layer on NiFe-layered double hydroxide on carbon cloth required only 444 mV or 363 mV in 0.1 M and 0.5 M

KBi respectively to deliver 10 mA/cm^2, and had a TOF of 0.5 s^{-1} at 600 mV.[50] 3) Ni-Bi-Pi (nickel-borate-phosphate) nanoarray on carbon cloth delivered 10 mA/cm^2 at 440 mV in 0.1 M KBi. This 3D catalyst contained 0.77 $\mu mol/cm^2$ of active sites and had a TOF = 0.2 s^{-1} at 600 mV.[51] 4) Ultrathin Ni-Bi layer on Ni_3N nanosheet on Ti mesh in 0.1 M KBi yielded 10 mA/cm^2 at 382 mV in 0.5 M KBi, and the Tafel slope was 190 mV/dec.[52] 5) NiBi nanosheet array on Ti mesh was reported to deliver 10 mA/cm^2 at 430 mV, and the TOF equaled 0.13 s^{-1} at 400 mV and 0.53 s^{-1} at 600 mV in 0.1 KBi, and the Tafel slope was 276 mV/dec with NiBi loading of 1.9 mg/cm^2.[53] 6) NiBi nanoarray on carbon cloth (containing Ni-Bi loading of 2.3 mg/cm^2) delivered 10 mA/cm^2 at 470 mV in 0.1 KBi, with a Tafel slope of 107 mV/dec, and a TOF of 0.45 s^{-1} at 600 mV.[54] For emphasis, Ni-Bi$)_{1mc}$ that yielded an average apparent TOF_{ss} of 2.7 s^{-1} at ca. 460 mV in our study contained only ca. 3 $nmol/cm^2$ of Ni.