Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Catalytic Open-circuit Passivation by Thin Metal Oxide Films of p-Si Anodes in Aqueous Alkaline Electrolytes

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Supplementary Information

Supplemental Experimental Methods

The procedure for determining Si etch rate in KOH (Fig. S1) can be found in a previous work.[1] Briefly, a Si wafer was subjected to 950 ˚C for 6 h in air to grow a thermal oxide. A 10 µm by 100 µm array of rectangles was patterned using the same photolithography procedures as above. The patterned wafers were etched in BOE for 3 min to create trenches and the photoresist was removed with acetone. The samples were cleaved and made into electrodes. The electrodes were tested in a standard 3-electrode cell with 1 M KOH(aq) and a potential was applied. After 20 h, the sample was removed from the electrode and submerged in BOE for 5 min to remove the thermal oxide. AFM was used to quantify height differences between the not etched Si surface (previously underneath the thermal oxide) and the exposed trenches.

The p^+-Si/Ni islands (µNi) electrode depicted in Fig. S7 was fabricated using photolithography and Ni sputtering as described in a previous work.[1] Briefly, the Si wafer was RCA2 cleaned and dried before applying primer and Shipley 1813 positive photoresist via spin coater. The wafer was cured on a hot plate at 110 ˚C for 1 min and then exposed to UV light under a mask aligner. The chrome mask used produced an array of 3 µm diameter holes in the photoresist with 7 µm pitch. The pattern was developed in MF-319 for 2 min and baked at 110 ˚C for 1 min. 60 nm of Ni was sputter deposited. The photoresist was removed by sonicating the sample in acetone.

Amorphous TiO_2 films used in Fig. S9, S10, and S12 were deposited on cleaned Si via ALD (Cambridge Nanotech S200). For each ALD cycle, a 0.10 s exposure to TDMAT was followed by a 15 s, 20 sccm N_2 purge, a 0.015 s exposure to H_2O, and another N_2 purge. The deposition chamber was held at 150 ˚C and the TDMAT precursor was held at 75 ˚C throughout the deposition. A 1500 cycle was prepared leading to a 70 nm film as measured by spectroscopic ellipsometry (J.A. Woollam Co., alpha-SE).

Supplementary Information Figures

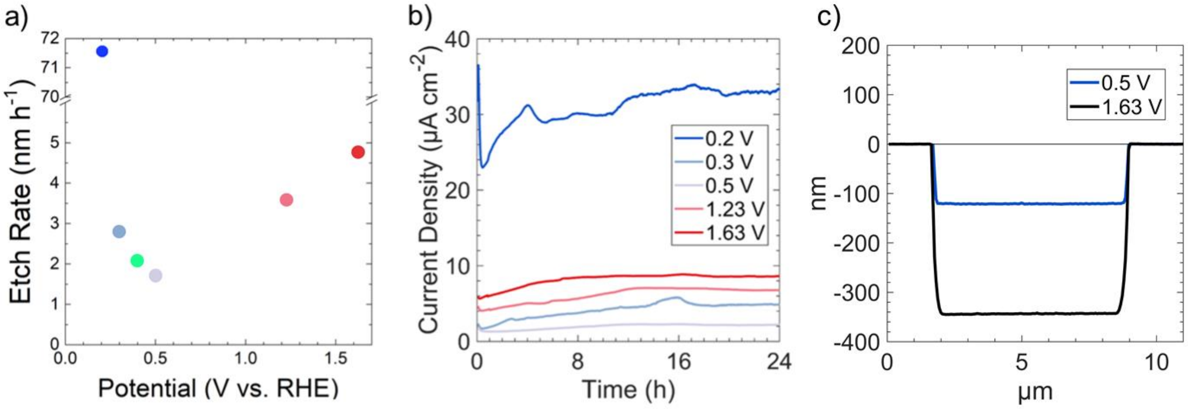

Figure S1. (a) Dissolution rate of p$^+$-Si(100) in 1 M KOH(aq) in the dark at various potentials and (b) the corresponding chronoamperogram over a 24 h period. (c) Cross-section of p$^+$-Si(100) representative etch pits under 0.5 V (blue) and 1.63 V (black) vs RHE in 1 M KOH(aq) for 72 h.

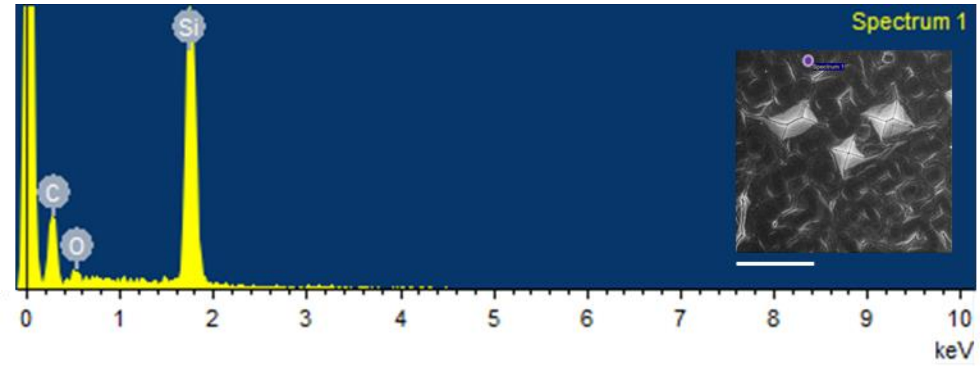

Figure S2. Energy dispersive X-ray spectrum of p$^+$-Si/Ni (5 nm) after 120 h in N_2-saturated 1 M KOH(aq). Inset shows corresponding scanning electron micrograph; the purple dot indicates location of scan. Scale bar is 10 µm.

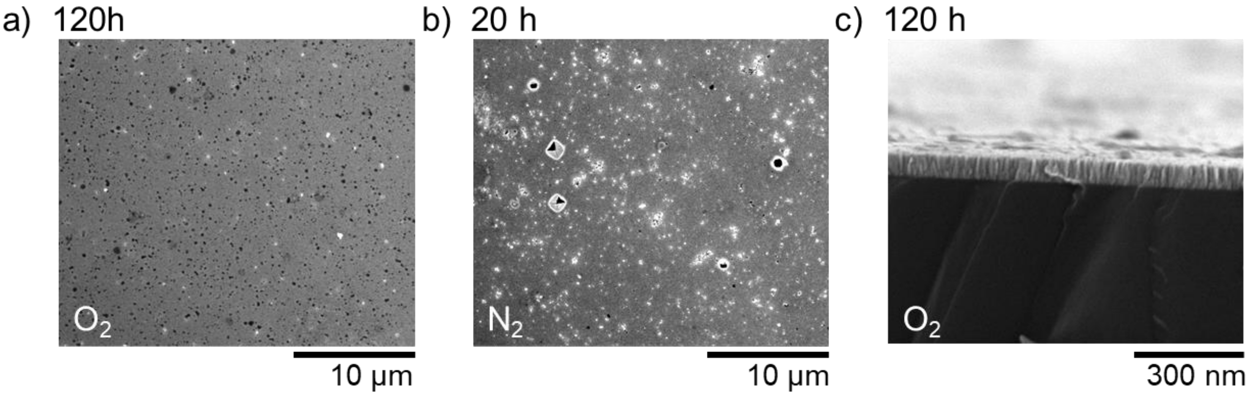

Figure S3. (a-b) Top-down scanning electron micrographs of p$^+$-Si(100)/NiO$_x$ electrodes in 1 M KOH(aq) at open circuit saturated with (a) O_2 for 120 h and (b) N_2 for 20 h. (c) Cross section of sample in (a) showing the NiO$_x$ coating on the Si substrate.

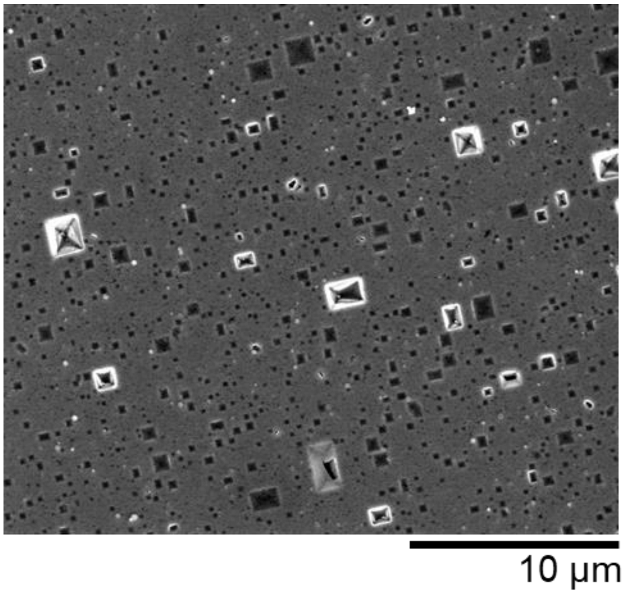

Figure S4. Scanning electron micrograph of p$^+$-Si(100)/Ni (5 nm) after being potentiostatically held at -0.1 V vs RHE for 20 h in O_2-saturated 1 M KOH(aq).

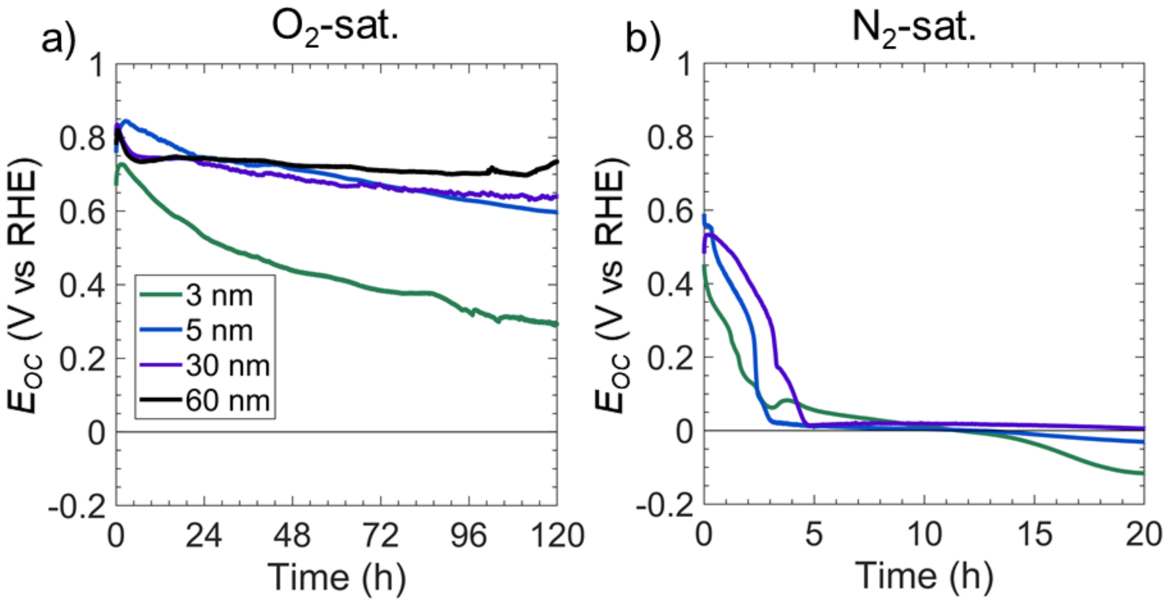

Figure S5. Comparison of open-circuit potential vs time for p$^+$-Si/Ni electrode with Ni film thicknesses at 3 nm (green), 5 nm (blue), 30 nm (purple), and 60 nm (black, (a) only) in (a) O_2- and (b) N_2-saturated 1 M KOH(aq) solution.

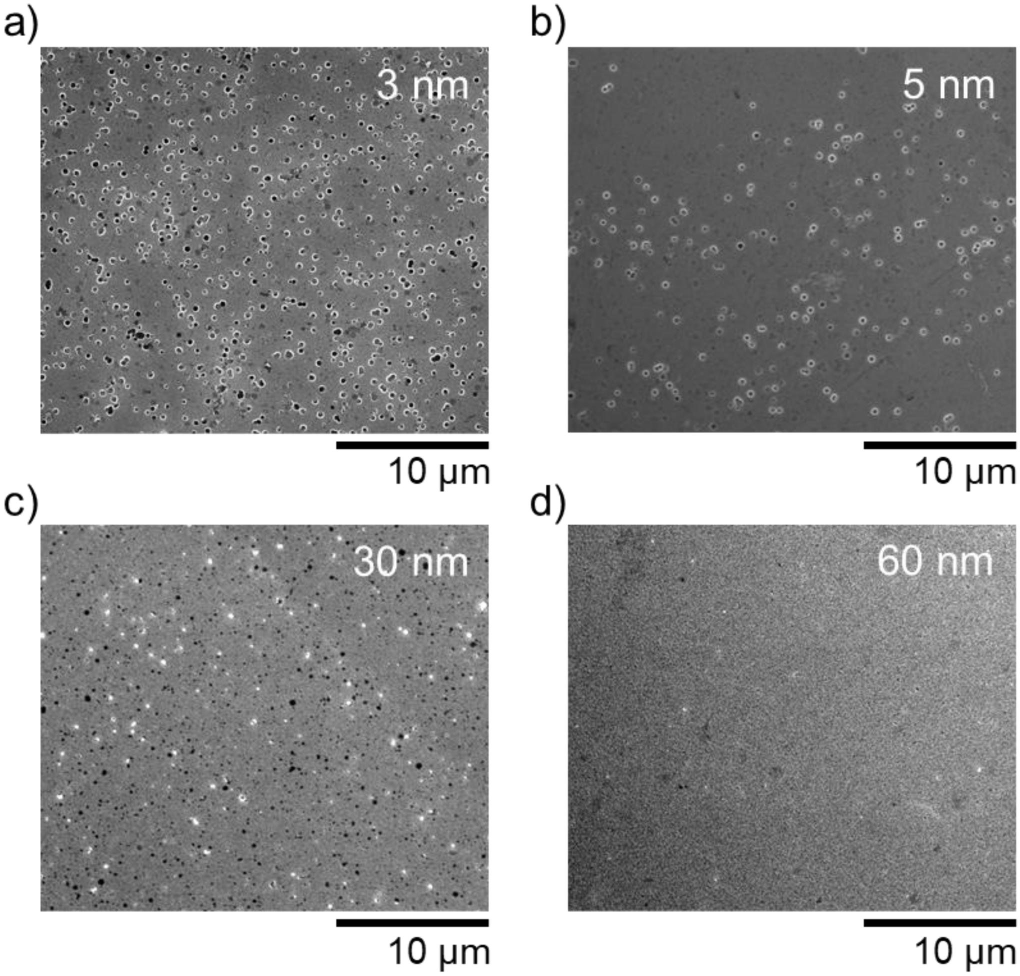

Figure S6. Scanning electron micrographs of p$^+$-Si deposited with Ni film thicknesses at (a) 3 nm, (b) 5 nm, (c) 30 nm, and (d) 60 nm after 120 h at open circuit in O_2-saturated 1 M KOH(aq).

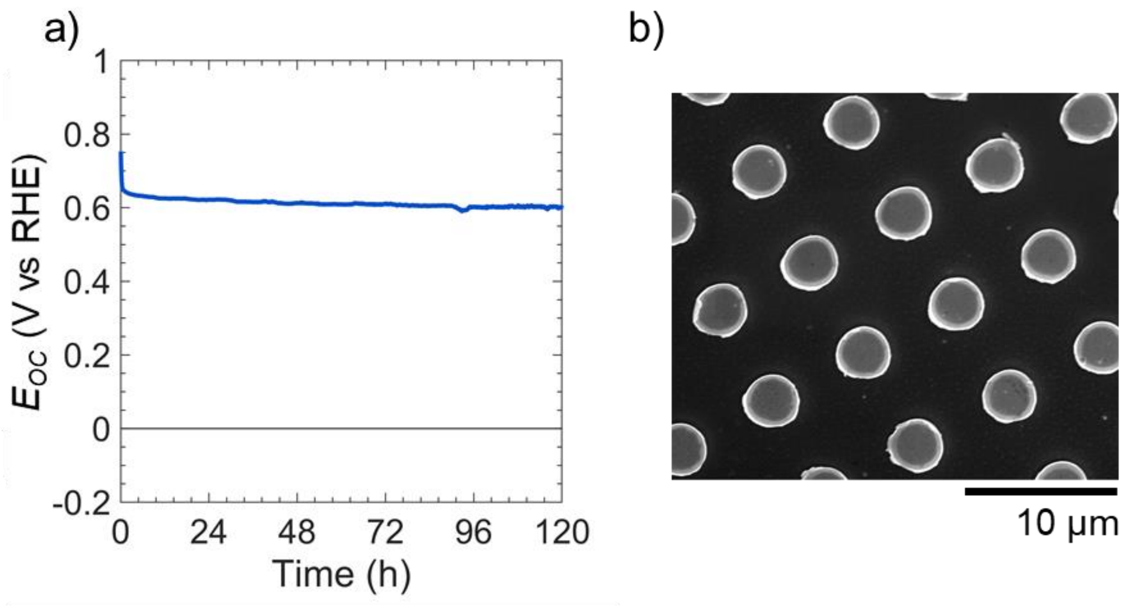

Figure S7. Catalyzed passivation of exposed Si using Ni islands (μNi) in 1 M KOH. (a) Open-circuit potential vs time of p$^+$-Si decorated with 60 nm thick μNi in O_2-saturated, 1 M KOH(aq). (b) Scanning electron micrograph of p$^+$-Si/μNi after testing for 120 h. An array of 3 μm diameter μNi covered ~ 14% of the Si surface.

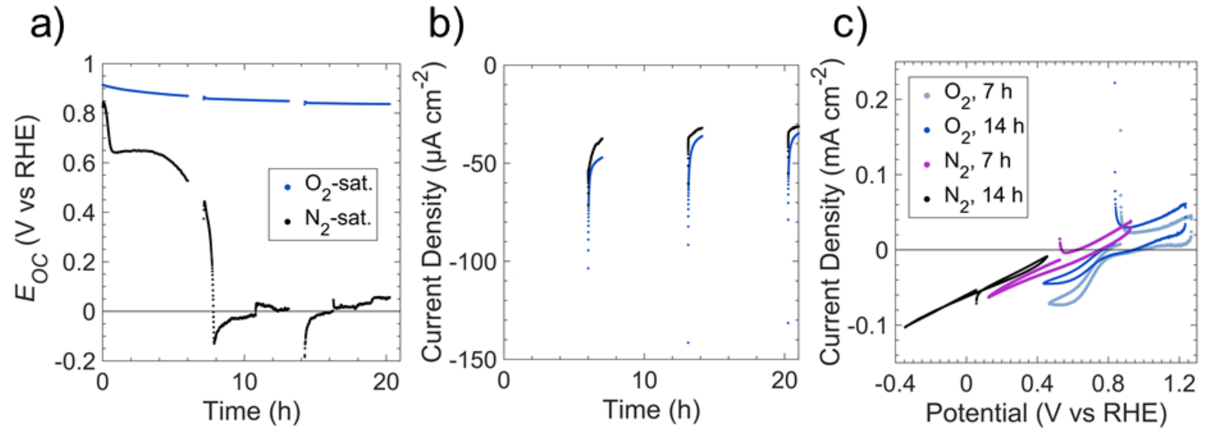

Figure S8. Electrochemical data of p$^+$-Si/NiO_x (60 nm) electrodes in 1 M KOH(aq) in the dark. (a) Open-circuit potential (E_{oc}) vs time over 6 h intervals in O_2-saturated (blue) or N_2-saturated (black) solutions. (b) Chronoamperogram at 0.3 V vs RHE for 1 h taken at 6, 13, and 20 h after the E_{oc} measurements in (a). (c) Cyclic voltammograms in O_2- (light blue and blue) or N_2-saturated (purple and black) solutions taken after 7 and 14 h cycles, respectively. The scans were cycled from E_{oc} to +0.4 V to -0.4 V vs E_{oc} at 10 mV s^{-1}.

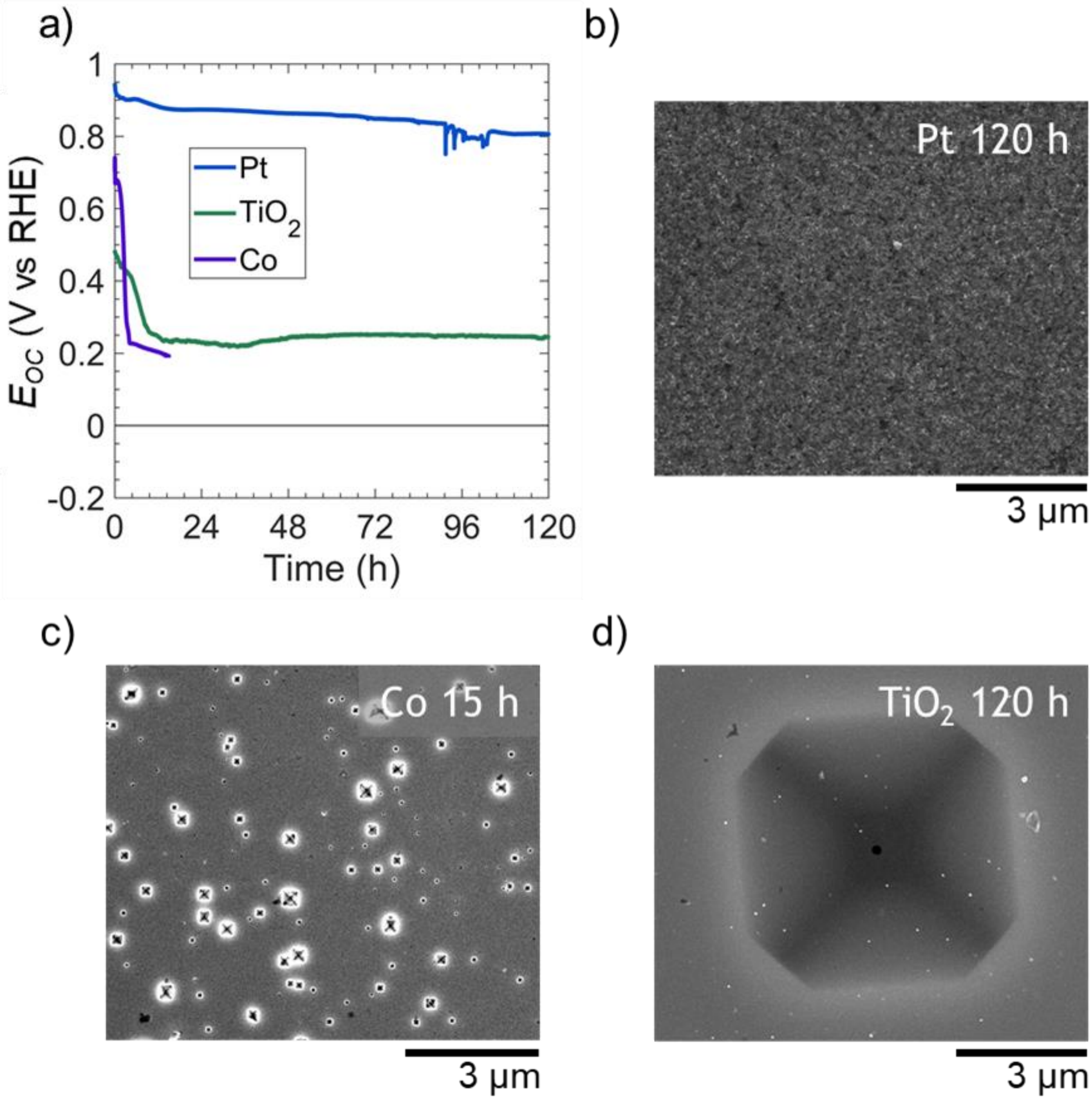

Figure S9. (a) Open-circuit potential vs time for p^+-Si coated with Pt (blue), amorphous TiO_2 (green), or Co (purple) thin films in O_2-saturated 1 M KOH(aq). (b-d) Scanning electron micrographs of p^+-Si coated with (b) Pt, (c) Co, or (d) TiO_2 imaged after submerging in KOH for 120 h, 15 h, and 120 h, respectively.

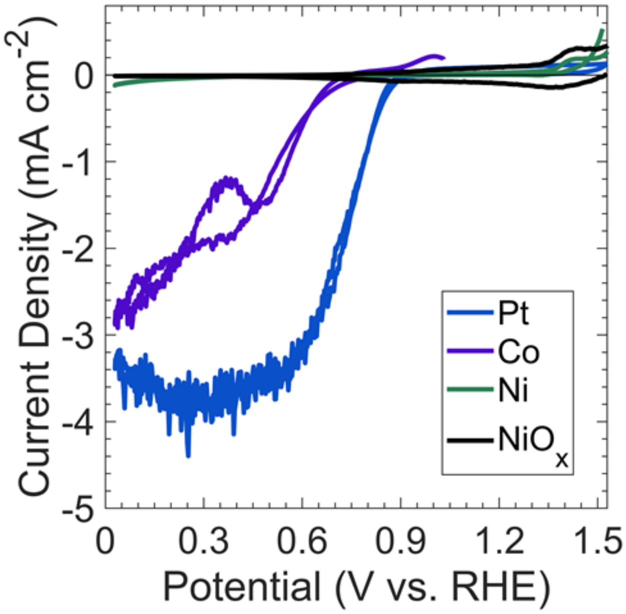

Figure S10. Cyclic voltammograms for the oxygen reduction reaction for Pt (blue), Co (purple), Ni (green), and NiO$_x$ (black) thin films on n$^+$-Si in 1 M KOH(aq) under O$_2$-saturation and vigorous stirring.

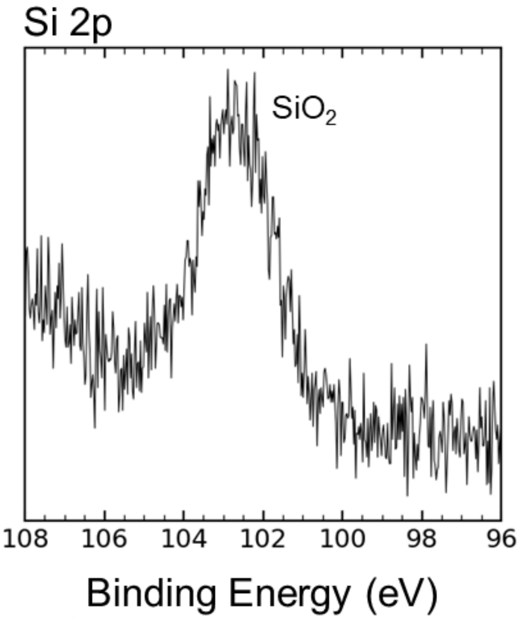

Figure S11. X-ray photoelectron spectrum in the Si 2p region of an np$^+$-Si/NiO$_x$ photoelectrode after extended stability testing under day/night cycling. The y-axis is in arbitrary units.

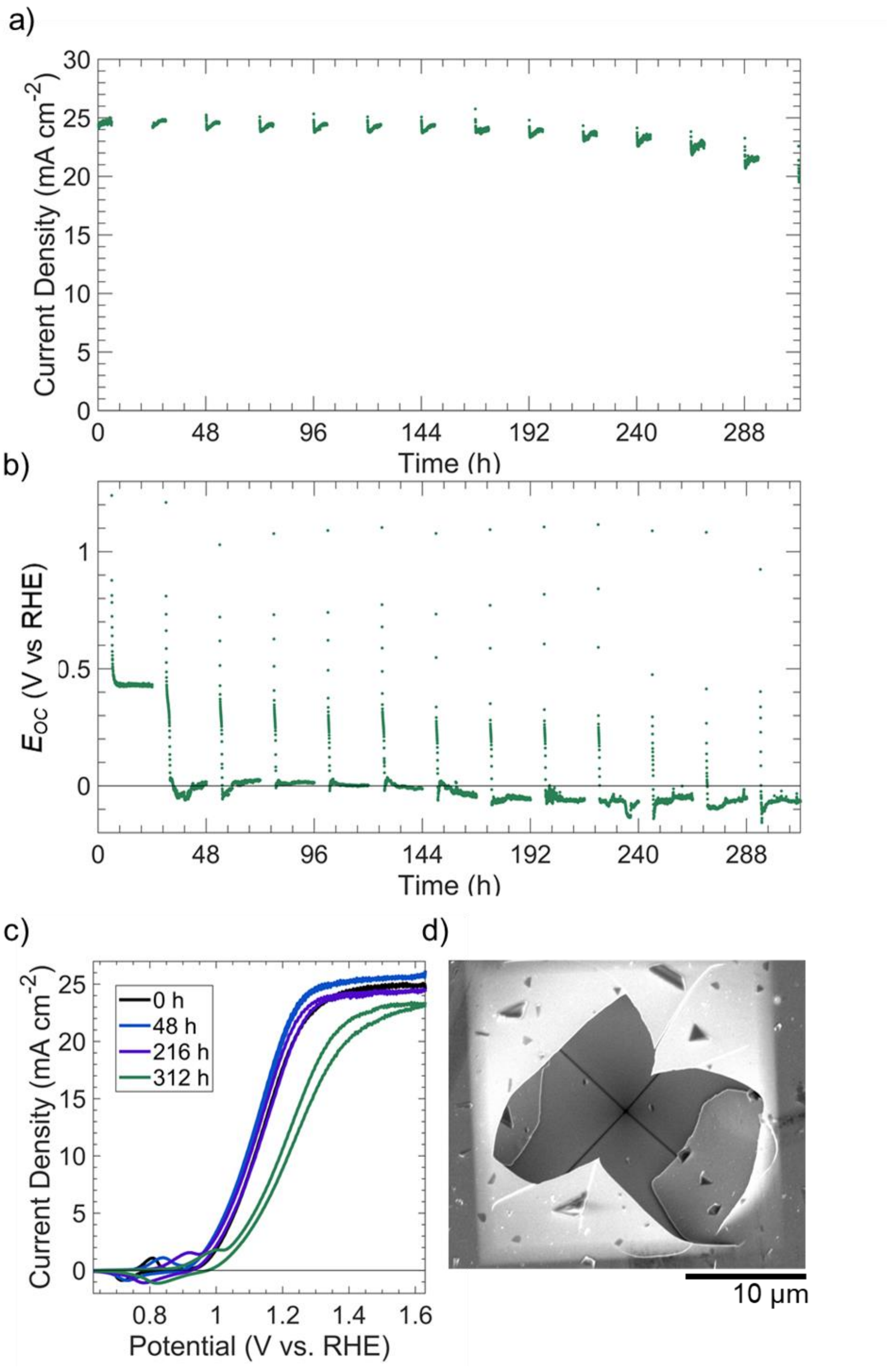

Figure S12. Stability and performance of np$^+$-Si/TiO_2/Ni photoanode under day/night cycling in O_2-saturated 1 M KOH(aq). (a) Chronoamperogram under 100 mW cm^{-2} illumination and 1.63 V vs RHE for 6 h intervals. (b) Open-circuit potential vs time in the dark for 18 h intervals. (c) Cyclic voltammograms under 1 sun simulated illumination after 0 h (black), 48 h (blue), 216 h (purple), and 312 h (green) of testing (d) Scanning electron micrograph of photoanode after testing depicting a Si etch pit undercutting the TiO_2/Ni layers.

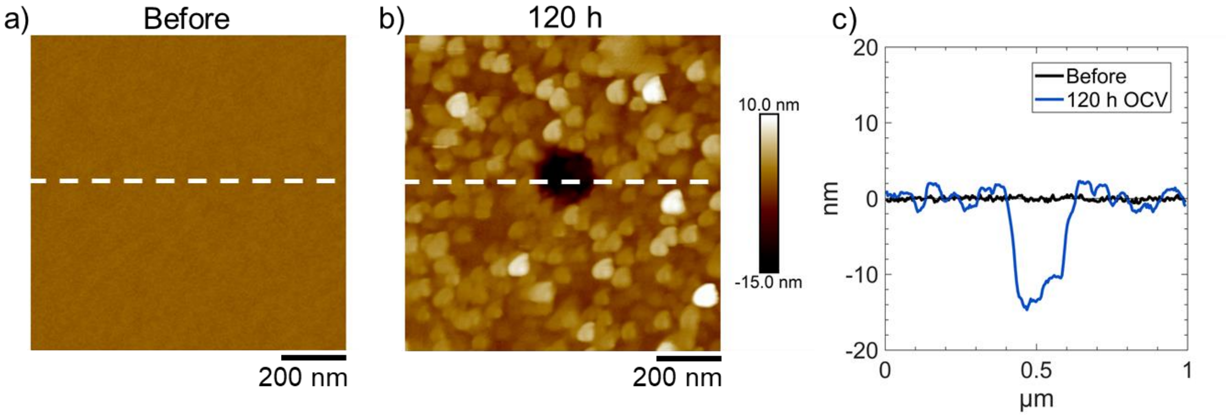

Figure S13. Atomic force microscope images of p$^+$-Si/Ni topography (a) before and (b) after 120 h submerging in 1 M KOH(aq) at open circuit. (c) Cross-section of electrode before (black) and after submerging in KOH (blue) at the indicated white dashed line in (a-b).

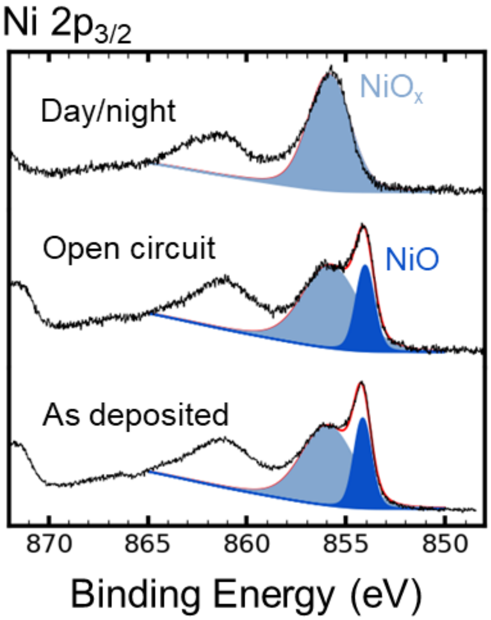

Figure S14. X-ray photoelectron spectroscopic data in the Ni 2p$_{3/2}$ region of np$^+$-Si/NiO$_x$ electrodes. Electrodes were measured as deposited, after 20 h in O_2-saturated 1 M KOH(aq) at open circuit, and after 410 h in 1 M KOH(aq) under simulated day/night cycling as described in Fig. 4. The Ni 2p$_{3/2}$ emission was fitted to two peaks. The dominant phase of the light blue peak is likely a mix of NiO. Ni(OH)$_2$, and NiO(OH) while that of the low energy peak (darker blue) is likely NiO. The y-axis is in arbitrary units.

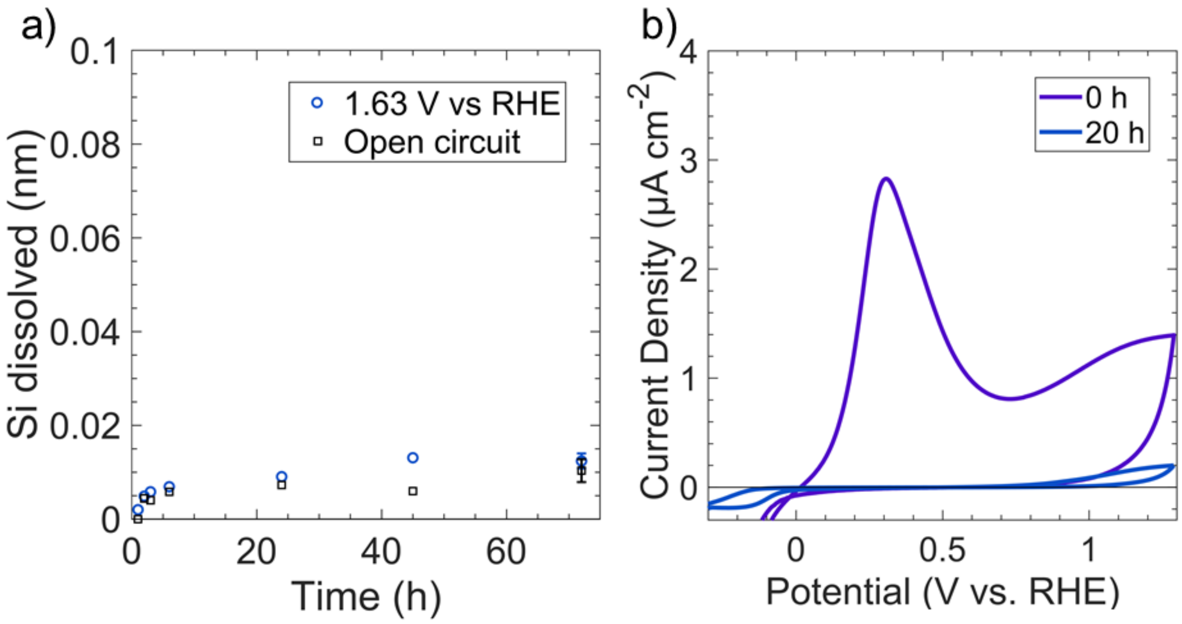

Figure S15. Stability of SiO_x in O_2-saturated 0.5 M K-borate buffer (pH 9.5). (a) Si dissolved over time in solution from p^+-Si electrodes at open circuit (black square) and at 1.63 V vs RHE (blue circle) as determined by inductively coupled plasma mass spectrometry. (b) Cyclic voltammograms of p^+-Si electrodes measured either immediately after immersion (purple) or after 20 h at open circuit (blue). The voltammetric scan rate was 1 mV s^{-1}. To remove any native oxide, the electrodes were immersed in buffer oxide etch for 30 s prior to electrochemistry.

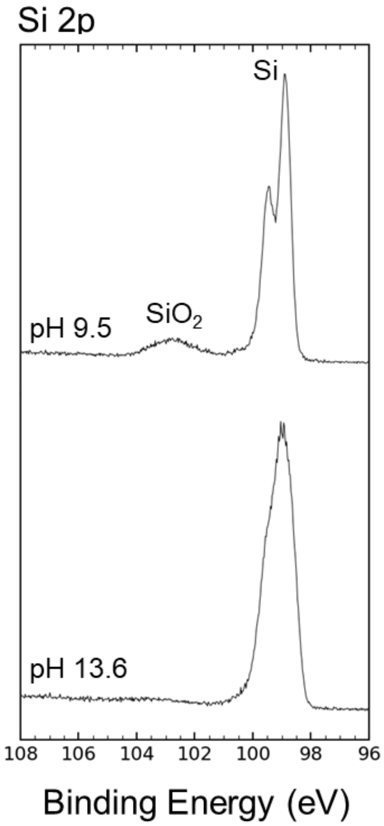

Figure S16. XPS data in the Si 2p region of p$^+$-Si electrodes. Electrodes were measured after 20 h in 1 M KOH(aq) at open circuit in either 1 M KOH(aq) (bottom) or 0.5 M K-borate buffer (top). The electrode was submerged in buffer oxide etch for 30 s to remove any native oxide prior to testing. The y-axis is in arbitrary units.

References

1. H. J. Fu, I. A. Moreno-Hernandez, P. Buabthong, K. M. Papadantonakis, B. S. Brunschwig and N. S. Lewis, *Energy & Environmental Science*, 2020, **13**, 4132-4141.