Supporting Information for

10% solar-to-fuel conversion with non-precious materials

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Additional Experimental Details

Mini-module fabrication

Mini-modules were fabricated using commercially available single-junction Czochralski silicon solar cells. Mini-cells were cut out of commercial size wafers by laser scribing with a 1064 nm pulsed laser and mechanical cleaving. Mini-cells were electrically connected via solar tabbing wire and silver epoxy. The mini-module was constructed by sequentially layering glass, EVA, solar cells, and EVA. The glass maintains structural integrity while EVA provides water protection. The mini-module was encapsulated using a double layer vacuum press heated to 120 °C. With the module in the lower chamber of the vacuum press, both the upper and lower chambers were held under vacuum for 5 min. The upper chamber was vented to atmospheric pressure for 5 min to remove air bubbles through the induced pressure difference between the two chambers. The lower chamber was vented and the mini-module was allowed to cool to room temperature. Excess EVA was removed and the mini-module was stored to protect against mechanical and water degradation.

Estimation of current associated with crossover on SFE

The impact on the SFE due to H_2 oxidation can be estimated by examining the mass-transport limited current density, which is given by:

$$J_L = \frac{nFDc_b}{\delta}$$

where, n is the number of electrons, F is Faraday's constant, c_b is the bulk concentration of species in solution, D is the diffusion coefficient (5.11×10^{-5} cm^2 s^{-1} for H_2 in water), and δ is the Nernst diffusion layer thickness. Assuming H_2 saturation in water (7.8×10^{-7} mol cm^{-3}), and a reasonable value for δ given a planar electrode with no artificially imposed convection is around 0.05 cm (*1*), which gives a J_L at the anode for H_2 oxidation of 0.15 mA cm^{-2}. This implies that for a 10% SFE (or 8.13 mA cm^{-2}) the contribution from product crossover would is at most 0.15 mA cm^{-2}, giving a SFE of 9.8%. Figure S1 shows that the experimental measurement of H_2 crossover by the NiB_i catalyst is less than that predicted from this calculation; no current from H_2 oxidation is observed, speaking to the selectivity of the catalyst.

1. Bockris JO, Reddy AKN, and Gamboa-Aldeco ME, (1998) *Modern electrochemistry* (New York: Plenum Press, c1998-c2000).

Table S1. PV characteristics for the 3 and 4-cell c-Si mini-modules.

PV module characteristics	4- cell	3-cell
V_{OC} (V)	2.46	1.79
I_{SC} (mA)	51.0	52.2
Active Area (cm^2)	6.0	4.5
Fill Factor	76.9	76.2
Efficiency (%)	16.0	15.8

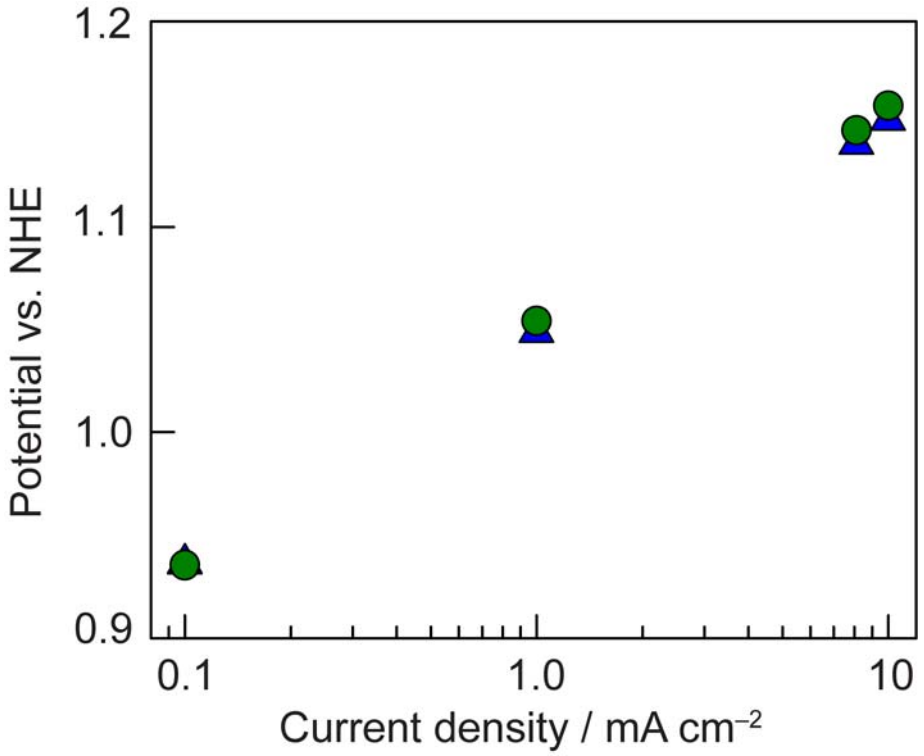

Figure S1. Steady-state current voltage behavior for the NiB_i operating in 0.5 M KB_i /0.5 M K_2SO_4 pH 9.2 in H_2 saturated solution (green circles) and in Ar saturated solution (blue triangles). The voltage required to achieve a given current density under both conditions is nearly identical, indicating that the contribution of H_2 oxidation at the anode is negligible.

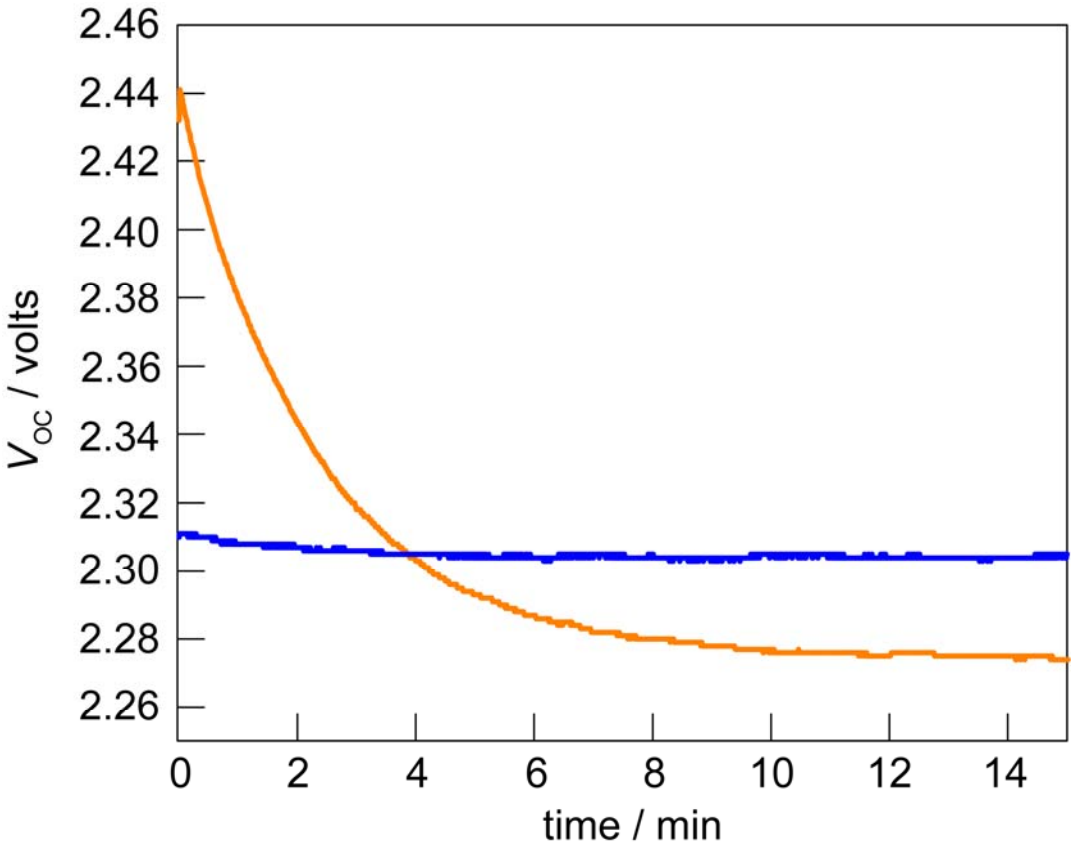

Figure S2. Decay of the open circuit voltage of the 4-cell PV mini-module over the course of ~1 h. The initial V_{OC} starts at 2.42 V and decays to a steady-state of 2.27 V after the first 10 min (orange line), which contributes to the initial decline in SFE of the coupled PV-EC device. After overnight illumination the V_{OC} was measured (blue line) and shows a recovery to 2.31 V, which corresponds to the initial increase in SFE of the PV-EC device during the first 24 h.

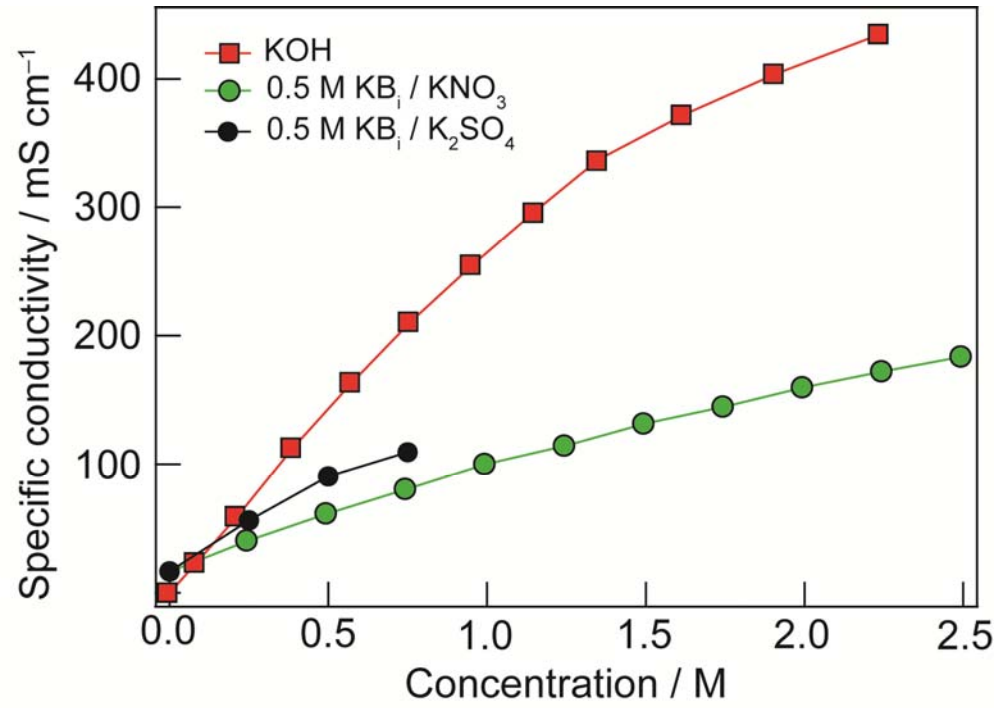

Figure S3. Specific conductance measurements for the various electrolytes considered to minimize R_{SOL}. KOH is the most conductive electrolyte; in order to operate in pH near neutral regimes 0.5 M KB_i was used with additional supporting electrolyte.

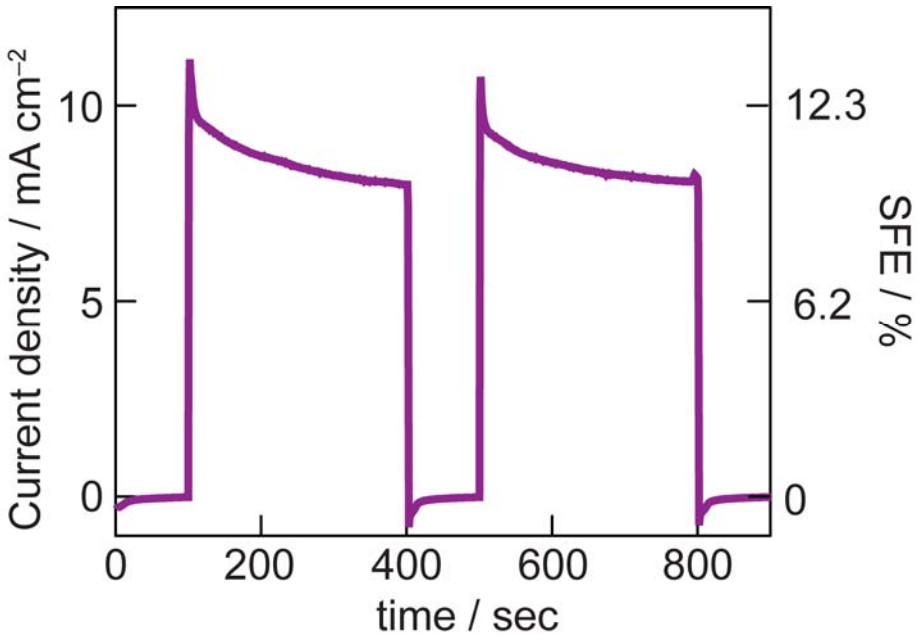

Figure S4. Current under chopped illumination representing J_{OP} for the PV-EC device composed of a 3-cell PV-module, a NiB_i anode and NiMoZn cathode operating in 1 M KOH (pH 14). Because KOH is a conductive electrolyte, a 12% SFE can be obtained with a 3-cell mini-module as opposed to a 4-cell module. The initial drop in SFE is due to the decrease in PV efficiency, due to heating of the PV module. The chopped illumination illustrates the recovery in SFE.

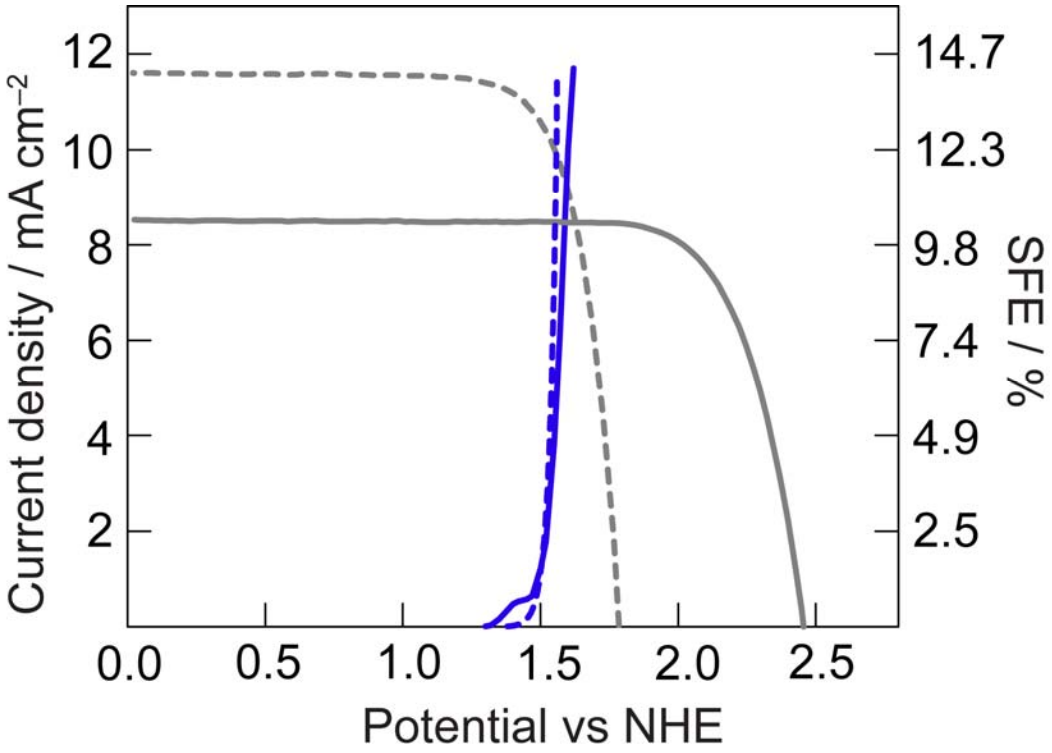

Figure S5. *J-V* curves of the individually measured 3 (grey dashed) and 4 (grey solid) cell PV mini-modules and EC curve measured in 1 M KOH. The blue dashed curve shows the ideal *J-V* curve obtained for NiB_i and NiMoZn catalysts based on previously reported Tafel analysis and the solid blue curve is the experimentally measured EC curve.