Supplementary Information

Utilizing three-terminal, interdigitated back contact Si solar cells as a platform to study the durability of photoelectrodes for solar fuel production

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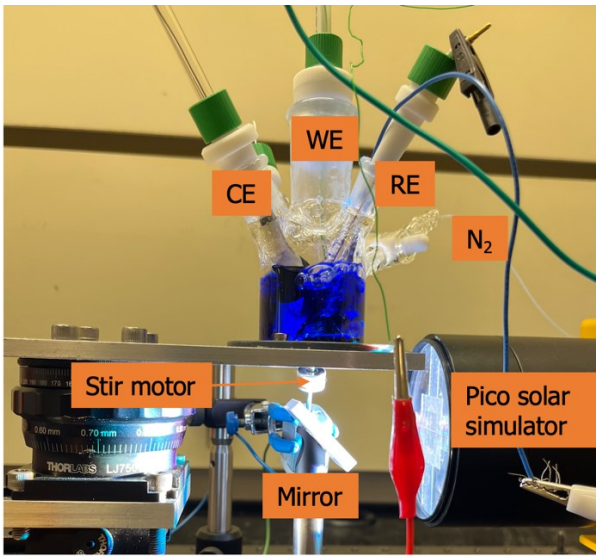

Figure S1: A picture of the three-electrode electrochemical experimental setup immersed in $MV^{2+/+}$ as described in Figure 3. The Pico solar simulator is to the right. The cell has a quartz window bottom and is bottom illuminated with a mirror angled at 45 degrees. The stirring motor is behind the mirror. N_2 is introduced into the cell through the stopcock port. The working, counter, and reference electrodes are respectively denoted as WE, CE, and RE.

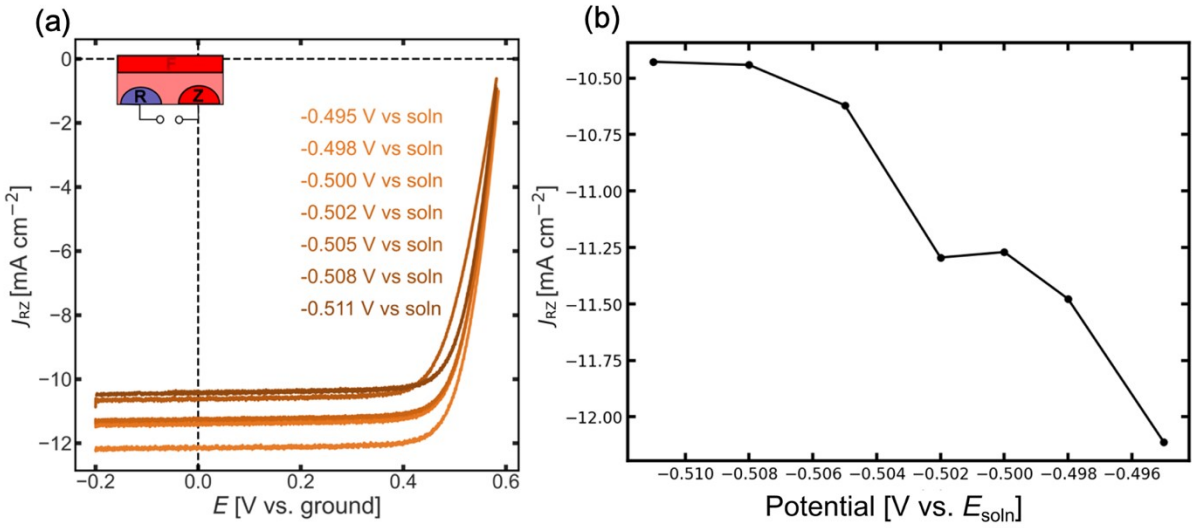

Figure S2: (a) Illuminated RZ CV data of a 3T nuIBC Si electrode immersed in $MV^{2+/+}$ electrolyte with varying solution potentials, to demonstrate how solution potential impacts light absorption by MV^{2+} and the resulting photocurrent in the 3T Si electrode. The solution potential was measured immediately prior to each CV and ranged from –0.495 V vs solution to –0.511 V vs solution. The range in current density was ~2 mA cm^{-2}. (b) The short circuit J_{RZ} measurements plotted vs the solution potential (E_{soln}). A more negative E_{soln} means more MV^{+} species is present, so the solution absorbs more light, and the photocurrent decreases.

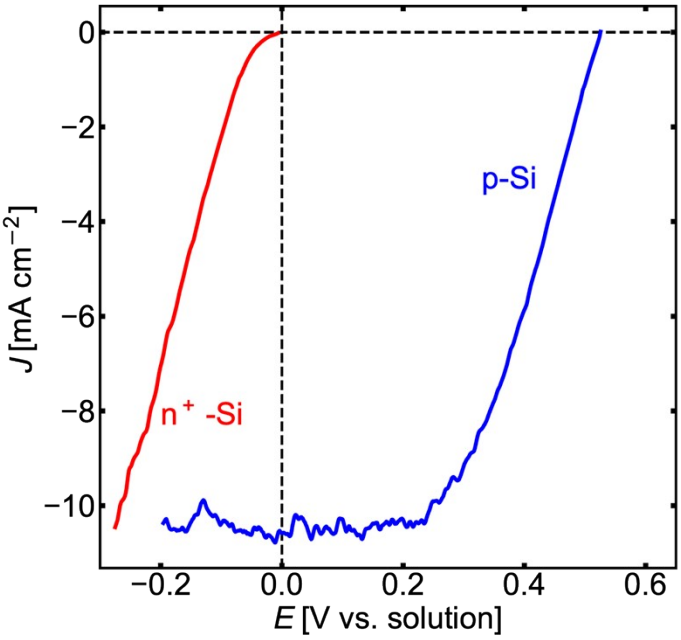

Figure S3: Illuminated CV data of p-Si and n^+-Si electrodes immersed in $MV^{2+/+}$ electrolyte (AM1.5G illumination).

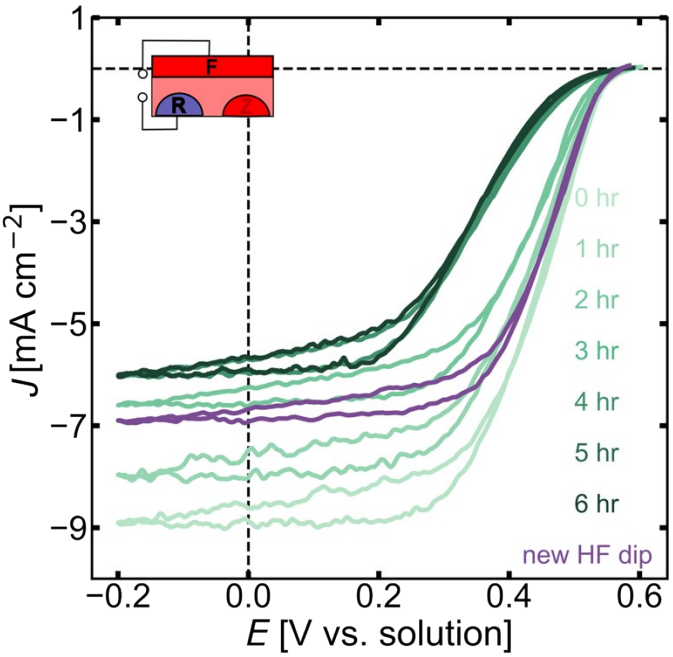

Figure S4: Illuminated FR CV data (forward and reverse sweeps) for a 3T nuIBC electrode taken hourly during a durability study where the electrode was left at open circuit in the dark over a 6 hour period in $MV^{2+/+}$ electrolyte. The forward sweep of this data is shown in Figure 5a. The electrode was illuminated under AM1.5G illumination for each CV taken. The purple CV was taken after the 6-hour experiment concluded and the electrode was dipped in HF, then remeasured.

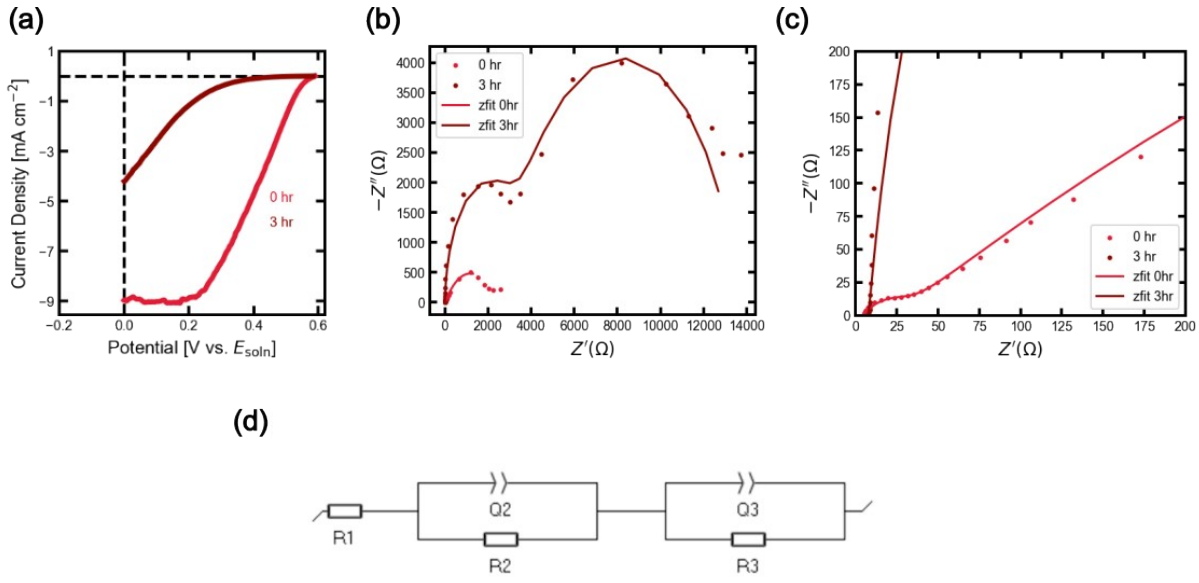

Figure S5: (a) Illuminated FR CV data for a 3T nuIBC device taken before and after three hours of unprotected dark operation at open circuit. All CVs were taken under simulated AM1.5G in a $MV^{2+/+}$ electrolyte; (b) Dark GEIS data in FZ mode taken before and after three hours of steady state dark operation without cathodic protection (The points represent the data and the lines represent the fit.); (c) shows the same EIS data at higher magnification; (d) The circuit used to fit the EIS data (R represents resistor, Q represents imperfect capacitance).

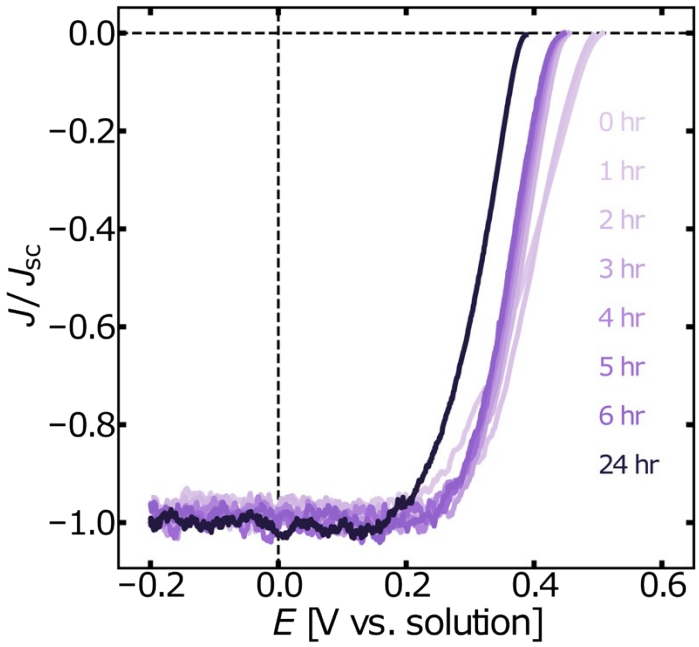

Figure S6: Illuminated CV data for a p-Si electrode taken hourly during a durability study where the electrode was left at open circuit in the dark over a 24-hour period. The electrode was immersed in $MV^{2+/+}$ electrolyte and CVs were taken each hour under simulated AM1.5G illumination. This study had the same conditions as described in Figure 5a. The current is normalized to the short circuit due to differences light absorption. The open circuit potential changed over time, (Table S1).

Table S1: Open Circuit potential values of p-Si during the durability experiment shown in Figure S6.

Time (hour)	Open Circuit Voltage [V vs solution]
0	0.51
1	0.50
2	0.45
3	0.45
4	0.45
5	0.45
6	0.44
24	0.39

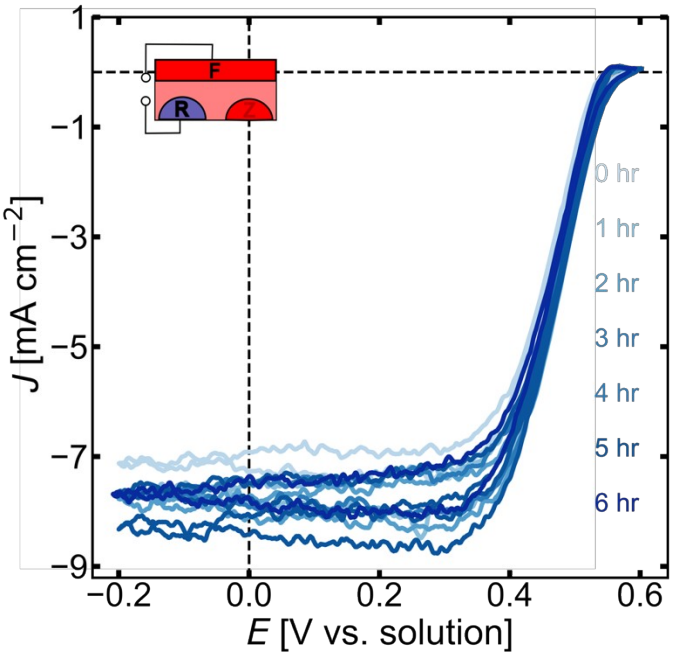

Figure S7: Illuminated FR CV data taken hourly during the durability study of the 3T nuIBC electrode in dark conditions with cathodic protection. The forward sweep of this data can be seen in Figure 5c. The electrode was immersed in $MV^{2+/+}$ solution, light was left off, and a voltage of –0.16 V vs E_{soln} was applied for 1 hr between each CV. The electrode was illuminated under AM1.5G illumination for each CV taken.

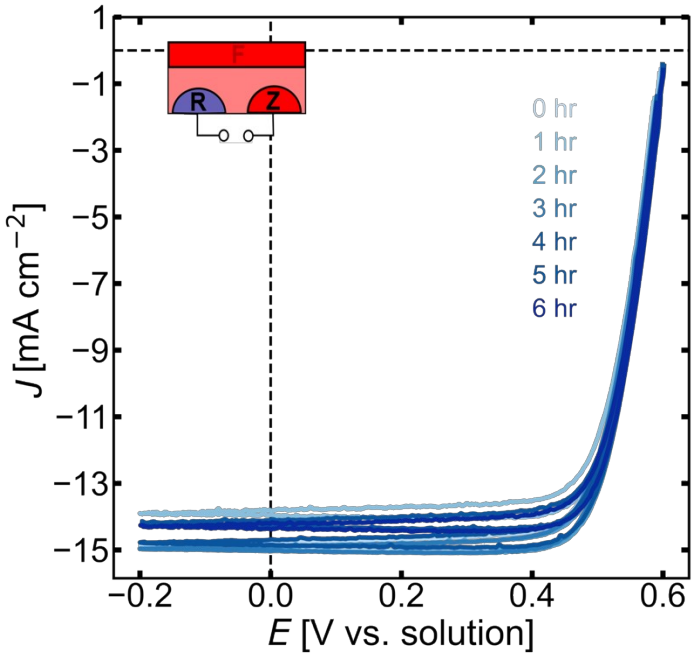

Figure S8: Illuminated RZ CV data taken hourly during the durability study of the 3T nuIBC electrode in dark conditions with cathodic protection (Figure S7). The electrode was immersed in $MV^{2+/+}$ solution, light was left off, and a voltage of –0.16 V vs E_{soln} was applied for 1 hr between each CV. The electrode was illuminated under AM1.5G illumination for each CV taken. They follow the same trend as the lines in Figure 5c, which explains the variability in the CVs.

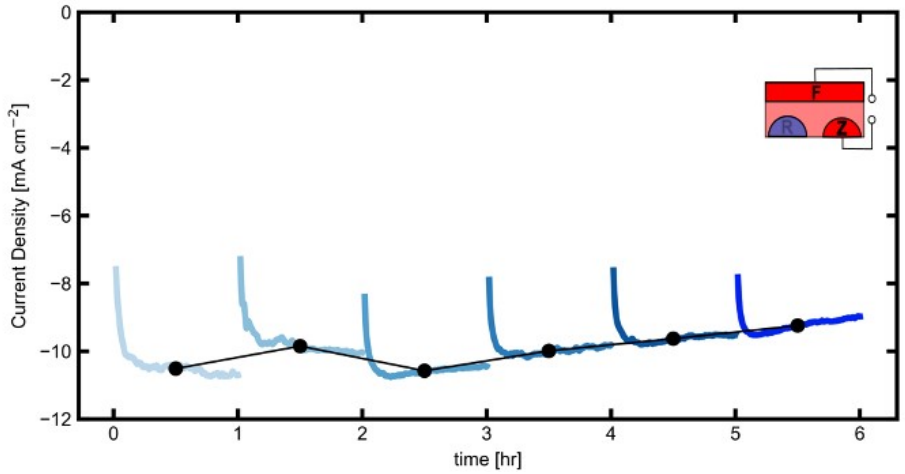

Figure S9: Chronoamperometry (CA) data for a 3T nuIBC electrode operated in FZ mode at a cathodic bias of –0.16 V vs E_{soln} in $MV^{2+/+}$ electrolyte in the dark. Between each hour-long CA experiment, an illuminated CV sweep was taken (Figure S7). The overlaid data points are the 1 hr mean current density for each hour of dark CA. The first 5 min of each hour was excluded from the mean calculation to exclude the initial current transient in the calculation.

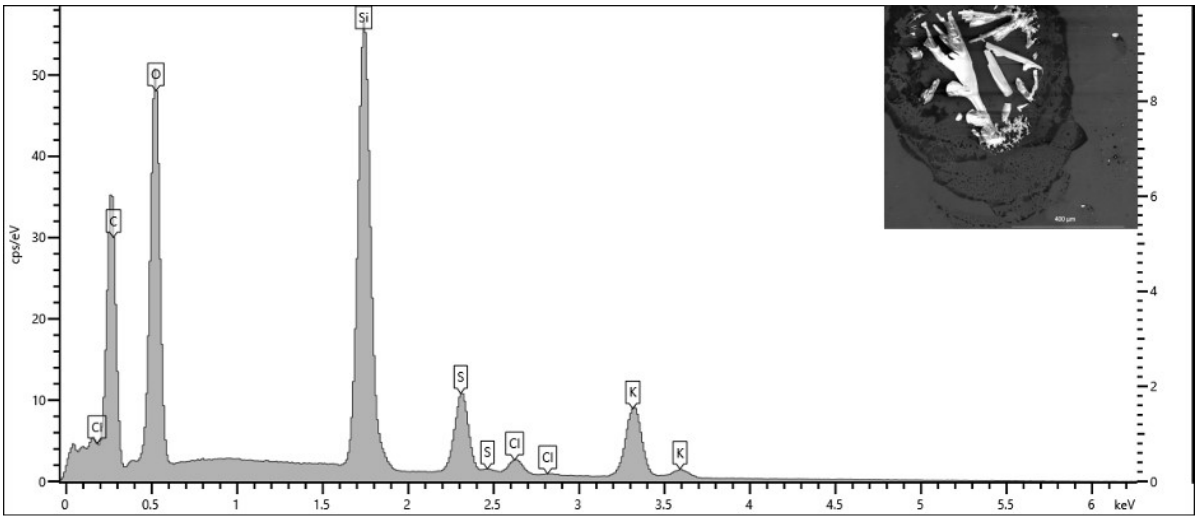

Figure S10: EDS of cathodically protected 3T Si after a 6-hour durability experiment. C, O, Cl, Si, S, and K all are present on the surface. The Cl, K, S, and C are concentrated on the crystalline salt structure. The SEM image (inset) shows a salt crystal which was likely deposited on the surface during the experiment and could explain losses in PEC activity.

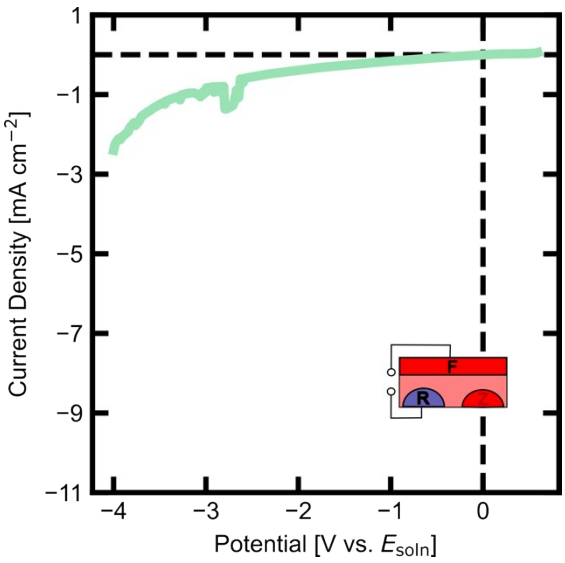

Figure S11: Electrochemical characterization of a 3T nuIBC device operated in FR mode in the dark in a $MV^{2+/+}$ electrolyte. The potential was swept from 0.6 V to –4.0 V vs $E_{soln.}$ At –4.0 V vs $E_{soln,}$ the photoelectrode was only able to reach cathodic currents of –2.8 mA cm^{-2} due to reverse bias breakdown of the diode in the device.

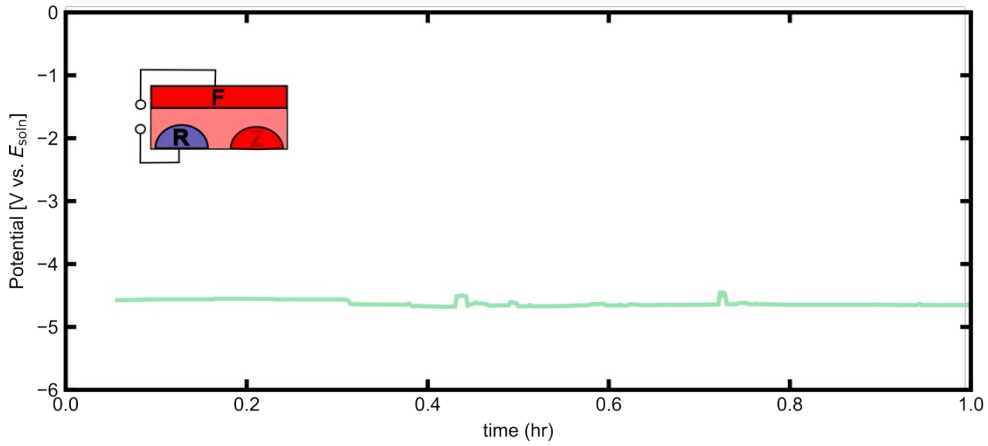

Figure S12: Chronopotentiometry (CP) of a 3T nuIBC device operated in FR mode in the dark in a $MV^{2+/+}$ electrolyte. A cathodic current of –8.2 mA cm^{-2} was applied for one hour. The average potential required to maintain that current was –4.5 V vs E_{soln}.

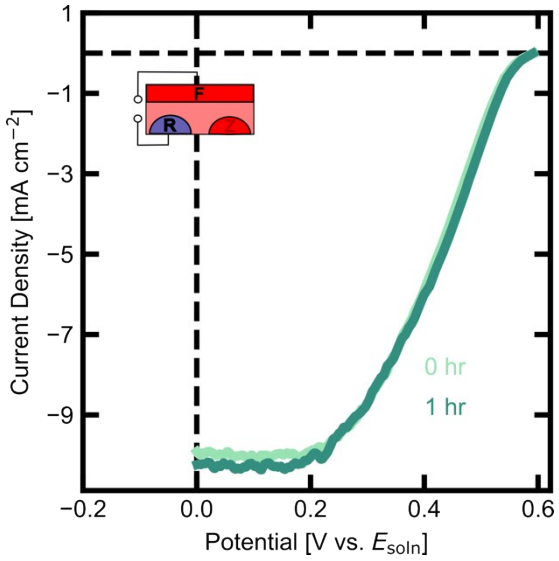

Figure S13: Illuminated FR CV data for a 3T nuIBC device taken before and after an hour of steady state dark operation, where the electrode was held in FR mode in reverse bias (J_{FR} = –8.2 mA cm^{-2}), as seen in Figure **S12**. The CVs were taken under simulated AM1.5G illumination in a $MV^{2+/+}$ electrolyte.

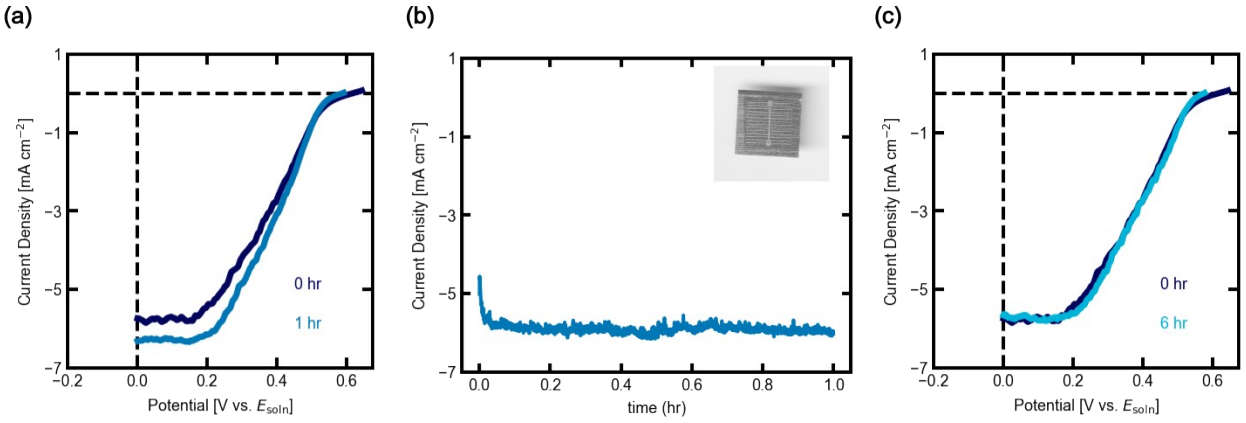

Figure S14: Characterization of 3T nuIBC electrodes with Pt catalyst. All CVs were taken under simulated AM1.5G in a $MV^{2+/+}$ electrolyte. (a) Illuminated FR CV data taken before and after 1 hour of dark conditions with cathodic protection; (b) Chronoamperometry data (–0.3 V vs E_{soln}) in FZ mode in the dark. [Inset shows photograph of shadow mask used to deposit Pt/ Ti on the electrode surface]; (c) Illuminated FR CV data taken before and after six hours of steady state dark operation without cathodic protection (open circuit).

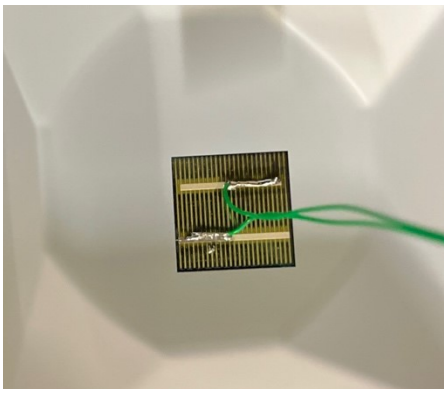

Figure S15: Image of the back of a 3T Si solar cell with wires soldered on the busbars. The wires were soldered with SN60/Pb40 solder. The wire on the top is connected to the Ag busbar with electrical connection to the p^+-Si back contact and the wire on the bottom is connected Ag busbar with electrical connection to the n^+-Si back contact.

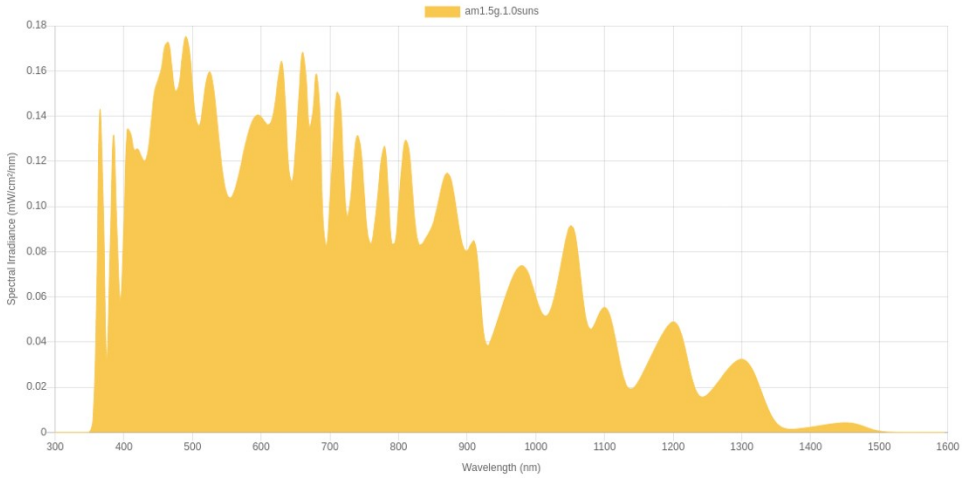

Figure S16: The spectral irradiance from the Pico solar simulator given by G2V Optics. Incident illumination given by the solar simulator is 87.6 mW cm^{-2} at a working distance of 7 cm.