Redesigning photoelectrodes so they can work in the light and dark

NREL Transforming ENERGY

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Summary

- A major challenge limiting fuel-forming systems is maintaining long term performance and efficiency under real-world operating conditions.
- Real-world PEC systems will need to be stable across the day and night. In the dark, the photoelectrode sits at the solution potential, which allows deleterious reactions that cannot occur under illumination.
- New semiconductor architectures of three-terminal (3T) Si cells utilize an extra electrical contact to bypass the diode in the semiconductor and enable cathodic protection of the photoelectrode and catalysts to improve the durability.

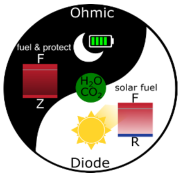

Figure 1: 3T photoelectrode can make fuel using sunlight or an external electricity source

Introduction

- PEC systems are primed to take advantage of cost reductions and performance improvements made over the past decade in photovoltaic (PV) devices.
- Small band gap semiconductors, like Si, are efficient at utilizing a large portion of the solar spectrum but are not stable in aqueous environments without protection. *There is a great need to understand and improve photoelectrode stability overnight.*
- Metals can be protected from degradation reactions by passing a protective cathodic current – attempting this with traditional photoelectrodes causes damage or requires prohibitively large voltages.
- New PV fabrication techniques have produced 3T Si devices with an extra contact bypassing the p-n junction in the device. *We hypothesize this alternative current pathway could be used for cathodic protection of the bare photoelectrode surface in dark conditions.*

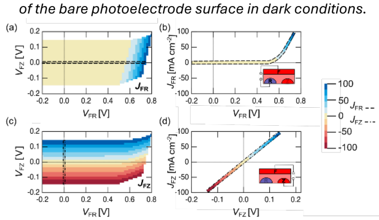

Figure 2: Electrical characterization of a 3T Si solar cell in the dark. The front of the device (F) was contacted with an evaporated Ag grid. (a) Contour plot of J_{FR} as a function of V_{FZ} and V_{FR}; (b) J_{FR}–V_{FR} data corresponding to V_{FZ} = 0 (black dashed line in the J_{FR} contour plot); (c) contour plot of J_{FZ} as a function of V_{FZ} and V_{FR}; (d) J_{FZ}–V_{FZ} data corresponding to V_{FR} = 0 (black dashed line in the J_{FZ} contour plot).

What is a three terminal solar cell?

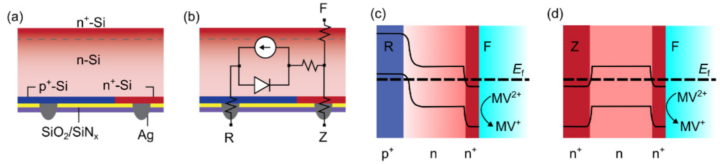

Figure 3: Cross sectional schematics of 3T Si devices: (a) doping, passivation layers, and contacts; (b) equivalent electrical circuit, showing how FR and RZ pass current through a diode, while FZ measurements only have resistive losses; (c) schematic of one-dimensional band bending at equilibrium between F and R contacts; (d) schematic of one-dimensional band bending at equilibrium between the F and Z contacts.

- 3T Si solar cell were fabricated out of crystalline n-type Czolchralski grown Si wafers with interdigitated p^+-type (R) and n^+-type (Z) back contacts formed from laser ablation and low temperature diffusion.
- Adding a conductive front (F) creates a 3T interdigitated back contact (IBC) solar cell with 1 electrochemical contact (F) and 2 electrical contacts (R & Z).
- To characterize bare Si photoelectrode we use an aqueous redox couple, methyl viologen (MV).

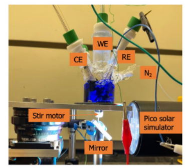

Figure 4: A picture of the three-electrode electrochemical experimental setup immersed in $MV^{2+/+}$. The cell has a quartz window bottom and is bottom illuminated with a mirror angled at 45 degrees. A stir motor sits near the mirror. N_2 is introduced into the cell through a stopcock port.

Dark stability of 3T Si photocathode

- Cathodic protection is not possible for a 2T photoelectrode in the dark, due to the diode behavior of the device (negative bias leads to reverse breakdown).
- Durability studies show that without cathodic protection, the device performance degrades after extended periods in the dark at open circuit (Figure 6a) and under illumination at open circuit (Figure 6b).
- With the extra electrical contact (Z) in the 3T Si, we can utilize cathodic protection to maintain bare photocathode activity in the dark by applying a small negative potential of –0.16 V *vs.* E_{soln} (Figure 6c)

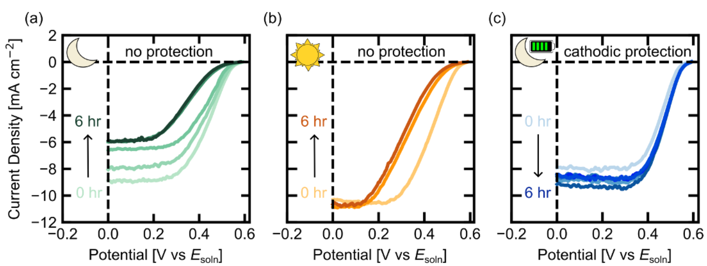

Figure 6: Durability studies of the 3T Si electrodes in dark conditions in $MV^{2+/+}$ electrolyte. (a)–(c) FR mode light CVs under simulated AM1.5G illumination (a) were taken each hour in between steady state dark operation holding an electrode in FZ mode open circuit (J_{FZ} = 0), (b) were taken every three hours in between continuous illumination and open circuit (J_{FZ} = 0) illuminated operation (c) were taken each hour in between steady state dark operation holding an electrode in FZ mode at –0.16 V *vs.* E_{soln}.

Collins, D.K. and Schichtl, Z.G.; Nesbitt, N.T.; Greenaway, A.L.; Mihailetchi, V.D.; Tune, D.; Warren, E.L. Utilizing Three-Terminal, Interdigitated Back Contact Si Solar Cells as a Platform to Study the Durability of Photoelectrodes for Solar Fuel Production. *Energy & Environmental Science* **2024**.

Three modes of operation

- 3T Si functionality is comparable to familiar two terminal (2T) photocathode architectures.
- FR mode: the photoelectrochemical behavior shows a positive voltage onset and light-limited cathodic current (e.g. p-Si).
- FZ mode: the device does not form a rectifying junction with the electrolyte and can pass cathodic current freely (e.g. n^+-Si).
- RZ mode: can act as an *in situ* photodiode to monitor incident illumination intensity. (e.g. IBC Si solar cell).
  - Maximum photocurrent achievable by the device under investigation.

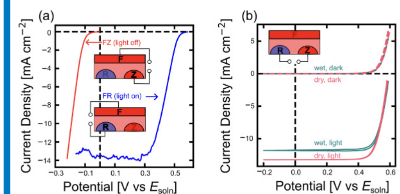

Figure 5: Photoelectrochemical, electrochemical, and electrical characterization of the three-operating modes of 3T nuIBC Si in both the light and in the dark. (a) Illuminated FR mode CV and dark FZ mode CV *vs.* E_{soln} immersed in $MV^{2+/+}$ solution. (b) Illuminated and dark RZ mode CVs for an electrode measured in air (dry) and in $MV^{2+/+}$ electrolyte (wet, E_{soln} = –0.5 V *vs.* Ag/AgCl). All illuminated data measured under simulated AM1.5G spectra. Insets show schematics of the contacts used for FR, FZ and RZ measurements.

Conclusions/Outlook

- 3T semiconductors provide more degrees of freedom when operating PEC systems.
- Cathodic protection could be an important approach for deploying PEC systems in real-world conditions.
- Prolonged operation under cycled illumination and low-cost fabrication of the 3T Si architecture suggests utilization in a scalable PEC-based system
- Future plans: addition of catalysts for specific fuel-forming reactions where cathodic protection can extend to the catalytic components and create integrated systems capable addressing the intermittency of sunlight

ACKNOWLEDGEMENTS

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