



Review Article

Improving the stability of photosystem I–based bioelectrodes for solar energy conversion

Kody D. Wolfe¹, Dilek Dervishogullari²,
Joshua M. Passantino³, Christopher D. Stachurski²,
G. Kane Jennings³ and David E. Cliffl²



Abstract

Isolated photosystem I (PSI) has been integrated into numerous technologies for solar energy conversion. Interest in PSI is a consequence of its high internal quantum efficiency, thermal stability, ease of extraction, and adaptability. While there has been success in improving performance to elevate PSI biohybrid technologies toward a practical realm, the stability of PSI bioelectrodes is also of critical importance. Commercial solar energy conversion technologies are expected to achieve lifetimes of the order of ten years; however, many research-scale PSI bioelectrodes have only been tested for tens of days. Key areas affecting PSI bioelectrode stability include the effects of reactive oxygen species, immobilization strategies, and the environment within solid-state PSI biohybrid photovoltaics. At the current state, further investigation of long-term stability is necessary in enabling the development of PSI bioelectrodes for both photoelectrochemical cells and solid-state biohybrid photovoltaics.

Addresses

¹ Interdisciplinary Materials Science & Engineering Program, Vanderbilt University, Nashville, TN, 37235-1822, United States

² Department of Chemistry, Vanderbilt University, Nashville, TN, 37235-1822, United States

³ Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN, 37235-1822, United States

Corresponding author: Cliffl, David E (d.cliffl@vanderbilt.edu)

Current Opinion in Electrochemistry 2020, 19:27–34

This review comes from a themed issue on **Bioelectrochemistry**

Edited by **Shelley D. Minteer**

For a complete overview see the [Issue](#) and the [Editorial](#)

Available online 3 October 2019

<https://doi.org/10.1016/j.coelec.2019.09.009>

2451-9103/© 2019 Elsevier B.V. All rights reserved.

Keywords

Photosystem I, Reactive oxygen species, Stability, Protein electronics.

Abbreviations

PSI, photosystem I; DSSC, dye-sensitized solar cell; ROS, reactive oxygen species; PEGDGE, poly(ethylene glycol diglycidyl ether); ITO, indium tin oxide; cyt c, cytochrome complex; DET, direct electron transfer; SPECM, scanning photoelectrochemical microscopy; LR, lumogen red; SAM, self-assembled monolayer; PLGA, polylactic-co-glycolic acid; MPs, microparticles; PCE, power conversion efficiency;

PTTA, polytriarylamine; PEDOT:PSS, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate.

Introduction

Photoactive protein complexes that drive photosynthesis are internally efficient, with more than 99% of captured photons resulting in electron–hole pairs, or excitons, used for the production of chemical energy [1,2]. Photosystem I (PSI) is one of the two primary protein complexes found within the thylakoid membrane of plants, algae, and cyanobacteria [1–3]. PSI is a plastocyanin–ferredoxin oxidoreductase that captures photonic energy via delocalization of electrons within a network of chlorophyll antennae [2]. Electron transfer within PSI begins with the excitation of the P₇₀₀ reaction center, followed by transport of the electron to an iron–sulfur cluster, F_B, where ferredoxin reduction occurs [2]. PSI has been targeted as a low-cost and benign photosensitizer, primarily owing to its high reduction potential and exceptional thermal stability [1–6]. Interest in PSI has also been attributed to its ease of extraction, compatibility with inorganic materials, reactivity with common electrochemical mediators, and capacity for genetic engineering [4,7–9]. Thanks to these desirable properties, isolated PSI has been implemented in a variety of energy conversion technologies including photoelectrochemical cells, biohybrid photovoltaics, and dye-sensitized solar cells [4,7,9–12]. Research on PSI has been focused on its integration with electrode materials, electrochemical mediators, and electron and hole transport layers [4,7–9,13,14]. Several recent investigations have also explored its incorporation into solid-state devices to improve performance and practicality in the field of solar energy conversion [4,7,9,15].

The long-term stability of PSI within bioelectrodes is becoming increasingly important, especially in technologies such as biohybrid photovoltaics [7,9,16]. Long-term stability is critical when incorporating biological materials into energy conversion systems that are expected to have lifetimes of the order of ten years [17]. The stability of the PSI protein complex is largely related to its immediate environment; the natural

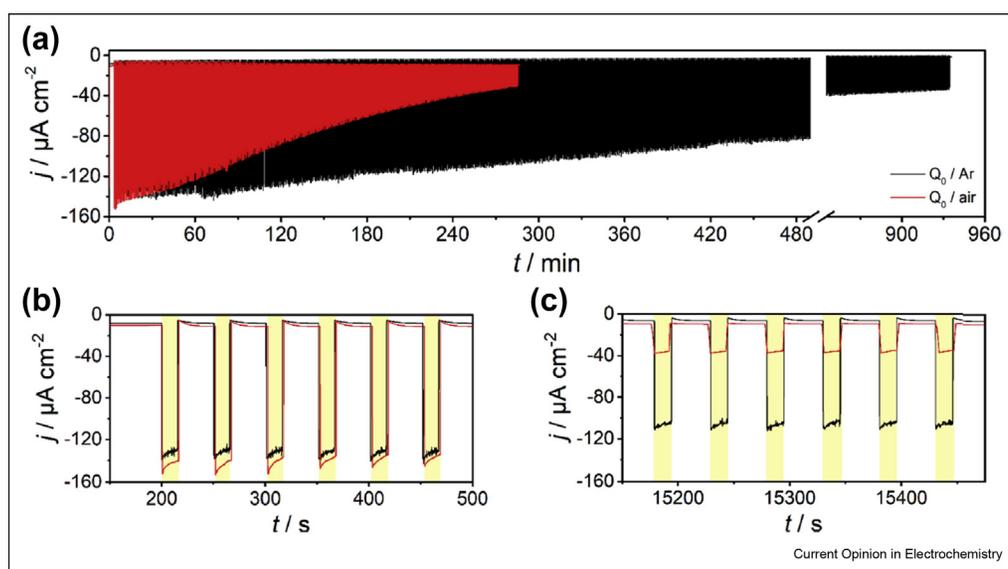
environment of PSI is dynamic, and PSI is responsive to stresses including changes in temperature, fluctuations in metabolite concentrations, and protein complex conformation within chloroplasts [16]. One avenue for retaining stability of photosynthetic protein complexes is to incorporate the entire thylakoid membrane into biohybrid devices. Recent advances in this field include the addition of osmolytes to improve thermal stability and the immobilization of thylakoid membranes onto graphene scaffolds, which increases the likelihood of the desired electron transfer pathway and minimizes damaging internal processes [18,19]. However, when designing biohybrid systems using isolated PSI, the extraction procedure, solvent and surfactant properties, and the environment surrounding the protein complex are critical in determining the stability — both structural and performance-related stability — within bioelectrodes [9,16]. Herein, we discuss and evaluate the current state of PSI bioelectrodes with respect to the overall stability of the protein complex outside of its native environment. We highlight three areas regarding PSI stability: the effects of aerobic electrolytes, including damage by reactive oxygen species (ROS), immobilization strategies for improvement of photocurrent production and physical bioelectrode stability, and the incorporation of PSI into solid-state biohybrid photovoltaics. We conclude that although solid-state devices require protein immobilization and may mitigate known stability issues such as ROS damage, gaps

remain in the understanding of PSI stability in these systems, and there is a great need for further research.

Aerobic electrolytes and degradation by ROS

Owing to both practicality and knowledge from previous research efforts, aerobic electrolytes are commonly used to produce high-performing bioelectrodes [7]. Despite the advantages of dissolved oxygen as a mediator, it is reported to be problematic, allowing for the production of ROS and the consequential degradation of the PSI structure and function [20,21*]]. The production of ROS by PSI within chloroplasts of plants is well known [22]. ROS is known to stimulate photoinhibition *in vivo* by damaging the active sites of photosynthetic protein complexes [20]. Superoxide (O_2^-) and singlet oxygen (1O_2) may be produced by PSI and are detoxified by superoxide dismutase and ascorbate peroxidase enzymes [20]. The absence of essential protective enzymes in PSI bioelectrodes means that the presence of ROS is detrimental and has been reported to cause damage to the P₇₀₀ site [20]. Zhao et al. [21*] reported that PSI deposited within the biocathode containing a mixture of an osmium redox polymer and poly(ethylene glycol) diglycidyl ether produces ROSs that are detectable through the collection of hydrogen peroxide via scanning photoelectrochemical microscopy. Zhao et al. [21*] also found that the production of ROS occurs even in the presence of other artificial mediators, and

Figure 1



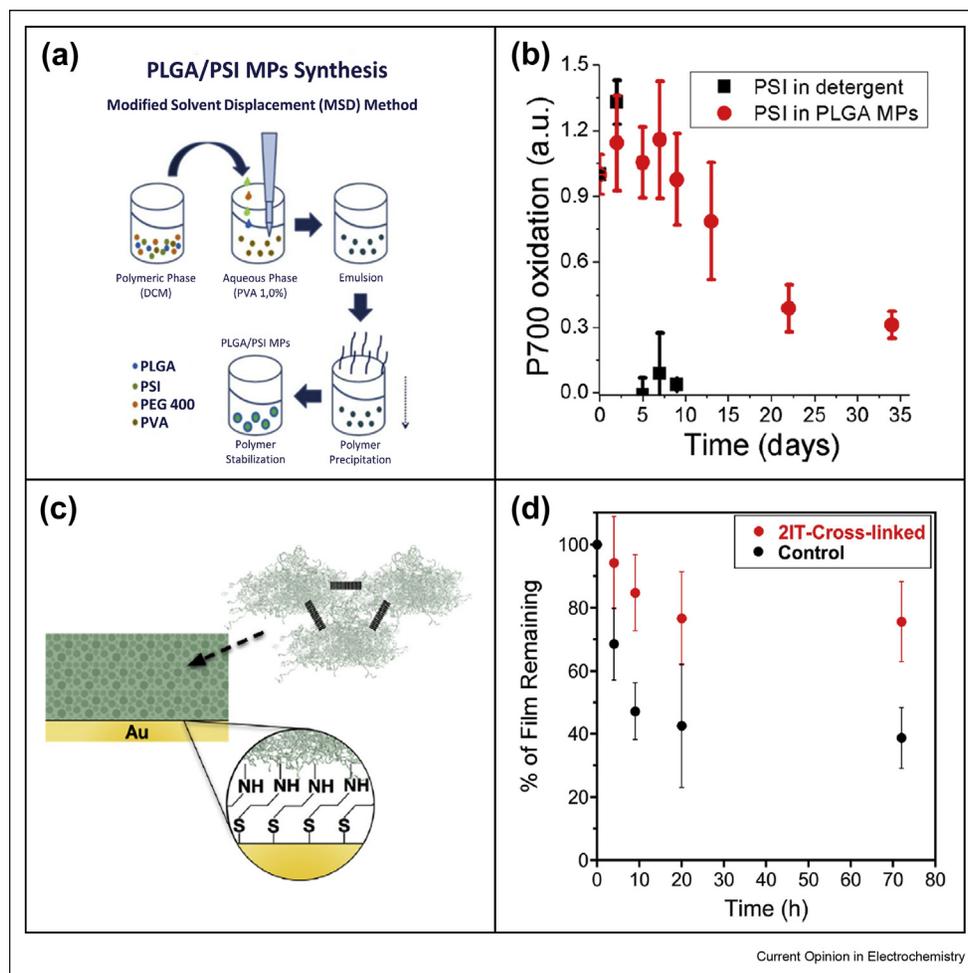
Stability study of PSI–Os_p–PEGDGE biocathodes. (a) A comparison of photocurrent density stability in air-equilibrated (red) and anaerobic argon (black) conditions. (b) Expanded views of the data from panel a are given for the initial few minutes of the study. (c) Expanded views of the data from panel a are given after 4 h of the study. Yellow sections denote illumination by a light source of 80 mW/cm² in the presence of a phosphate–citrate buffer (pH = 4.0) electrolyte containing 2.5 mM Q₀. The applied potential of the cell was 300 mV vs. SHE (reproduced with permission from Zhao et al [24**], Copyright 2019 American Chemical Society). PSI, photosystem I; PEGDGE, poly(ethylene glycol) diglycidyl ether; SHE, standard hydrogen electrode.

they claim that the suppression of ROS production within PSI bioelectrodes will be difficult owing to the high reactivity and short diffusion time of ROS [21].

Other studies have proven that the presence of oxygen is vital to the performance of PSI bioelectrodes using specific mediators, further complicating stability issues related to ROS [23,24**]. Zhao et al. [24**] showed that within the osmium redox polymer–poly(ethylene glycol) diglycidyl ether biocathode, the presence of oxygen is necessary for electron transfer when using methyl viologen as an electron acceptor, making a performance stability study using this mediator impossible

in deaerated conditions. To circumvent the problem, ubiquinone (Q_0) was used as a replacement electron acceptor owing to its similar performance in the presence and absence of oxygen. As shown in Figure 1, the degradation of a PSI biocathode in the presence of Q_0 was found to be linear and slower in the absence of oxygen, retaining 77% of its photocurrent performance after 4 h. In the presence of oxygen, the degradation rate increased dramatically, after a first-order decay with a k_{app} of $1.05 \times 10^{-4} \text{ s}^{-1}$ and retaining only 32% of the original photocurrent after 4 h [24**]. Ciornii et al. [25*] showed that adding the electron-scavenging Q_0 to porous indium tin oxide–cytochrome complex (cyt *c*)–

Figure 2



Examples of PSI immobilization strategies designed to improve PSI bioelectrode stability. (a) The modified solvent displacement method as used to produce poly lactic-co-glycolic acid (PLGA)-PSI microparticles (MPs) (reproduced and adapted with permission from Cherubin et al [47**], Copyright 2019 American Chemical Society, further permissions regarding this material should be directed to the ACS, <https://pubs.acs.org/doi/abs/10.1021/acssuschemeng.9b00738>). (b) P_{700} oxidation as a function of time demonstrates that PSI entrapped within PLGA MPs resists photobleaching over time (reproduced with permission from Cherubin et al [47**], Copyright 2019 American Chemical Society, further permissions regarding this material should be directed to the ACS, <https://pubs.acs.org/doi/abs/10.1021/acssuschemeng.9b00738>). (c) A schematic of a cross-linked PSI multilayer produced by introducing 2IT into a PSI multilayer deposited onto an amine-terminated self-assembled monolayer (SAM) (reproduced with permission from Yang et al [48], Copyright 2016 Elsevier). (d) A PSI multilayer film and cross-linked multilayer film retention study performed in aqueous electrolyte showing 75 h of stability (reproduced with permission from Yang et al [48], Copyright 2016 Elsevier). PSI, photosystem I; 2IT, 2-iminothiolane; DCM, dichloromethane; PVA, polyvinyl alcohol.

PSI electrodes lowers the rate of photocurrent degradation in a 30-min short-pulse (20-s) light stability study. In addition to anaerobic aqueous electrolytes and the addition of electron scavengers, a cobalt^{II/III}-based mediator in an organic solvent and a designer surfactant peptide, A₆K, was used by Merzhin et al. [26] to improve the structure–function stability of PSI [27]. These findings, along with the previously mentioned issues related to ROS, should be considered as a testament to the need for novel anaerobic electrolytes and other methods for mitigating ROS production as a direction for improving PSI bioelectrode stability.

Immobilization: covalent attachment and entrapment strategies

The immobilization of PSI onto various electrode surfaces has been a common direction for increasing photoactivity and stability of PSI bioelectrodes [4,7,9,28,29]. In general, there have been two directions for improvement via PSI immobilization. The first is to immobilize PSI through either covalent linkage or physical attraction to an electrode or another active component to enhance electron transfer [30–35]. Despite improved performance, there are few findings supporting stability beyond a single day in these PSI bioelectrodes. However, efforts aimed toward achieving direct electron transfer should be noted because they indirectly provide physical stability through immobilization. A number of recent studies have investigated the use of cyt *c* as an electron shuttle for PSI in biocathodes [14,25,33,36–38]. The mechanism of binding and electron transfer to PSI via cyt *c* has been extensively studied for the purpose of improving the electron transfer between the cathode and P₇₀₀ [39–42]. Alternative linking agents have also been investigated, including a perylene diimide derivative, which transfers charge from PSI to platinum nanoparticles for hydrogen evolution, and lumogen red as an artificial antenna for electron transfer on a titanium dioxide electrode [30,34]. PSI has been linked or immobilized via chemical and physical methods onto other materials, including alkanethiol self-assembled monolayers on gold, graphene, glassy carbon via an osmium polymer, and fullerene C₇₀ [29,43–45]. Finally, other strategies such as phage display, plasmon coupling, and linking to dehydrogenase have been developed for improving electron transfer in PSI bioelectrodes [31,35]. Each of these linking strategies has improved electron transfer from PSI to a substrate electrode. Although stability is not the primary focus, efforts toward achieving improved electron transfer may indirectly improve the PSI–electrode interface by physically or chemically binding the protein to a surface.

PSI immobilization has also been targeted as a direct strategy for improving the physical stability of the PSI–electrode interface. Examples include covalent linkage

of PSI complexes within a thick multilayer film and entrapment of the protein complex within gels, microspheres, or porous electrodes [23,33,46,47**,48]. These strategies improve physical stability by minimizing desorption and dissolution of the multilayer films into the electrolyte. Entrapment also brings the protein into a new environment, protecting it from hazardous species in solution or from flow in the bulk electrolyte. To improve stability, Cherubin et al. [47**] encapsulated PSI into chitosan and polylactic-co-glycolic acid–based microparticles (MPs) using a modified solvent displacement method (Figure 2 (a)). The polylactic-co-glycolic acid–PSI MPs increased resistance to photobleaching from 5 to more than 34 days, as shown in Figure 2 (b) [47**]. Resistance to photobleaching was attributed to protection of the protein within the amphiphilic MPs. Badura et al. [23] showed that covalent linkage to an osmium-based redox polymer protects the protein complex. Specifically, the redox polymer shields PSI from direct contact with the bulk electrolyte. In addition, Zhao et al. showed that interactions within a similar osmium-based hydrogel may be tuned via the pH-dependent moieties within the polymer [49]. In a general effort to improve PSI multilayer stability, Yang et al. [48] cross-linked multilayers of PSI to minimize desorption into solution over time. Cross-linking of PSI via disulfide bonds using 2-iminothiolane, as depicted in Figure 2 (c), increased the percentage of PSI complexes retained on the bioelectrode over a 3-day exposure to the electrolyte (Figure 2 (d)) [48]. In summary, the overall stability of PSI bioelectrodes within liquid electrochemical cells can be improved through covalent linkage and cross-linking, physical interactions, and encapsulation, which effectively mitigate desorption, dissolution, and interaction with the bulk electrolyte.

Solid-state biohybrid photovoltaics

PSI photovoltaics composed of all solid components have advantages in regard to practicality, performance, and stability [7,9]. By eliminating the liquid electrolyte, the PSI protein complex is protected from soluble species, such as ROS, and is immobilized between electrodes. In addition, liquid electrolytes add unnecessary weight to the cell, may evaporate in hot environments, and can leak, causing corrosion of metal components over time. Many aspects of solid-state biohybrid systems are not well understood, especially regarding the stability of the photoactive biological species within these novel environments. The standard analysis of a solid-state PSI biohybrid photovoltaic begins with a layered device schematic and a band energy diagram showing the electron energy within each distinct layer and the path of electron flow. Solid-state PSI biohybrid photovoltaics comprise two current collectors (one being transparent), electron and hole transport layers, and a PSI-based photoactive layer.

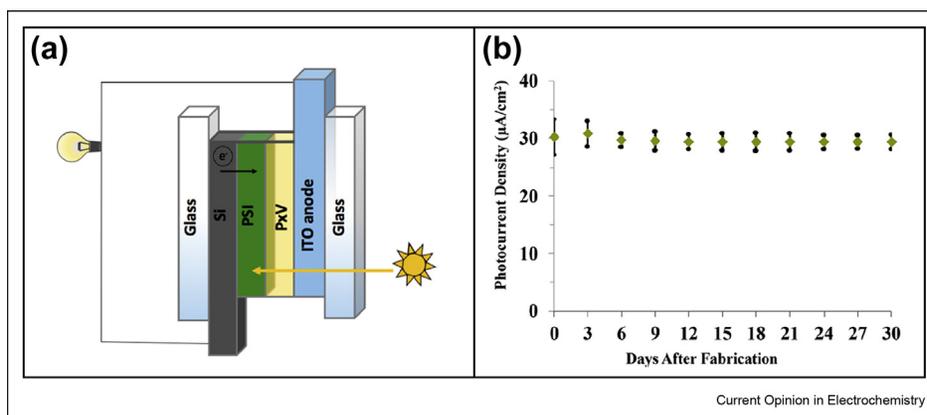
Materials are chosen based on their energetics, with the final photopotential of the cell determined by the electron energy at the two current collectors and the total resistance of all layers.

Solid-state devices differ from photoelectrochemical cells with a liquid electrolyte in both the chosen materials and in deposition techniques. The deposition technique is an important consideration in preparing the PSI active layer. Common deposition strategies include low-vacuum deposition, spin coating, and entrapment within conducting polymer matrices [50,51*,52,53*,54–57]. These techniques are chosen because their benign conditions are unlikely to cause damage to or denature PSI. Furthermore, the hydration of the protein complex within the film is critical to its performance and structural stability, favoring solution-phase deposition techniques [51*,58]. Designer peptide detergents have been used by Kiley *et al.* [58] to improve structural stability during the deposition of solid-state PSI films and by Matsumoto *et al.* [59] for long-term structural stability in aqueous solvents. Within biohybrid photovoltaic devices, PSI active layers must be deposited in a manner that allows for moisture retention, and subsequent layers must be deposited with caution [51*,53*,54]. While the need for hydration of the protein complex within solid devices is established, little has been reported on structure–function properties or stability for various states of hydration or within different environments.

Performance within solid-state PSI biohybrid photovoltaics has improved drastically in the past five years. Improvements are attributed to novel material choices and deposition strategies, including those aimed toward improved PSI orientation. Performance of solid-state

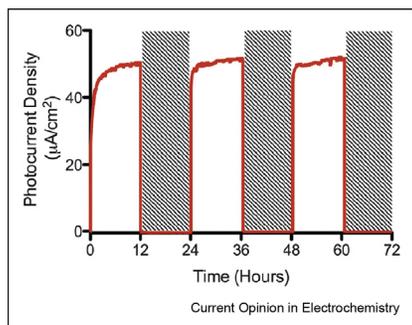
devices is most often represented using a power curve, from which the fill factor and power conversion efficiency (PCE) can be ascertained. Gordiichuk *et al.* [50] produced a solid-state PSI device that incorporates a titanium oxide anode, a semiconducting polytriarylamine polymer hole transport layer, and a molybdenum oxide cathode, achieving a fill factor of 45%. Zeynali *et al.* [51*] produced a solid-state device yielding one of the highest reported PCEs of a PSI solid-state photovoltaic, achieving 0.51% by incorporating high-performing hole and electron transport layers. Other recently reported all-solid-state PSI biohybrid photovoltaics include a solid-state device based on a PSI multilayer interfaced with poly(3,4-ethylenedioxythiophene):polystyrene sulfonate prepared by Kazemzadeh *et al.* [54], a PSI-cyt *c* composite device prepared by Olmos *et al.* [56], and a PSI-polyaniline solid-state device prepared by Gizzie *et al.* [55]. Although solid-state devices are generally assumed to offer improved stability, thanks to their mitigation of both dissolution or desorption and the absence of hazardous soluble species, little experimental evidence has been demonstrated. Figure 3(a) shows a schematic of a high-performing solid-state PSI biohybrid photovoltaic prepared by Dervishogullari *et al.* [53*], which was tested for photocurrent performance stability for 30 days (Figure 3(b)). Beam *et al.* [57] also highlighted the stability of a p-type silicon/PSI/zinc oxide device for 20 days. In another multiday stability study, a polyaniline–PSI composite device yielded a photocurrent of more than $60 \mu\text{A}/\text{cm}^2$ after 3 days of continuous testing under 12-h light cycles, showing this device may be used on a practically relevant daily timescale (Figure 4) [55]. Although these studies are promising, further improvement of performance along with a heavier emphasis on long-term stability is necessary for PSI biohybrid solid-

Figure 3



Dervishogullari *et al.* [53*] fabricated a solid-state PSI biohybrid photovoltaic incorporating a polyviologen electron transport layer. (a) A device schematic highlighting the transparent indium tin oxide (ITO) anode and polyviologen electron transport layer (reproduced with permission from Dervishogullari *et al.* [53*], Copyright 2018 American Chemical Society). (b) A 30-day performance stability study showing the photocurrent produced as a function of days passed since the device fabrication scale (reproduced with permission from Dervishogullari *et al.* [53*], Copyright 2018 American Chemical Society). PSI, photosystem I.

Figure 4



A 12-h light cycle stability study highlighting the stability of the PSI– polyaniline solid-state device produced by Gizzie et al. [55] on a practically relevant timescale (reproduced with permission from Gizzie et al [55], Copyright 2015 Royal Society of Chemistry). PSI, photosystem I.

state photovoltaics to be used in practical applications, especially in regard to the presence of oxygen within solid-state devices.

Conclusions

The rapid development of PSI bioelectrodes warrants consideration of the stability of the protein complex in a variety of environments. Aerobic electrolytes are both practical and have high performance; however, the production of damaging ROS may limit the possibility of long-term stability [24**]. Means of protecting the protein complex from ROS are therefore necessary for the use of mediators that require an aerobic environment, such as methyl viologen. Immobilization strategies have been developed to retain the PSI protein complex in a structurally stable environment and to protect it from the electrolyte. Both entrapment and cross-linking have been used to improve the stability of PSI [47**,48]. A push toward solid-state PSI biohybrid photovoltaics may offer a solution to both ROS degradation and protein immobilization, while also eliminating other limitations associated with liquid electrolytes. Many promising materials and deposition strategies have been developed, and PCEs near the single-digit range have been reported [51*]. However, the longest reported duration of a performance stability study for a solid-state device is only 30 days [53*]. Researchers should begin to consider factors such as hydration, the presence of oxygen, photobleaching, and the structure of PSI in these novel solid-state environments in an effort to improve long-term stability. Solid-state devices show promise for the future of PSI-based technologies, and their stability will become increasingly important in the development of PSI biohybrid photovoltaics

Conflict of interest

None declared.

Acknowledgements

The authors greatly acknowledge financial support from the US Department of Agriculture (2019-67021-29857) and the National Science Foundation (DMR-1507505).

References

Papers of particular interest, published within the period of review, have been highlighted as:

- * of special interest
- ** of outstanding interest

1. Raghavendra AS: *Photosynthesis: a comprehensive treatise*. 1st ed. Cambridge: Cambridge University Press; 2000.
2. Nelson N, Junge W: **Structure and energy transfer in photosystems of oxygenic photosynthesis**. *Annu Rev Biochem* 2015, **84**:659–683.
3. Amunts A, Nelson N: **Functional organization of a plant Photosystem I: evolution of a highly efficient photochemical machine**. *Plant Physiol Biochem* 2008, **46**:228–237.
4. Nguyen K, Bruce BD: **Growing green electricity: progress and strategies for use of Photosystem I for sustainable photovoltaic energy conversion**. *Biochim Biophys Acta Bioenerg* 2014, **1837**:1553–1566.
5. Shubin V, Terekhova IV, Bolychevtseva YV, El-Mohsnawy E, Rögner M, Mäntele W, Kopczak MJ, Džafić E: **Thermostability of photosystem I trimers and monomers from the cyanobacterium *Thermosynechococcus elongatus***. *Spectrochim Acta A* 2017:17–22.
6. Ivanov AG, Velitchkova MY, Allakhverdiev SI, Huner NPA: **Heat stress-induced effects of photosystem I: an overview of structural and functional responses**. *Photosynth Res* 2017, **133**:17–30.
7. Robinson MT, Gizzie EA, Mwambutsa F, Cliffl DE, Jennings GK: **Mediated approaches to Photosystem I-based bio-photovoltaics**. *Curr Opin Electrochem* 2017, **5**:211–217.
8. Chen G, LeBlanc G, Jennings GK, Cliffl DE: **Effect of redox mediator on the photo-induced current of a photosystem I modified electrode**. *J Electrochem Soc* 2013, **160**:H315–H320.
9. Friebe VM, Frese RN: **Photosynthetic reaction center-based biophotovoltaics**. *Curr Opin Electrochem* 2017, **5**:126–134.
10. Kamran M, Delgado JD, Friebe V, Aartsma TJ, Frese RN: **Photosynthetic protein complexes as bio-photovoltaic building blocks retaining a high internal quantum efficiency**. *Biomacromolecules* 2014, **15**:2833–2838.
11. Robinson MT, Armbruster ME, Gargye A, Cliffl DE, Jennings GK: **Photosystem I multilayer films for photovoltage enhancement in natural dye-sensitized solar cells**. *ACS Appl Energy Mater* 2018, **1**:301–305.
12. Ciesielski PN, Hijazi FM, Scott AM, Faulkner CJ, Beard L, Emmett K, Rosenthal SJ, Cliffl D, Kane Jennings G: **Photosystem I – based biohybrid photoelectrochemical cells**. *Bioresour Technol* 2010, **101**:3047–3053.
13. LeBlanc G, Chen G, Gizzie EA, Jennings GK, Cliffl DE: **Enhanced photocurrents of photosystem I films on p-doped silicon**. *Adv Mater* 2012, **24**:5959–5962.
14. Stieger KR, Feifel SC, Lokstein H, Lisdat F: **Advanced unidirectional photocurrent generation via cytochrome c as reaction partner for directed assembly of photosystem I**. *Phys Chem Chem Phys* 2014, **16**:15667–15674.
15. Das R, Kiley PJ, Segal M, Norville J, Yu AA, Wang L, Trammell SA, Reddick LE, Kumar R, Stellacci F, Lebedev N, Schnur J, Bruce BD, Zhang S, Baldo M: **Integration of photosynthetic protein molecular complexes in solid-state electronic devices**. *Nano Lett* 2004, **4**:1079–1083.
16. Schlaue-Cohen GS: **Principles of light harvesting from single photosynthetic complexes**. *Interface Focus* 2015, **5**:1–6.
17. Fu Q, Tang X, Huang B, Hu T, Tan L, Chen L, Chen Y: **Recent progress on the long-term stability of perovskite solar cells**. *Adv Sci* 2018, **5**:1–17.

18. Voloshin RA, Brady NG, Zharmukhamedov SK, Feyziyev YM, Huseynova IM, Najafpour MM, Shen J-R, Veziroglu TN, Bruce BD, Allakhverdiev SI: **Influence of osmolytes on the stability of thylakoid-based dye-sensitized solar cells.** *Int J Energy Res* 2019;1–12.
19. Pankratova G, Pankratov D, Di Bari C, Goñi-Urtiaga A, Toscano MD, Chi Q, Pita M, Gorton L, De Lacey AL: **Three-dimensional graphene matrix-supported and thylakoid membrane-based high-performance bioelectrochemical solar cell.** *ACS Appl Energy Mater* 2018, 1:319–323.
20. Takagi D, Takumi S, Hashiguchi M, Sejima T, Miyake C: **Superoxide and singlet oxygen produced within the thylakoid membranes both cause photosystem I photoinhibition.** *Plant Physiol* 2016, 171:1626–1634.
21. Zhao F, Hardt S, Hartmann V, Zhang H, Nowaczyk MM, Rögner M, Plumeré N, Schuhmann W, Conzuelo F: **Light-induced formation of partially reduced oxygen species limits the lifetime of photosystem 1-based biocathodes.** *Nat Commun* 2018, 9:1–9.
- Zhao *et al.* deposit photosystem I (PSI) within an osmium polymer and poly(ethyleneglycol)diglycidyl ether (PEGDGE) and use cyclic voltammetry and scanning photoelectrochemical microscopy to study the lifetime and production of reactive oxygen species (ROS), respectively. They conclude that in the presence of methyl viologen and dissolved oxygen, PSI generates partially reduced oxygen species.
22. Asada K: **Production and scavenging of reactive oxygen species in chloroplasts and their functions.** *Plant Physiol* 2006, 141:391–396.
23. Badura A, Guschin D, Kothe T, Kopczak MJ, Schuhmann W, Rögner M: **Photocurrent generation by photosystem 1 integrated in crosslinked redox hydrogels.** *Energy Environ Sci* 2011, 4:2435–2440.
24. Zhao F, Ruff A, Rögner M, Schuhmann W, Conzuelo F: **Extended operational lifetime of a photosystem-based bioelectrode.** *J Am Chem Soc* 2019, 141:5102–5106.
- Zhao *et al.* further develop a system incorporating photosystem I (PSI) within an osmium polymer and poly(ethyleneglycol)diglycidyl ether (PEGDGE) and give clear evidence that PSI has a shorter lifetime within aerobic conditions. This is a result of the production of partially reduced oxygen species, otherwise known as reactive oxygen species (ROS). It is reported that the PSI lifetime decay curve follows a first order decay with $k_{app} = 1.05 \times 10^{-4} \text{ s}^{-1}$ in the presence of oxygen, whereas in the absence of oxygen the decay is linear.
25. Ciornii D, Kölsch A, Zouni A, Lisdat F: **A precursor-approach in constructing 3D ITO electrodes for the improved performance of photosystem I-cyt c photobioelectrodes.** *Nanoscale* 2019:1–9.
- Ciornii *et al.* produced porous indium tin oxide (ITO) electrodes via a solution phase precursor approach to be interfaced with photosystem I (PSI) and the cytochrome complex (cyt *c*). They found that a nominal 460 nm pore size provided the greatest photocurrent production and attributed the performance to a maximum in the areal loading of cyt *c*-PSI onto the ITO surface. Additionally, they provided stability data showing that with the addition of a ubiquinone (Q_0) electron scavenger, short-pulse (20 s) light induced photocurrent degradation was partially mitigated over a 30 min test.
26. Mershin A, Matsumoto K, Kaiser L, Yu D, Vaughn M, Nazeeruddin MK, Bruce BD, Graetzel M, Zhang S: **Self-assembled photosystem-I biophotovoltaics on nanostructured TiO₂ and ZnO.** *Sci Rep* 2012, 2:1–7.
27. Nusbaumer H, Zakeeruddin SM, Moser J-E, Grätzel M: **An alternative efficient redox couple for the dye-sensitized solar cell system.** *Chem: Eur J* 2003, 9:3756–3763.
28. Trammell SA, Spano A, Price R, Lebedev N: **Effect of protein orientation on electron transfer between photosynthetic reaction centers and carbon electrodes.** *Biosens Bioelectron* 2006, 21:1023–1028.
29. Badura A, Kothe T, Schuhmann W, Rögner M: **Wiring photosynthetic enzymes to electrodes.** *Energy Environ Sci* 2011, 4:3263–3274.
30. Nagakawa H, Takeuchi A, Takekuma Y, Noji T, Kawakami K, Kamiya N, Nango M, Furukawa R, Nagata M: **Efficient hydrogen production using photosystem I enhanced by artificial light harvesting dye.** *Photochem Photobiol Sci* 2019, 18:309–313.
31. Tapia C, Milton RD, Pankratova G, Minter SD, Åkerlund H-E, Leech D, DeLacey AL, Pita M, Gorton L: **Wiring of Photosystem and hydrogenase on an electrode for photoelectrochemical H₂ production by using redox polymers for relatively positive onset potential.** *ChemElectroChem* 2017, 4:90–95.
32. Killiszek M, Harputlu E, Szalkowski M, Kowalska D, Unlu CG, Haniewicz P, Abram M, Wiwatowski K, Niedziółka-Jönsson J, Maćkowski S, Ocakoglu K, Kargul J: **Orientation of photosystem I on graphene through cytochrome: C 553 leads to improvement in photocurrent generation.** *J Mater Chem A* 2018, 6:18615–18626.
33. Stieger KR, Feifel SC, Lokstein H, Hejazi M, Zouni A, Lisdat F: **Biohybrid architectures for efficient light-to-current conversion based on photosystem I within scalable 3D mesoporous electrodes.** *J Mater Chem A* 2016, 4:17009–17017.
34. Takekuma Y, Nagakawa H, Noji T, Kawakami K, Furukawa R, Nango M, Kamiya N, Nagata M: **Enhancement of photocurrent by integration of an artificial light-harvesting antenna with a photosystem I photovoltaic device.** *ACS Appl Energy Mater* 2019:3986–3990.
35. Gordichuk P, Pesce D, Ocampo OEC, Marcozzi A, Wetzelaer G-JAH, Paul A, Loznik M, Gloukhikh E, Richter S, Chiechi RC, Herrmann A: **Orientation and incorporation of photosystem I in bioelectronics devices enabled by phage display.** *Adv Sci* 2017, 4:1–7.
36. Stieger KR, Ciornii D, Kölsch A, Hejazi M, Lokstein H, Feifel SC, Zouni A, Lisdat F: **Engineering of supramolecular photoactive protein architectures: the defined co-assembly of photosystem I and cytochrome c using a nanoscaled DNA-matrix.** *Nanoscale* 2016, 8:10695–10705.
37. Ciornii D, Riedel M, Stieger KR, Feifel SC, Hejazi M, Lokstein H, Zouni A, Lisdat F: **Bioelectronic circuit on a 3D electrode architecture: enzymatic catalysis interconnected with photosystem I.** *J Am Chem Soc* 2017, 139:16478–16481.
38. Feifel SC, Stieger KR, Hejazi M, Wang X, Ilbert M, Zouni A, Lojou E, Lisdat F: **Dihemic c4-type cytochrome acting as a surrogate electron conduit: artificially interconnecting a photosystem I supercomplex with electrodes.** *Electrochem Commun* 2018, 91:49–53.
39. Kölsch A, Hejazi M, Stieger KR, Feifel SC, Kern JF, Müh F, Lisdat F, Lokstein H, Zouni A: **Insights into the binding behavior of native and non-native cytochromes to photosystem I from *Thermosynechococcus elongatus*.** *J Biol Chem* 2018, 293:9090–9100.
40. Proux-Delrouyre V, Demaille C, Leibl W, Sétif P, Bottin H, Bourdillon C: **Electrocatalytic investigation of light-induced electron transfer between cytochrome c6 and photosystem I.** *J Am Chem Soc* 2003, 125:13686–13692.
41. Efrati A, Tel-Vered R, Michaeli D, Nechushtai R, Willner I: **Cytochrome c-coupled photosystem I and photosystem II (PSI/PSII) photo-bioelectrochemical cells.** *Energy Environ Sci* 2013, 6:2950–2956.
42. Friebe VM, Millo D, Swainsbury DJK, Jones MR, Frese RN: **Cytochrome c provides an electron-funneling antenna for efficient photocurrent generation in a reaction center biophotocathode.** *ACS Appl Mater Interfaces* 2017, 9:23379–23388.
43. Manocchi AK, Baker DR, Pendley SS, Nguyen K, Hurley MM, Bruce BD, Sumner JJ, Lundgren CA: **Photocurrent generation from surface assembled photosystem I on alkanethiol modified electrodes.** *Langmuir* 2013, 29:2412–2419.
44. Kothe T, Pöller S, Zhao F, Fortgang P, Rögner M, Schuhmann W, Plumeré N: **Engineered electron-transfer chain in photosystem 1 based photocathodes outperforms electron-transfer rates in natural photosynthesis.** *Chem: Eur J* 2014, 20:11029–11034.
45. Gunther D, LeBlanc G, Prasai D, Zhang JR, Cliffl DE, Bolotin KI, Jennings GK: **Photosystem I on graphene as a highly transparent, photoactive electrode.** *Langmuir* 2013, 29:4177–4180.
46. Qiu X, Castañeda Ocampo O, De Vries HW, Van Putten M, Loznik M, Herrmann A, Chiechi RC: **Self-regenerating soft**

- biophotovoltaic devices. *ACS Appl Mater Interfaces* 2018, **10**: 37625–37633.**
47. Cherubin A, Destefanis L, Bovi M, Perozeni F, Bargigia I, de la Cruz Valbuena G, D'Andrea C, Romeo A, Ballottari M, Perduca M: **Encapsulation of Photosystem I in organic microparticles increases its photochemical activity and stability for ex vivo photocatalysis.** *ACS Sustain Chem Eng* 2019:10435–10444.
- Cherubin et al. encapsulate photosystem I (PSI) within both chitosan and polylactic co-glycolic acid (PLGA) microparticles and measured the oxidation of P700 optically to study stability in both methyl viologen and sodium ascorbate mediators. PSI encapsulated within PLGA was stable for over 34 days. Without encapsulation, stability was observed for just 5 days. Not only was stability increased within electrolytes, but decay after lyophilization was also decreased.
48. Yang S, Robinson MT, Mwambutsa F, Cliffel DE, Jennings GK: **Effect of cross-linking on the performance and stability of photocatalytic photosystem I films.** *Electrochim Acta* 2016, **222**:926–932.
49. Zhao F, Sliozberg K, Rögner M, Plumeré N, Schuhmann W: **The role of hydrophobicity of Os-Complex-Modified polymers for photosystem 1 based photocathodes.** *J Electrochem Soc* 2014, **161**:H3035–H3041.
50. Gordiichuk PI, Wetzelaer GJAH, Rimmerman D, Gruszka A, De Vries JW, Saller M, Gautier DA, Catarci S, Pesce D, Richter S, Blom PWM, Herrmann A: **Solid-state biophotovoltaic cells containing photosystem i.** *Adv Mater* 2014, **26**:4863–4869.
51. Zeynali A, Ghiasi TS, Riazi G, Ajeian R: **Organic solar cell based on photosystem I pigment-protein complex, fabrication and optimization.** *Org Electron* 2017, **51**:341–348.
- Zeynali et al. produced a solid-state photosystem I (PSI) photovoltaic through benign deposition methods including low temperature and low vacuum deposition. Their device features a tyrosine hole transport layer, a PSI multilayer, and a fullerene C₆₀ electron transport layer to achieve one of the highest reported power conversion efficiencies of a PSI device, 0.51%. The hydration of the PSI multilayer is discussed with respect to function and stability.
52. Robinson MT, Simons CE, Cliffel DE, Jennings GK: **Photocatalytic photosystem I/PEDOT composite films prepared by vapor-phase polymerization.** *Nanoscale* 2017, **9**:6158–6166.
53. Dervishogullari D, Gizzie EA, Jennings GK, Cliffel DE: **Polyviologen as electron transport material in photosystem I-based biophotovoltaic cells.** *Langmuir* 2018, **34**: 15658–15664.
- Dervishogullari et al. showed that a polyviologen electron transport layer increased performance within a photosystem I (PSI) solid-state device. It was clearly shown that the layer acted as an electron transport layer through the fabrication of devices with varied layer order. Additionally, the devices were tested for 30 days, highlighting the stability of solid-state PSI photovoltaics.
54. Kazemzadeh S, Riazi G, Ajeian R: **Novel approach of biophotovoltaic solid state solar cells based on a multilayer of PS1 complexes as an active layer.** *ACS Sustain Chem Eng* 2017, **5**:9836–9840.
55. Gizzie EA, Scott Niezgoda J, Robinson MT, Harris AG, Kane Jennings G, Rosenthal SJ, Cliffel DE: **Photosystem I-polyaniline/TiO₂ solid-state solar cells: simple devices for biohybrid solar energy conversion.** *Energy Environ Sci* 2015, **8**: 3572–3576.
56. Olmos JDJ, Becquet P, Gront D, Sar J, Dąbrowski A, Gawlik G, Teodorczyk M, Pawlak D, Kargul J: **Biofunctionalisation of p-doped silicon with cytochrome c553 minimises charge recombination and enhances photovoltaic performance of the all-solid-state photosystem I-based biophotocathode.** *RSC Adv* 2017, **7**:47854–47866.
57. Beam JC, LeBlanc G, Gizzie EA, Ivanov BL, Needell DR, Shearer MJ, Jennings GK, Lukehart CM, Cliffel DE: **Construction of a semiconductor–biological interface for solar energy conversion: p-doped silicon/photosystem I/zinc oxide.** *Langmuir* 2015, **31**:10002–10007.
58. Kiley P, Zhao X, Vaughn M, Baldo MA, Bruce BD, Zhang S: **Self-assembling peptide detergents stabilize isolated photosystem ion a dry surface for an extended time.** *PLoS Biol* 2005, **3**:1180–1186.
59. Matsumoto K, Vaughn M, Bruce BD, Koutsopoulos S, Zhang S: **Designer peptide surfactants stabilize functional photosystem-I membrane complex in aqueous solution for extended time.** *J Phys Chem B* 2009, **113**:75–83.