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Solar Redox Flow Batteries with Organic Redox Couples in Aqueous Electrolytes: A Mini-review

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ABSTRACT

In recent years, research in solar energy storage with photoelectrochemical cells (solar redox flow batteries: SRFBs) has resurged. This development is emerging in parallel with the growing field of research into organic redox couples intended for aqueous redox flow batteries (RFBs) in a range of different pH environments. In a solar flow battery, the dissolved electroactive molecules are charged directly from solar radiation by semiconductor photoelectrodes, The charged solution can then at a later stage be converted into electricity and solar flow batteries are as such an approach to build integrated solar energy generation and storage devices. Research in RFBs and SRFBs has from their beginning been mutually linked by use of the same organic redox molecules in the electrolyte, such as quinones. Despite the long research history (since 1976), metallic-based, acidic SRFBs have shown only incremental development, while research in use of organic redox pairs appear more promising. This review focuses on historical development of use of organic redox pairs in both RFBs and SRFBs and in particular on the mutual exchange *of methods and materials between the two fields*.

1) Introduction

Globally tremendous efforts are made to replace fossil-based electricity production with renewables. The EU alone aims at a greenhouse gas reduction of 80-95% by 2050, by a combination of renewable energy and increased energy efficiency.¹ In 2016 the contribution from renewables to the electricity consumption totaled 29.6%, of which 31.8% was wind power and 11.6% solar, while the remainder primarily came from hydro power and biomass.² However, continued implementation is faced with challenges concerning grid stability and the security of supply because of the intermittent nature of sun and wind. Based on historical hourly weather

data, modeling of a fully renewable power grid with 45% solar and 55% wind has shown that Europe alone would need 400–480 TWh of storage capacity.³ There are widespread attempts to develop technologies to mitigate particularly the daily fluctuation, such as batteries, or on a longer timescale electrolysis hydrogen storage coupled with fuel cells or further chemical fuel conversion.⁴ In this context, Solar Redox Flow Batteries (SRFBs) have received renewed attention in recent years. An SRFB is a combination of a Redox Flow Battery (RFB) and a photoelectrochemical (PEC) cell, which may be fully integrated in a single cell or separated into an RFB and a PEC cell/panel component (here both configurations are denoted SRFB). In this way, the SRFB is a rechargeable PEC cell, converting solar energy into a storable electrochemical fuel that later can be converted into electricity. In these devices, energy is stored in soluble redox couples that are charged by photo-excited charge carriers from semiconductor-based photoelectrode(s) under solar radiation in direct contact with the redox couples as schematically outlined in Figure 1.

In RFBs, the redox couples are dissolved in solutions of supporting electrolytes (hereafter denoted redox electrolytes) and kept in external tanks and pumped through an electrochemical flow cell for charge or discharge.⁵ This configuration offers flexibility in terms of power (electrode area) and capacity (volume of redox electrolytes) that can be scaled independently. RFBs are regarded as a promising technology for future large-scale energy storage because of this design flexibility and potential low levelised-cost-of-electricity-storage.^{5,6} Here it is noted that to date, the world's largest battery facility being constructed is a 200 MW/800 MWh all-vanadium RFB (Dalian-Rongke Power facility in Liaoning, China) intended for peak-shaving, grid support, and black-start options.⁷

In addition to the solar charging function, SRFBs share, in principle, most of the positive traits

of an RFB,. They can be charged both directly from solar radiation and with excess electricity from the grid, and thereby fulfill multiple functions in the future renewable electricity system. Not excluding large-scale applications, SRFBs could also be a technology for micro-grid applications or as a behind-the-meter solution for domestic buildings. Furthermore, the conjoint solar heating of the redox electrolytes can be utilized for building/water heating through heat exchangers.⁴ This also opens up exploiting the battery temperature coefficient (redox reaction entropy effect). Provided that the temperature coefficient is negative, the cell potential is lower during solar charging (high temperature) and higher during discharging (low temperature). Hereby heat is additionally converted into electricity and increases the overall efficiency of the system even further.

Overall, a SRFB is a simpler and more integrated solution for stationary energy generation and storage than PEC water splitting, that need hydrogen gas-collectors and -compression and fuel cells. At the same time research in SRFBs can exploit the extensive technical advances in the field of photoelectrodes for water splitting.^{4,8,9} However, the process of integrating such photoelectrodes with standard metallic and acidic RFBs, such as all-vanadium and iron-chromium systems⁵, has been challenged due to lack of flexibility in redox electrolyte properties such as redox potential, pH, and solubility. To meet this, efforts in the SRFB field has recently turned towards organic/metal-organic redox couples and follows the same trends of research on aqueous organic redox couples for RFBs, where a series of high-impact publications on systems operating in a wide pH range has emerged since 2014.¹⁰⁻¹⁴ In principle organic redox couples offer tailored properties where the solubility, redox potential, and pH can be optimized by introduction or substitution of functional groups on core organic redox active component, as specifically reviewed earlier.^{5,15} The types of organic molecules and metal-organic complexes

that have been used both for RFBs and SRFBs (or older rechargeable PEC cells) can be seen in Chart 1. Substantial research on this topic was carried out in the 1980s, but is not well recognized today. To gain a more comprehensive understanding of the progress made in the SRFB field to date, this review is therefore dedicated to recount both early work on rechargeable PEC cells and recent efforts in the field of organic, aqueous SRFBs and evaluate performance comparatively.

2) Fundamental aspects of SRFBs

SRFB System Design: There are multiple ways to integrate photoelectrodes with RFBs that each come with various drawbacks and opportunities, and Figure 1a-d outlines several different types of cell designs.^{8,9} Considering a simple PEC storage cell in Figure 1a, it consists of a single photoelectrode (here a photoanode) immersed in the anolyte chamber, where it is illuminated from either the front or the back side. Given a suitable fit between the energy levels of the redox potentials of the electrolyte and the semiconductor band edges, band bending at the interface causes a charge separation (uphill towards to the electrolyte in the case of Figure 1a), which leads to the positive hole transport to the surface and oxidizing the anolyte redox couple. This happens while electrons are conducted through the external circuit to reduce the catholyte on the other side of a separator, usually an ion-exchange membrane, without the need for external electrical bias. Overall, the net photo-induced reactions bring the redox species into their charged state until a later time where they are discharged and electrical power harvested . Figure 1a is to be viewed as an example where the photoelectrode is front-side illuminated *i.e.*, chemical reaction and light irradiation on the same side. This design is experimentally straightforward and the most common in experimental studies.¹⁶ However, in practice it requires a photoelectrode immersed inside a cell and illuminated through a window, from this design it follows that the

photoelectrode substrate blocks the transport of counter-ions in the electrolyte, leading to higher internal cell resistance. Furthermore, the redox solutions are normally strongly absorbing in the UV/VIS spectrum and large fractions of the total solar energy can be lost by absorption, and the space between the photoelectrode and window glass must be minimized. The other option is back-side illumination, which is an approach that seems more ideal in terms of solar-to-current efficiency as demonstrated for solar water splitting.^{17,18} Such a design is challenged by optimization of the photoelectrode layer thickness, where a high absorbance (thick layer) in many cases will lead to lower photocurrents because of a low charge carrier mobility.

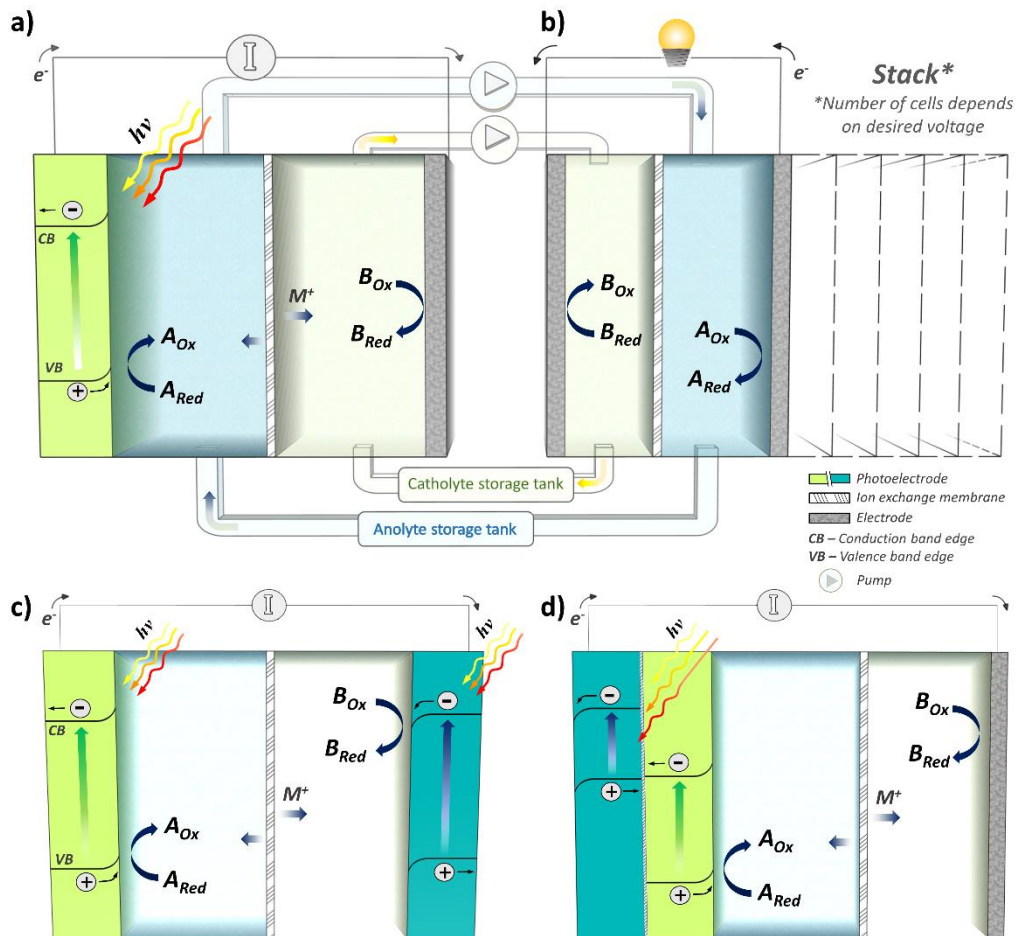


Figure 1. Schematic solar RFB designs. a) PEC redox cell with an n-type photoelectrode (photoanode) in the anolyte (with redox couple A) chamber and an inert, polarizable counter electrode in the catholyte (with redox couple B) chamber separated by an ion exchange membrane. b) RFB stack consisting of several RFB single cells connected in series or parallel for discharging the solar charged electrolytes. c) PEC redox cell with both an n-type (photoanode; left) and a p-type (photocathode; right) semiconductor (tandem device architecture) with a recombination layer (diagonal pattern) in between two electrodes. d) A PEC redox cell with a tandem device configuration which has both photoanode and photocathode connected in series.¹⁹ Subscripts (Ox and Red) denote the oxidized form and reduced form of the redox couples, respectively. Note that the illustration is not to scale.

The voltage of single cell RFBs are too low for efficient conversion in inverters to useful > 100 V AC power, and RFB cells are for this reason series connected in stacks to produce voltages with nominal powers of 48 V or higher. As outlined in Figure 1b, one option for discharge of the solar charged redox electrolytes is by pumping it into an optimized RFB stack for discharge and back to the PEC system again for solar charging. Alternatively, and the approach used in the earliest reports on these kinds of cells, electrodes for discharging can be integrated into the PEC cell.¹⁶ Most recent publications do not follow this solution since, in this case, the cell can only be efficiently discharged under dark conditions, and the considerable cell resistance of PEC cells compared to optimized RFB stacks, diminishes the output power density.

Despite of the simplicity, one of the major drawback of the single photoelectrode PECs is the relatively low available photovoltage (≈ 0.8 V). Alternatively, integration of both a photoanode and a photocathode into the PEC compartment as shown in Figure 1c can increase the photovoltage to a level that is typically used in normal RFBs (≈ 0.8 V).^{20–22} Nonetheless, solar

irradiation from two sides as depicted in Figure 1c appears unfeasible and a more practical cell design is a dual-bed configuration, where the photocathode and photoanode are placed side by side and facing upwards. The overall performance of such an integrated system can be estimated by overlapping the individual *current-voltage* curves for each photoelectrode. The intersection of the two curves (*i.e.*, current matching) indicates the overall operating current density (J_{op}) as described elsewhere.¹⁷ Owing to the additional photovoltage from a second photoelectrode, such a dual-bed system can exhibit J_{op} for redox couples with a higher redox potential gap than in the case of single-photoelectrode cells. However, this will lead to a more complex cell design with higher internal resistance, but with geometric optimization it is not an unrealistic approach as demonstrated in recent studies using silicon-based photoelectrodes.^{20–22} While this configuration can give a sufficient photovoltage to potentially suit existing used RFB redox couples, *e.g.* vanadium $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ with a standard cell potential of 1.3 V, it comes with increased complexity of the PEC charging component design. Notably, this dual-bed approach naturally has only half of the limit in photocurrent since two electrodes share the illuminated area. Figure 1d shows a configuration that is similar to Figure 1a, except that the photoelectrode has a tandem configuration with two photon-absorber in series, as has become a common choice for solar water splitting.^{23–25} The challenge here is the selection of suitable semiconductor photoelectrode materials that does not only fit with respect to the band energy levels but also have absorption in the low and high wavelength spectrum for the first and second photoelectrode, respectively.

Redox Couples: In recent years research in aqueous organic and metal-organic complexes redox couples for RFBs and SRFBs have emerged. The ones used in SRFBs are collected in Chart 1.^{5,10,12–15,26–29} and many of the same molecules were already explored for PEC

rechargeable cells in the 1980s. Despite the well-studied electrochemistry of metal ions and their predominance in almost all battery technologies to date, it deserves attention why metals largely have been suppressed by organic molecules for SRFBs. We attempt to answer this question by a chronological review (Section 2) and a performance evaluation of photoelectrochemical storage cells with focus on aqueous systems and tunability of the organic redox couples with respect to redox potential and operating pH, which is a critical factor to the stability of the system.

In recent SRFBs research either conventional vanadium metal-ion RFB electrolytes are used, or alternatively, a fully organic or halogen/metal-organic and organic redox electrolyte combination.³⁰ Notably, other recent reviews discuss non-aqueous organic RFBs and PEC cells. However, at the moment it appears more likely that conjoint advantages with the RFB field and integration with solar heating systems can be realized in aqueous systems, rather than in non-aqueous.^{8,9,31} To date no non-aqueous RFB are commercialized due to the inherent limitations of the low electrolyte conductivity, membrane selectivity, and (fire) safety concerns of organic solvents.³²

3) History and progress of SRFBs: Timeline – from 1976 to 2018

The first study of photoelectrochemical storage cells, with stagnant rather than flowing electrolytes that resembles a SRFB, was published in 1976 by Hodes et al.³³ They used an n-type CdSe polycrystalline photoelectrode and an alkaline solution with 1 M sodium sulfide in combination with a solid silver counter electrode (anode in two-electrode system), thereby creating a hybrid redox storage cell. At this point, the RFB technology was under development, primarily by NASA, who worked on development of the iron-chromium RFB.³⁴ This is seen in Figure 2 that shows the conjoint chronological developments of organic, aqueous SRFBs and RFBs, and it is overall clear that a variety of organic redox couples combined with mainly

selenide-based photoelectrodes were studied from 1976 to 1987. Simultaneously, many investigations of other PEC/redox electrolyte systems were conducted, as summarized in a previous review of solar rechargeable batteries by Sharon et al. in 1991.¹⁶ Their conclusions included the insights that the solar rechargeable batteries had failed to attract commercial attention due to insufficiencies with respect to i) efficient and low-cost photoelectrodes, ii) stable and selective ion-exchange membranes or redox systems that work without a membrane, and iii) development of efficient (low resistance) cell designs. Nonetheless, considering the advancements, for the past decades, of photoelectrode materials and stability combined with new RFB chemistries and stack design, it is not unlikely that high efficiency, power density and stability SRFBs can be discovered.³⁵⁻³⁷

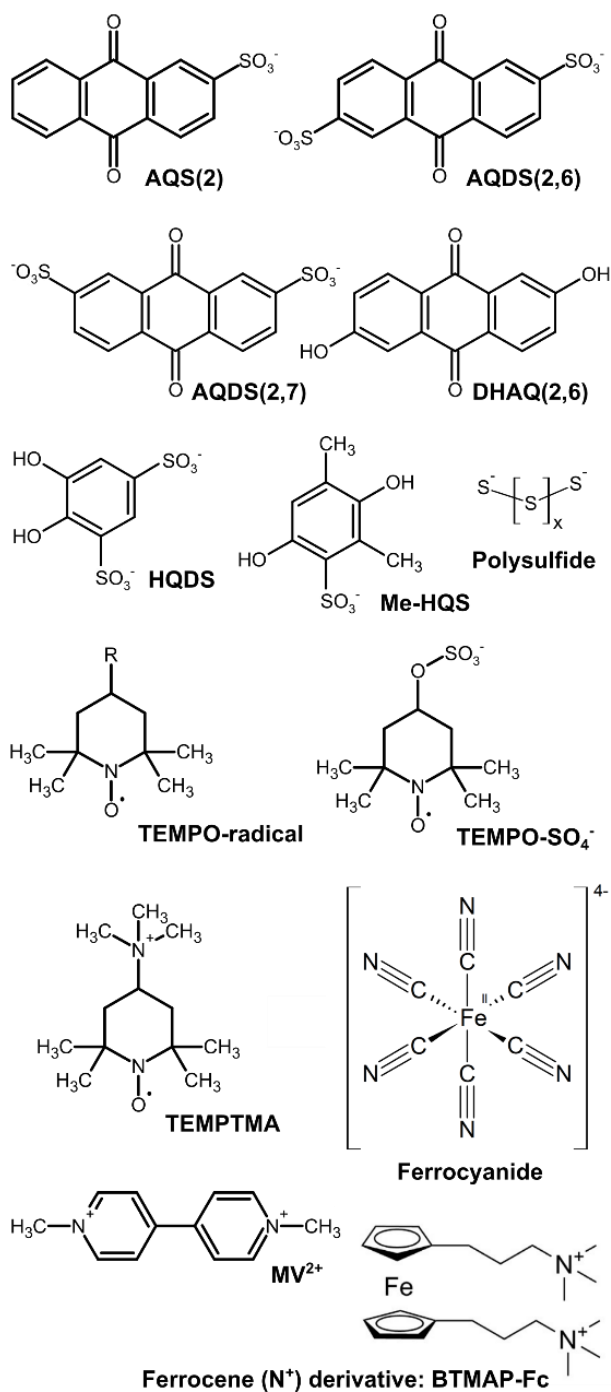


Chart 1. Organic and metal-organic structures described in this work and their names or abbreviations.

As shown in Figure 2, various semiconductor materials have been tested: chalcogenides, metal-oxides, and III-V group semiconductors were demonstrated in the early period and are denoted as *PEC Golden Age*. In the early studies, the PEC charging cell was not physically separated from the discharging cell and they operated under no-flow conditions, and a more correct term may, therefore, be solar redox storage cells than SRFBs. When not considering PEC water splitting, the *PEC Golden Age* was followed by a dormant period until 2016. Reasons for the resurgence of the SRFB field include an increased focus on integrated electrochemical devices, and as illustrated by the timeline in Figure 2, also a consequence of the new interest in the organic redox couples for RFBs. In recent SRFBs studies, it is apparent that the organic redox electrolytes are inspired by the ones used for RFBs.

Additionally, many of the redox couples that were used in the 1980s PEC storage cells have recently been investigated again as redox couples for RFBs. Quinones, polysulfide, methyl viologen (MV^{2+}) and metal-organic complexes are recurring themes, for which the structures are found in Chart 1 and the Supporting Information Tables S1-S3. Especially sulfonated anthraquinones AQDS(2,7), AQDS(2,6) and AQS(2) which were described for RFBs in 2014 have become popular in SRFBs.^{10,12} AQDS(2,6) was used in two PEC storage cells in 1983 and 1984 with both n and p-type WSe₂ and iodine in acidic supporting electrolyte.^{38,39} This cell is quite similar to one investigated in 2017 and illustrates the resurged interest in this field.⁴⁰

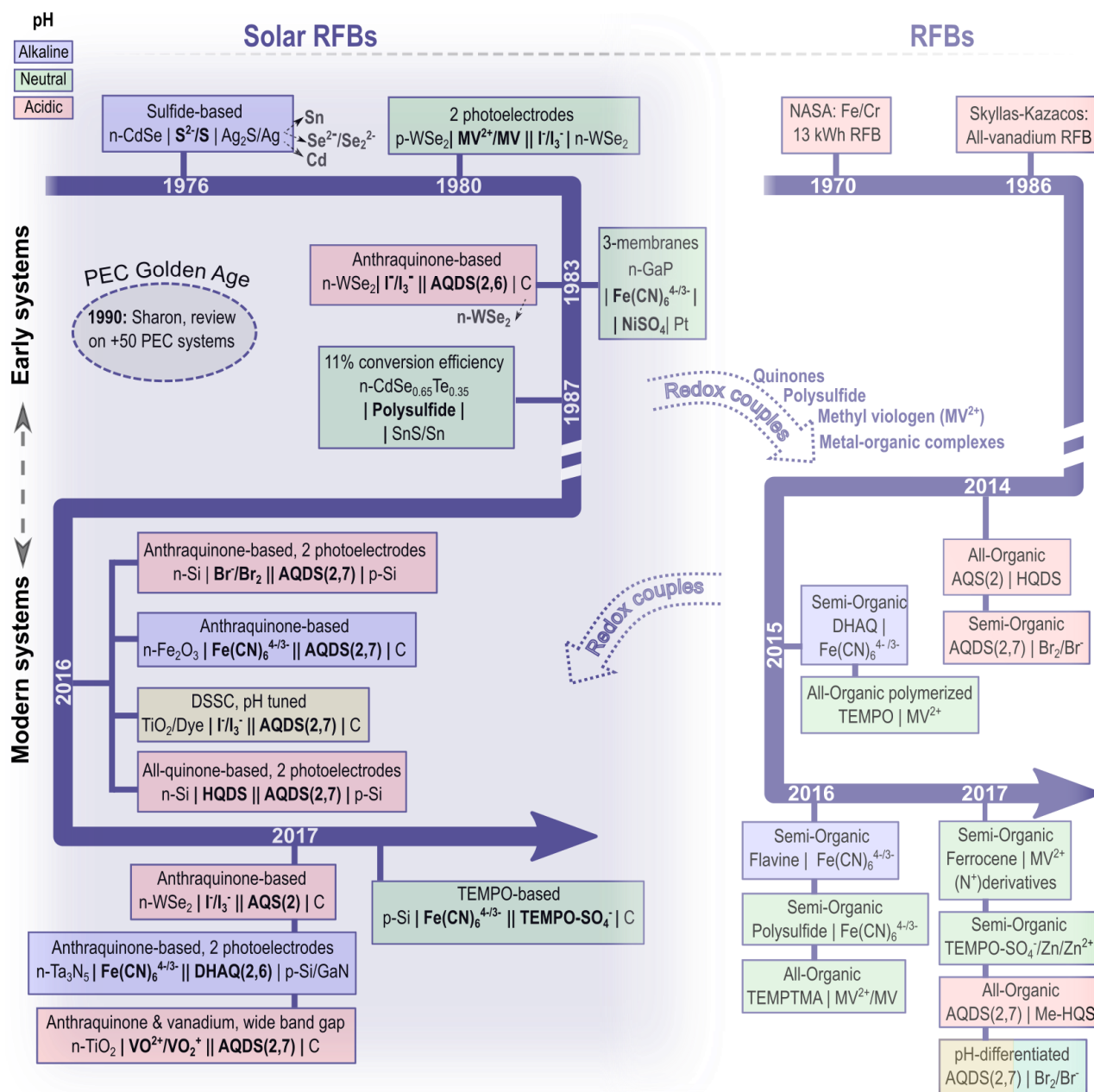


Figure 2. Timeline of key developments within organic, aqueous solar flow batteries. To the left the photoelectrochemical systems are summarized and to the right the RFB systems. The color of the boxes indicates the pH environment (blue: alkaline, green: neutral, yellow: mild acidic and red: acidic). References, full cell configuration and details for each photoelectrochemical work are given in Table S1-S3 in the Supporting Information, while the organic and semi-organic structures and abbreviations are given in Chart 1 and are from references^{10–14,26–29,34,41–46}

In particular, quinones have received considerable attention concerning energy storage applications. Experimental screenings of ensembles of quinone variants have been published since 1972.⁴⁶⁻⁴⁹ One of these screenings we did in 2016, and it collects redox potentials and solubility data on +30 different commercially available mainly quinone compounds at acidic, natural and alkaline pH.⁴⁶ We concluded that the anthraquinones are most suitable for the low-potential side of an RFB (usually around -0.5 to 0.2 V_{NHE} depending on the pH). The positive side remains a challenge, since stable quinones with a high redox potential (hydro/benzoquinones) are rare, as also recognized by other researchers.^{28,50} To the best of our knowledge, there is only one SRFB publication from 2016 which uses a benzoquinone on the high-potential side, and in that the authors also find that the cell potential is significantly lower than expected due to a chemical reaction (hydroxylation) of the benzoquinone taking place in the aqueous electrolyte.^{20,50} Side-group functionalization of the quinones can increase the stability, however, this can be at the cost of lower redox potential and lower solubility, as demonstrated recently.²⁸ Notably, the hydro/benzoquinones are stable enough to be used for theoretical photoelectrochemical investigations, as recognized already in 1979.⁵¹

Likewise, in 1980 it was found that methyl viologen (MV²⁺) is a suitable low redox potential molecule with a high solubility in neutral solution. It was used to construct the first two-photoelectrode (dual-bed) aqueous PEC storage cell.⁵² Nowadays, the compound finds its place in quite a few recent high-performing RFBs after its reevaluation in this field in 2015 as seen from the publications included in Figure 2.^{11,14,26,27,44} However, it remains unexplored in modern SRFBs. This is probably because the required neutral supporting electrolyte has been an uncommon choice in SRFB systems for a long time. In fact, until our recent report on a system using a silicon photoelectrode with Fe(CN)₆³⁻/TEMPO-SO₄⁻ at pH 7, no neutral SRFB had been

explored after the GaP/ferrocyanide cell was reported in 1983 and the CdSe/polysulfide cell in 1987.^{30,53,54}

Another interesting point is that polysulfide works quite well as a redox couple in SRFBs. For example, a two-days outdoor operation of an SRFB with a CdSe photoanode was shown in 1987, and the performance of this system concerning efficiency and energy density remains unsurpassed in SRFBs to date.⁵⁴ However, polysulfide is so far absent as a redox couple in recent SRFBs, despite the fact that the polysulfide-bromine RFB have been investigated to the point that demonstration projects at scale have been undertaken.⁷ It could be on the verge of a renaissance, since in 2016 a neutral, ferrocyanide/polysulfide RFB was reported with a cell voltage of close to 1 V (0.91 V) and stated raw material cost of only one third of that for the all-vanadium RFB.⁴³ In that RFB the other redox couple, ferrocyanide, was notably operated in a neutral environment. This is in contrast to most recently reported organic, aqueous RFBs, where it is operated in strong alkaline solution, partnering with molecules such as anthraquinones and alloxazines.^{13,42,55} However, it has recently been (re)shown that (potassium)ferrocyanide is unstable at $\text{pH} > 12$ in the long term in RFBs, because it decomposes to (K)CN, while in neutral solution it was found to be stable.^{56,57} As appears to be the theme, ferrocyanide was already used in a neutral SRFB in 1983⁵³ and not in alkaline SRFBs, maybe due to its instability as shown by Luo et al.⁵⁶ In 2016, we re-investigated this metal-organic complex for use with AQDS(2,7) in an alkaline SRFB using hematite as the photoanode.⁵⁸ Here it appeared to be reasonably stable in alkaline solution during RFB battery cycling, though it decomposed to some extent under illumination.⁵⁸ We developed this system as Lin et al. published a similar RFB based on a hydroxylated quinone, dihydroxyanthraquinone(2,6) (DHAQ(2,6), cell potential 1.2 V compared to 0.74 V in our previous study).¹³ Afterwards, these redox couples, ferrocyanide and

DHAQ(2,6), were used in a two-photoelectrode SRFB as well.²² Notably, the long-term future of ferro/ferricyanide in SRFBs where it is illuminated (*i.e.* front-side illuminated SRFBs) is questionable, since it has been found to be inherently unstable under solar radiation in multiple reports.^{22,30,58,59} Recently, we attempted to use it in a neutral SRFB³⁰ on the illuminated side with quite detrimental consequences to the overall stability, and Cheng et al. were only able to suppress the reaction time scale to 12 hours as well.²²

Identification of stable organic redox molecules that are suitable for the high-potential side of both the RFB and SRFB is a major challenge and explains the choices of iodine, bromine, and vanadium in most studies, as seen from Figure 2 (redox potentials from about +0.5 to +1 V_{NHE}). To counteract this limitation, we made a study of an SRFB with TEMPO-SO₄⁻ a (redox potential +0.83 V_{NHE}) in an SRFB with ferricyanide as the counter redox couple (catholyte).³⁰ This type of radical redox molecule has been quite intensively investigated for neutral RFBs since 2015^{11,14,27,29,46}, and allowed us unprecedented redox reaction energy level and photovoltage matching. The stability of the SRFB was deteriorated mainly by the ferri/ferrocyanide light instability, and thus the overall performance of this system could be improved by keeping the ferri/ferrocyanide side in the dark and use a photoanode instead of a photocathode.³⁰ However, the work was intended to illustrate energy level matching rather than stability.

The overall conclusions from considering Figure 2 are that i) organic redox molecules that are investigated for RFBs soon turns up in SRFBs as well (such as AQDS(2,7), BQDS, DHAQ(2,6), Fe(CN)₆^{3-/4-}, and TEMPO-SO₄⁻), and ii) the combination of organic redox couples with halogens or metal-organic complexes will likely continue in future SRFBs. In 2017, a new family of metal-organic complexes, where the iron-complex ferrocene is modified with tetramethylammonium groups to increase water solubility, were explored for the high-potential

side of neutral RFBs and yielded promising results, especially concerning aqueous solubility and battery cycling stability.^{26,44} It is straightforward to believe that these modified ferrocene derivatives (such as BTMAP-Fc, see Chart 1) will be employed in SRFBs studies in the near future. These molecules can potentially be very interesting for SRFBs since they can replace the unstable ferrocyanide or the halogens for the high-potential side, which could lead to higher performing devices.

We have recently demonstrated a differential pH RFB, that exploits the strong pH dependence of most organic redox couples for increasing the cell potential.⁴⁵ This concept could also be used for SRFBs to tune the cell potential to fit the photoelectrodes. Operating each side of an SRFB at the pH that is most suitable for the specific redox couple *and* the photoelectrode could pave the way for both efficient and stable PEC storage cells. However, it remains a largely unexplored field of research and it is not clear whether pH differences can be sustained for long operating times, though we demonstrated differential pH stability over 200 cycles and 30 days.⁴⁵

It is clear from the history of this field that much research has already been conducted on organic, aqueous SRFBs, and the field is currently receiving renewed attention in parallel with the development of organic, aqueous RFBs. New research opportunities within SRFBs are emerging fast, however, there are still lessons to learn from older literature, making it worthwhile to revisit.

4) Energy level matching and the depth of solar charge

A specific focus point that we have anchored our work on is the matching of the energy levels between redox couples and photoelectrode.^{19,30,58} Successful solar charging depends on the relative energy levels of redox potential and band edges, and the Fermi level matching after the contact between the electrolyte and solid surface. Figure 3 shows a selection of redox couple

energy levels and semiconductor band edges, from which a number of metal-metal, metal-organic, or fully organic combinations can be identified. For instance, it can be recognized that solar irradiated c-Si could charge AQDS(2,7) and methyl viologen (MV^{2+}) without electrical bias. Considering the timeline and redox potentials found in Tables S1-S3 in the Supporting Information, it is evident that organic redox couples allows better energy level matching than with metal-based SRFBs. In particular, when considering that the redox potentials can be tuned by side-group functionalization and pH optimization of the supporting electrolyte.⁴⁶

As seen from Figure 3, if only vanadium-based or other metallic redox pairs (that generally perform poor in RFBs) are considered, the number of suitable photoelectrodes are limited. But when the wide selection of organic redox couples is included, a number of photoelectrodes comes into play, which is also reflected in the literature where there are far more aqueous SRFBs employing organic redox pairs than metallic. Nonetheless, the review by Sharon et al.¹⁶ gives an overview of the few 1980s SRFBs using the metals $Ce^{3+/4+}$ and $Fe^{2+/3+}$ and halogens, while we recently³⁰ compared reports on vanadium SRFB using CdS and TiO_2 photoelectrodes.^{19,60,61}

In literature on SRFBs, a thorough experimental/computational investigation of the energy levels of the redox electrolyte/semiconductor junction along with solar charging in the whole state-of-charge (SOC) range is rarely conducted.^{30,61} Here it is clear that in SRFBs with low SOC, high photocurrent and efficiency can be obtained, while these decreases significantly with increasing SOC. In some cases a full SOC cannot be reached because the available photovoltage is too low and these SRFBs are closer to *photo-assisted* cells. As shown in Figure 3, band gaps of most semiconductors studied for PEC applications falls within 1.1 eV to 2.4 eV and can only provide a photovoltage of roughly 0.5 ~ 1.1 V due to thermodynamic losses.⁶² In order to identify SRFBs that can be appreciably solar charged, it is necessary to evaluate both: i) the

energy level positions of redox potentials relative to valence and conduction band, and ii) the actual photo-potential delivered by the semiconductor/redox electrolyte junction(s). In the case of PEC devices with buried junctions (*e.g.*, p-n or p-i-n junctions), the photovoltage is determined by the built-in potential at the solid-state junction, and the energy level of the surface layer (not the bulk semiconductor) should be adequate for the selected redox couple. Theoretical cell potential for various redox couples and semiconductor band gap matching chart can be found in Figure S1 in the Supporting Information.

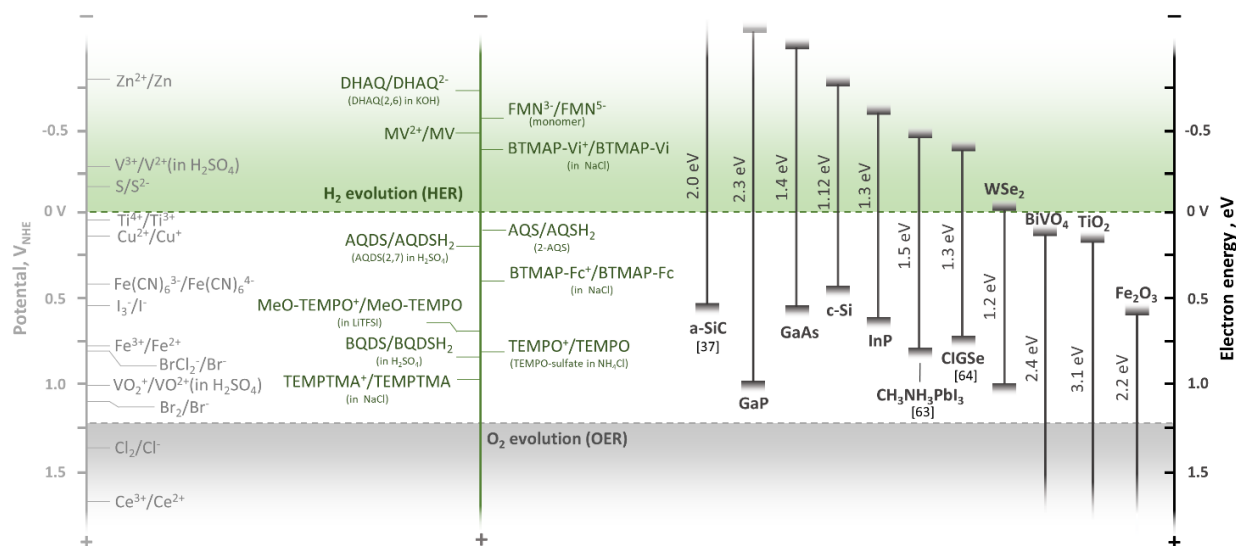


Figure 3. Redox potential of major inorganic (grey scale) and organic redox-active species (green scale) with band positions of photoelectrodes (vs. normal hydrogen electrode, at pH 0). Some potentials for redox potential and band edges vary with the pH, so the levels are indicative only. Potential range favorable for the hydrogen evolution (HER) and the oxygen evolution (OER) are colored with green and grey, respectively. Redox potential data and band edge positions were collected from the references of Figure 2 and previous studies [a]=63, [b]=64, [c]=37.

To illustrate these points further, Figure 4 shows the cell potential (E_{cell}^0), photocurrent and solar charging efficiency on an arbitrary scale as function of SOC. Here E_{cell}^0 has been calculated from the Nernst equation assuming 1:1 stoichiometric relationships between fully solubilized redox couples with unit activity and no protons involved in the redox reaction:^{30,65}

$$E_{cell} = E_{cell}^0 + \frac{RT}{F} \ln \frac{SOC^2}{(1-SOC)^2} \quad (1)$$

Where R is the gas constant, T the absolute temperature, and F is the Faraday constant. To calculate the current (i) the Butler-Volmer equation⁶⁶ is used with an overpotential equal to $U_p - E_{cell}$, where U_p is the available photovoltage assumed to be constant over the whole SOC range. The efficiency is defined as $i \cdot E_{cell}$ divided by the constant solar irradiation power. This is a crude model that neglects mass transport limitations, light absorption in the redox solution, internal ohmic resistance, and recombination mechanisms. Nonetheless, the model captures the charging features of a SRFB. The Nernst potential increases with SOC, whereby the overpotential available for charging the battery decreases, and this is reflected by a dramatic decrease in the Butler-Volmer current and efficiency (i_{BV}). The main point is that the conversion efficiency at high SOC is likely to be only fractions of the value at low SOC. At the same time, this indicates that one should select redox couples considering photovoltage margins of the PEC device to maximize the reachable SOC. Additionally, unfavorable redox couple selection and consequent low SOC lead to an increased reservoir volume to fulfil the required discharging capacity.

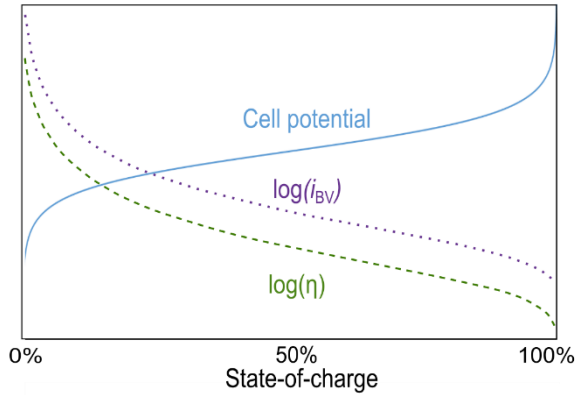


Figure 4. Generic illustration of the required potential to charge the full RFB cell in the absence of polarization losses as a function of the state-of-charge for a hypothetical RFB (blue full line, cell potential), the typical Butler-Volmer current behavior (purple dotted line) assuming constant available charging voltage from the photoelectrode, and the product of the current and potential interpreted as the conversion efficiency η .

5) Performance Review

There are multiple ways to evaluate the performance of an SRFB concerning efficiency, power, and energy density. Figure 5 and Figure 6 shows the most important performance indicators of a selection of SRFBs from the timeline in Figure 2. Figure 5 is dedicated specifically to the RFB properties of the system. It shows the engineering standard cell potential ($E_{cell}^{0'}$), which in the present case is defined as the cell potential at 50% state-of-charge where equal concentrations of the oxidized and reduced forms of the redox couples are present. Strictly, $E_{cell}^{0'} = E_{cell}^0$ only applies if the stoichiometric ratio in the reaction between the two redox pairs in the cell is one. Other ratios will lead to slightly modified dependences on SOC in Equation 1.

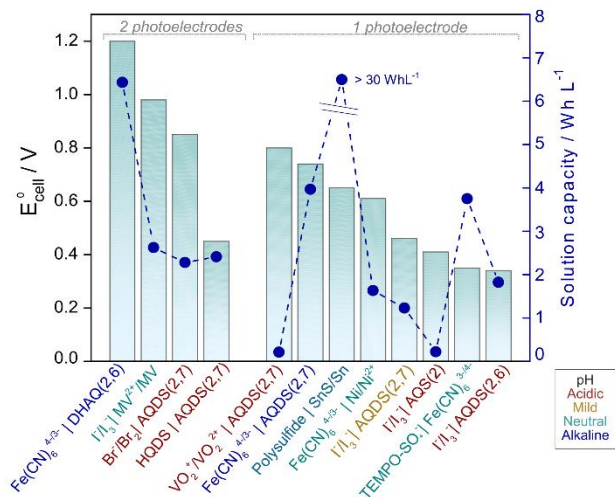


Figure 5. Performance evaluation concerning RFB properties: Rated cell potential for the redox electrolytes (green columns, left axis) and the theoretical limiting solution energy density (solution capacity, blue circles, right axis) calculated from the lowest redox couple concentration in the respective works. Data reproduced from³⁰ (recent works), and detailed in the Supporting Information (1980s works). References from the left:^{22,52,21,20,60,58,54,53,67,40,30,38}.

As seen from Figure 5 in connection with Figure S2 in the Supporting Information, it is clear that RFBs with $E_{cell}^{0'} > 0.8$ V can only be solar charged in dual-bed or tandem SRFBs, *i.e.* with two photoelectrodes. However, many of the SRFBs actually have $E_{cell}^{0'} < 0.8$ V and just one photoelectrode.

The standard all-vanadium flow battery, has $E_{cell}^{0'} = 1.3$ V and 1.6 M vanadium concentration that leads to a theoretical capacity of 28 WhL^{-1} . Most of the SRFBs have redox couple concentrations that limit the capacity to below one-tenth of this, a notable exception being the CdSe/polysulfide/SnS cell, where the energy density is just above 30 WhL^{-1} .⁵⁴ The low redox couples concentrations are in most cases not a consequence of low solubility of the redox couples, but is related to reduction of parasitic light absorption in the redox couples in the case of front-light illumination.^{21,30} On the other hand, the low cell potential is chosen for a better energy

level match between photoelectrode and redox couples. As discussed above, there is no obvious best strategy for optimizing the pH in organic RFBs or SRFBs, though acidic solutions are dominating in Figure 5 and Figure 6. This is most likely because most studied RFBs are acidic, while only a few are neutral or alkaline.

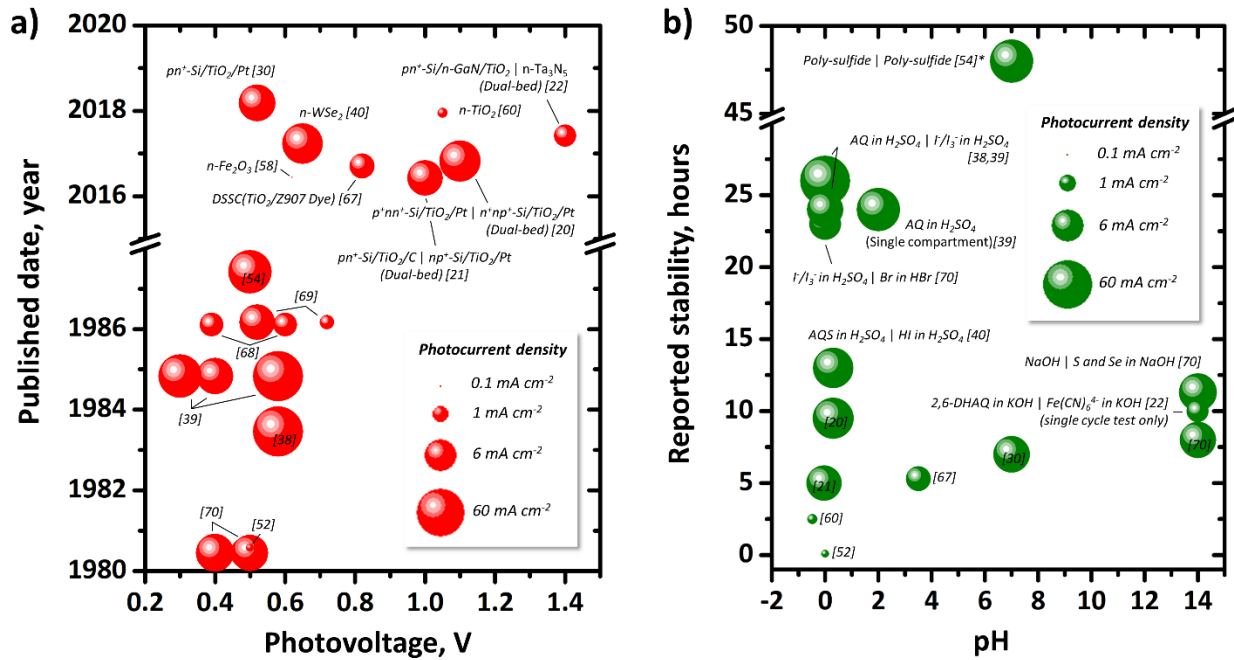


Figure 6: Performance evaluation concerning PEC properties of the SRFBs from the timeline in Figure 2 and selected works from Table S2 in the Supporting Information. a) The photovoltage and photocurrent density with publication year, and b) the reported stability of the operating SRFB and photocurrent density versus the pH. References [a] = 30, [b] = 60, [c] = 22, [d] = 40, [e] = 20, [f] = 67, [g] = 58, [h] = 21, [i] = 54 (no exact pH information, but NaOH and CsHS with same concentration), [j] = 68, [k] = 69, [l] = 39, [m] = 38, [n] = 52, [o] = 70.

From the photocurrents in Figure 6 and the corresponding solar conversion efficiencies (reported elsewhere³⁰ and in Figure S2 in the Supporting Information) it is clear that high solar conversion efficiency (5-12 %) comes from either having a low-potential redox couple combination (≤ 0.7

V) or from charging with two photoelectrodes. Interestingly, there has recently been many reports in which researchers have used dual-bed type PEC setups in order to provide sufficient photovoltage to drive chemical reactions with high redox potential gap. However, the data in Figure 5, Figure 6, and Figure S2 does not lead to the conclusion that two-photoelectrode system have superior performance, since the highest efficiency, solution capacity, and attainable state-of-charge is found in various one-photoelectrode systems. As shown in Figure 6a, the photocurrents from the dual-bed devices do not in general show a higher photocurrent, and in some cases even smaller than that of single device system (i.e., no benefit in overall conversion efficiency). The low conversion efficiency can potentially be overcome by using a tandem device approach as illustrated in Figure 1d. Unlike the dual-bed approach, the tandem configuration using semiconductors with two different band-gaps can provide sufficient photovoltage for driving a high-potential reaction with maximized light utilization as demonstrated with PEC solar water splitting.^{35,71}

Notably, in the vast majority of the SRFBs investigated, including dual-bed cells, the RFB is not appreciably charged, and the achieved state-of-charge is in most cases around or below 10% (see the Supporting Information Figure S2).³⁰ Only for few systems is it appreciably higher, e.g., the WSe₂ iodine/AQDS(2,6) cell³⁸, the dual-bed Si AQDS/BQDS cell²⁰, and our p-Si TEMPO-SO₄⁻/ferricyanide cell.³⁰ That means that the already low volumetric capacities (compared to state-of-the-art RFBs) observed in Figure 5 could be calculated to be correspondingly lower as well. This is challenging in terms of application as energy storage devices. In our recent study, we demonstrated SOC over 90% using a single p-Si photocathode with a photovoltage of 0.52 V for charging Fe(CN)₆^{3-/4-}/TEMPO^{0/+} (0.35 V) redox couples.³⁰ It is clear that silicon remains promising for SRFB applications, mainly in a dual-bed configuration since, in theory, two such

electrodes delivering each around 500 mV of photovoltage would be able to be integrated with a set of well-matched redox electrolytes with a rated cell potential of 0.7 V, for complete solar charge. A 0.9 V RFB (rated cell potential) could be solar charged up to 87% with a similar set of silicon photoelectrodes according to Equation (1).

Lastly, Figure 6b indicates the reported photoelectrode stability in terms of operational pH. The longest stability has been observed for n-Cd(Se,Te) photoelectrodes in neutral solution.⁵⁴

Interestingly, most studies have been performed with acidic and alkaline solutions, presumably due to lower ohmic losses in the electrolyte, but in terms of stability, there is no clear trend with the pH. In fact, a relatively limited semiconductor material selection has taken place so far. Here the general choices are i) silicon or chalcogenide photoelectrodes which are already well proven photovoltaic materials, and ii) the photoanode/anolyte configuration. This is somewhat surprising, given the variety of materials studied in the PEC water splitting field. Here, there is a wide material selection, however, the strong position of conventional PV materials (*e.g.*, Si) as a major choice remains unchanged. Unlike most stability reports in SRFB (Figure 6b), silicon-based photoelectrodes has shown outstanding stability both in acid and alkaline solutions.^{72,73}

Additionally, various thin film semiconductors have been used for long-term operation at various pH conditions after coupling with protection or passivation layer.³⁶ It is likely that in the future silicon-based photoelectrodes will be studied further, due to their low cost and high efficiency, while having many existing methods and procedures for adding protection layers against corrosion of the Si-electrode.³⁶ Since the stability of the photoelectrode could be a limiting factor of durability of the SRFB, corrosion studies and compatibility of the photoelectrode with chosen electrolytes should be studied even further.

It is clear that development of SRFBs requires excellent properties of, and match between, both the photoelectrodes and the redox couples. Silicon-based photoelectrodes are a good example, as they have in many ways been optimized to come close to their intrinsic performance limits, with photocurrents close to their theoretical limit and stability on the order of months^{18,17}. This puts emphasis on the importance of identifying redox couples that can work with these photoelectrodes to take full advantage of their photoelectrochemical properties. Considering Figure 3, this largely excludes conventional redox couple choices such as vanadium, iron and bromine, leaving the choice up to mainly the organic molecules and metal-organic complexes. Consequently, one strategy for future SRFBs will be to employ organic redox couples that emerges from the RFB field, or even use tailored organic molecules to the SRFB application concerning properties such as redox potential, pH stability, light absorption, and solubility.

6) Conclusion and outlook for the field

Numerous aqueous SRFBs and PEC rechargeable cells have been studied, some of the earliest date back to 1976, followed by many studies in the 1980s and then again within the recent years. From the beginning, studies have utilized organic redox pairs for the energy storage component, this approach has later been adopted by RFB research . In addition to the low-cost potential of organic-based redox couples they offer flexibility with respect to redox potential/pH and solubility in a wide pH range. Solar conversions efficiencies up to 10% have been demonstrated, however, there are several mutually linked parameters to optimize, and the demonstrated performance of SRFBs has not yet been consolidated. Breakthrough discoveries that show both high solar conversions efficiency, energy density, and high depth of solar charge remains elusive.

To aid the development, we suggest here a range of different research tasks that can be undertaken to propel the SRFB development into the future.

- Techno-economic modeling resembling what has already been done for RFBs to outline performance targets in terms of raw materials costs (semiconductors, redox couples, membrane, supporting electrolyte), cell resistance, cell potential, and energy density.⁶
- Further exploration of opto-electronic properties to combat both redox couple light-sensitivity and strong light absorption, thereby allowing for higher concentrations. For instance, back-illumination photoelectrode and cell design by using bifacial photoelectrodes.^{17,18}
- Theoretical work on the efficiency limits of these kinds of photoelectrochemical devices including imperfect light absorption, charge transport limitations (resistance), and Butler-Volmer kinetics of the redox reactions as done for PEC water splitting cells.⁷⁴
- Development of optimized SRFB flow cells and upscaled demonstrations with semiconductor areas above 10 cm².
- Standardized cell evaluations procedure that involves i) experimental or computational energy level evaluation, ii) stability evaluation by running multiple solar charging cycles with fresh electrolytes and the same photoelectrode(s) and vice versa, and iii) demonstrated ability to reach a high state-of-charge by solar radiation compared to discharge capacity.

ASSOCIATED CONTENT

Supporting Information.

PDF document containing Tables S1-S3 and Figures S1 and S2.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

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ABBREVIATIONS

RFB redox flow battery; SRFB solar redox flow battery, PEC photoelectrochemical, EU European Union

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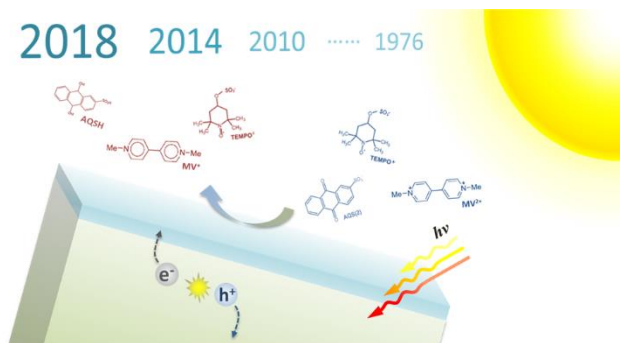
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<p>Wilson A. Smith</p>	<p>Wilson A. Smith is an Associate Professor in the Department of Chemical Engineering at TU Delft. He earned his B.Sc. in Physics from American University in 2005, and his Ph.D. in Physics from the University of Georgia in 2010, where he studied nanostructured photocatalysts. From there he moved to Paris, France, as a Postdoc at the Universite Pierre et Marie Curie/Sorbonne, where he studied the defect structure of doped semiconductors for solar water purification. In 2012 he began his current position at TU Delft. His group focus on fundamental processes related to PEC water splitting, electrocatalysis for water oxidation and CO₂ reduction processes.</p>	

Adélio Mendes	<p>Prof. Adélio Mendes received his PhD in Chemical Engineering from the University of Porto in 1993. He is currently full professor at the Chemical Engineering Department of the same university. Coordinates a large research team with interests in dye sensitized and perovskite solar cells, photoelectrochemical cells including water splitting, solar redox flow cells, CO₂ electro- and photoelectroreduction, redox flow batteries, fuel cells, methanol steam reforming, membrane and adsorbent-based gas separations processes. Prof. Mendes authored ca. 330 articles, filled 23 families of patents and he is the author of a textbook.</p>	
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