4.2 Photoelectrochemical Solar Energy Storage Cells

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4.2.1 Introduction

Although society’s electrical needs are largely continuous, clouds and darkness dictate that photovoltaic solar cells have an intermittent output. A photoelectrochemical solar cell (PEC) can generate not only electrical but also electrochemical energy and provide the basis for a system with an energy-storage component (PECS). Sufficiently energetic isolation incident on semiconductors can drive electrochemical oxidation/reduction and generate chemical, electrical, or electrochemical energy. Aspects include efficient dye-sensitized or direct solar to electrical energy conversion, phototetching, photoelectrochemical water-splitting, environmental cleanup, and solar energy storage cells. This chapter focuses on photoenergy storage concepts based on photoelectrochemical processes, but includes a necessary comparison to other methods proposed for the conversion and storage of solar energy. The PEC uses light to carry out a chemical reaction, converting light to chemical energy. This fundamental difference of the photovoltaic solar cell’s (PV) solid–solid interface, and the PEC’s solid–liquid interface has several ramifications in cell function and application. Energetic constraints imposed by single band gap semiconductors have limited the demonstrated values of photoelectrochemical solar to electrical energy conversion efficiency to 16%, and multiple band gap cells can lead to significantly higher conversion efficiencies [1, 2a,b].

Photoelectrochemical systems may facilitate not only solar to electrical energy conversion but has also led to investigations in photoelectrochemical synthesis, photoelectrochemical production of fuels, and photoelectrochemical detoxification of pollutants as discussed in other chapters in this volume.

4.2.1.1 Regenerative Photoelectrochemical Conversion

In illuminated semiconductor systems, the absorption of photons generates excited electronic states. These excited states have lifetimes of limited duration. Without a mechanism of charge separation their intrinsic energy would be lost through relaxation (recombination). Several distinct mechanisms of charge separation have been considered in designing efficient photoelectrochemical systems. At illuminated semiconductor–liquid interfaces, an electric field (the space charge layer) occurs concurrent with charge–ion redistribution at the interface. On photogeneration of electron-hole pairs, this electric field impedes recombinative processes by oppositely accelerating and separating these charges, resulting in minority carrier injection into the electrolytic redox couple.

This concept of carrier generation is illustrated in Fig. 1(a) (for an n-type PEC) and has been the theoretical basis for several efficient semiconductor-redox couple PEC cells. Illumination of the electrode surface with light, whose photon energy is greater than the band gap, promotes electrons into the conduction band leaving holes in the valance band. In the case of a photoanode, band-bending in the depletion region drives any electron that is promoted into the conduction band into the interior of the semiconductor and holes...
Excitation can also occur in molecules directly adsorbed and acting as a mediator at the semiconductor interface. In this dye sensitization mode, the function of light absorption is separated from charge carrier transport. Photoexcitation occurs at the dye and photogenerated charge is then injected into a wide band gap semiconductor. This alternative carrier generation mode can also lead to effective charge separation as illustrated in Fig. 1(b). The first high solar to electric conversion efficiency example of such a device was demonstrated in 1991 [3] through the use of a novel high surface area (nanostructured thin film) n-TiO₂, coated with a well-matched trimeric ruthenium complex dye immersed in an aqueous polyiodide electrolyte. The unusually high surface area of the transparent semiconductor coupled to the well-matched spectral characteristics of the dye leads to a device that harvests a high proportion of insolation.

4.2.1.2 Photoelectrochemical Storage

PECs can generate not only electrical but also electrochemical energy. Figure 2 presents one configuration of a PEC combining in situ electrochemical storage and solar-conversion capabilities; providing continuous output insensitive to daily variations in illumination. A high solar to
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Fig. 2 Schematic of a photoelectrochemical solar cell combining both solar conversion and storage capabilities. (a) Under illumination; (b) in the dark.

4.2.2 Comparative Solar-Storage Processes

4.2.2.1 Thermal Conversion and Storage
Solar insolation can be used to directly activate a variety of thermal processes; the enthalpy is stored physically or chemically and then either directly utilized or released upon reversal of the storage process. To date, the predominant nonbiologic utilization of solar energy is to heat a working fluid that is maintained in an insulated enclosure, storing a portion of the incident solar radiation for future use. Limitations of this approach include the low energy available per unit mass of the storage medium and low efficiencies of thermal to mechanical and thermal to electrical energy conversion. A variety of passive and dynamic optical concentrators have been studied to compensate for these limitations.

The high temperatures generated by concentrated solar power have been utilized to drive highly endothermic reactions. The reverse reaction releases the chemically stored energy as thermal energy. Various systems have been investigated such as in 1985 [5]:

\[
\text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2 \quad \Delta H = 98.94 \text{ kJ/mol}
\] (1)
4.2.2.2 Photochemical Storage

In photochemical processes, photon absorption creates a molecular excited state or stimulates an interband electronic transition in a semiconductor that induces a molecular change. Comprehensive reviews, including those by Gratzel [6], Kalyanasundaram [7], and Harriman [8], have discussed various aspects of photochemical energy conversion. A photoactivated molecular excited state can drive either (1) photodissociation (2) photoisomerisation or (3) photoredox reactions. Processes based on semiconductors may involve photovoltaic or photoelectrochemical systems.

A substantial photochemical effort research has centered on the photoredox storage of solar energy. Molecular photoredox processes use electron transfer from photoinduced excited states:

\[ A + \text{hv} \rightarrow A^* \]  
\[ \text{A}^* \rightarrow \text{A}^+ + e^- \]  

The electron transfer may be either direct or a variety of indirect processes as exemplified by either

\[ \text{A}^* \rightarrow \text{B}; \]  

followed by

\[ \text{B} \rightarrow \text{B}^+ + e^- \]  

or

\[ \text{A}^* + \text{B} \rightarrow \text{AB}; \]  

followed by

\[ \text{AB} \rightarrow \text{AB}^+ + e^- \]

Solar-activated photodissociation processes generally involve cleavage of a simple molecule into several energetic products. Limitations of this approach include the limited absorption of solar energy by the molecule, low quantum yield, rapid back reaction, and difficulties separating the product species. An example of storage by such photodissociation processes is exemplified by

\[ 2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2 \]  

In photoisomerization, an absorbed photon activates molecular rearrangement and conversion of organic molecules into strained isomers. The products are stored. Despite attractive features including a high heat storage capacity and good thermal stability, most systems tested have poor efficiencies. These systems necessitate transformation to strained conformations at high energies; energies consistent with wavelengths below 450 nm. This excludes much of the energy inherent in the AM1 solar spectra. The stored thermal energy is released on catalytic-induced reversion to the starting components. An example has been presented by Kutal for the photocatalytic transformation of norbornadiene to quadricyclane [9].

Photochemical redox reactions can generate fuel formation, including H2, CH3, and CH3OH. Because of its availability, the splitting of water to produce H2 has been the focus of particular attention. H2O is transparent to visible radiation, and therefore sensitization is required to drive the water-splitting process. In early attempts on photoredox-splitting of water by Heidt and McMillian, the process was sensitized by using solution redox species such as Ce3+/4+ [10].

\[ \text{Ce}^{4+}(aq) + \text{H}^+ \rightarrow \text{Ce}^{3+}(aq) + \frac{1}{2}\text{H}_2 \]  

\[ 2\text{Ce}^{4+}(aq) + \text{H}_2\text{O} \rightarrow 2\text{Ce}^{3+}(aq) + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \]  

These processes have displayed poor quantum yields. As in photoisomerization
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Sch. 1

processes, these reactions are also generally driven only by high-energy radiation (short wavelength) and cannot efficiently convert incident AM1 solar radiation.

H₂ or O₂ generation from water is a multielectron process. Optimization of photoredox-splitting of water necessitates the presence of a catalyst to mediate this complex multielectron transfer. In one such process, a sacrificial reagent triethanolamine (TEOA) is consumed irreversibly in the process, as denoted in Sch. 1 [9]:

Direct multielectron processes are rare and instead incorporate one or more radical intermediate steps. These reactive intermediates are susceptible to unfavorable side reactions, resulting in substantial losses in the energy-conversion process. Kinetically favored back reactions further reduce the overall conversion efficiency.

The engineering of these complex molecular organizations provides a substantial scientific challenge and have generally resulted in systems with low conversion efficiencies.

4.2.2.3 Semiconductor Photoredox Storage

Semiconductor surfaces have been used as sensitizers to drive photochemical conversion and storage of solar energy. In principle, this should lead to a higher level of photon absorption and more effective charge separation. Both effects can substantially increase solar photochemical-conversion efficiency, but these systems have not yet displayed high efficiencies of fuel generation or long-term stabilities.

Photoredox processes at semiconductor electrodes generating fuels or products other than hydrogen, including methanol and ammonia, have been attempted with low overall yields. The photoelectrolysis of HI into H₂ and I⁻ at p-InP electrodes has been described [11]. These H₂ and I⁻ photogenerated products are prime candidates for a fuel cell. Analogous advanced systems, in which the photoelectrochemically generated fuels have been successfully recombined to generate electrical energy, are discussed later in this section.

A system exemplifying photoelectrochemical synthesis to generate hydrogen is water photoelectrolysis. An early demonstration of water photoelectrolysis used TiO₂ (band gap 3.0 eV) and was capable of photoelectrolysis at ~0.1% solar to chemical energy—conversion efficiency [12]. The semiconductor SrTiO₃ was demonstrated to successfully split water in a direct photon-driven process by Bolts and Wrighton (1976), albeit at low solar energy—conversion efficiencies [13].
The high SrTiO$_3$ band gap, $E_g$, of 3.2 eV creates sufficient energetic charge to drive the photoredox process. This excludes the longer wavelength photons and corresponds to only a small fraction of incident solar radiation. To improve the solar response, $E_g$ has to be lowered; in a single band gap system, an optimum efficiency can be expected around 1.4 eV.

In photoelectrochemical water-splitting systems, corrosion of the semiconductor photoelectrodes can pose a significant problem. Most surface-stabilizing redox reactions compete with oxygen and hydrogen generation and must be excluded from these systems. To enhance the solar response of high band gap materials, techniques such as dye sensitization and impurity sensitization have been attempted, although with little improvement [14]. Semiconductor surfaces have been modified to protect low band gap materials against photocorrosion [15, 16]. A self-driven photoelectrochemical cell consisting of Pt-coated p-InP and Mn-oxide-coated n-GaAs has been demonstrated to operate at 8.2% maximum efficiency to generate H$_2$ and O$_2$ under simulated sunlight [17], and more recently a two band gap cell in a tandem arrangement has been used to split water at 12% efficiency [18]. A multijunction GaAs, Si cell has been recently used to drive water-splitting at over 18% solar to electrical-conversion efficiency [19].

Colloids and suspensions of semiconductors have been used for the photoredox-spliitting of water. The principle advantage of a fine suspension is the large active surface area available. Reaction rates of H$_2$ and O$_2$ generation have been enhanced by loading the particles with small deposit of precious metals, and although significant progress was made in this direction, a practical system is yet to be demonstrated [11].

### 4.2.3 Modes of Photoelectrochemical Storage

Conversion of a regenerative PEC to a photoelectrochemical storage solar cell (PESC) can incorporate several increasingly sophisticated solar energy conversion and storage configurations.

#### 4.2.3.1 Two-Electrode Configurations

A variety of two-electrode configurations have been investigated as PESC systems. Important variations of these photoelectrochemical conversion and storage configurations are summarized in Table 1. In each case, and as summarized in Fig. 3 for the simplest configurations, exposure to light drives separate redox couples and a current through the external load. There is a net chemical change in the system, with an overall increase in free energy. In the absence of illumination, the generated chemical change drives a spontaneous discharge reaction. The electrochemical discharge induces a reverse current. In each case in Table 1, exposure to light drives separate redox couples and current through the external load.

Consistent with Fig. 1, in a regenerative PEC, illumination drives work through an external load without inducing a net change in the chemical composition of the system. This compares with the two-electrode PECS configurations shown in Fig. 3(a) and (b). Unlike a regenerative system, there is a net chemical change in the system, with an overall increase in free energy. In the absence of illumination, the generated chemical change drives a spontaneous discharge reaction. The electrochemical discharge induces a reverse current. Utilizing two quasi-reversible chemical processes, changes taking place in the system during illumination can be reversed in the dark. Similar to
Tab. 1 Important two-electrode photoelectrochemical conversion and storage configurations

<table>
<thead>
<tr>
<th>SCHEME</th>
<th>Electrode 1</th>
<th>Electrolyte(s)</th>
<th>Electrode 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>SPE</td>
<td></td>
<td>Redox A Redox B</td>
</tr>
<tr>
<td>II</td>
<td>SPE</td>
<td></td>
<td>Redox A-membrane-Redox B</td>
</tr>
<tr>
<td>III</td>
<td>SPE</td>
<td></td>
<td>Redox A</td>
</tr>
<tr>
<td>IV</td>
<td>SPE-Redox A&lt;sub&gt;SPE&lt;/sub&gt;</td>
<td></td>
<td>Redox B</td>
</tr>
<tr>
<td>V</td>
<td>SPE</td>
<td></td>
<td>Redox A-membrane-Redox B</td>
</tr>
</tbody>
</table>

Note: Components of these systems include a semiconductor photoelectrode (SPE) and a counter electrode (CE). At the electrode–electrolyte interface, redox couples “A” or “B” are either in solution (| Redox |), counter electrode–confined (| Redox BCE-CE |) or confined to the semiconductor photoelectrode (SPE-Redox A<sub>SPE</sub>).

Fig. 3 Schematic diagram of a two-electrode storage cell. The storage electrode (a) an insoluble redox couple, (b) soluble redox couple.

R + O' \xrightarrow{hv} O + R'
cannot efficiently fulfill the duel role of being kinetically sluggish to reduction during illumination and yet being kinetically facile to the same reduction during dark discharge. The configuration represented in Fig. 3 has another disadvantage, the disparity between the small surface area needed to minimize photocurrent dark current losses and the large surface area necessary to minimize storage polarization losses to maximize storage capacity [20].

4.2.3.2 Three-Electrode Configurations
Several of the two-electrode configuration disadvantages can be overcome by considering a three-electrode storage cell configuration as shown in Fig. 4. In Fig. 4, the switches E and F are generally alternated during charge and discharge. During the charging, only switch E may be closed, facilitating the storage process, and during discharge, E is kept open while F is closed. In this case, chemical changes that took place during the storage phase are reversed, and a current flow is maintained from the storage electrode to a third (counter) electrode that is kept in the first compartment. To minimize polarization losses during the discharge, this third electrode should be kinetically fast to the redox couple used in the first compartment. Still an improved situation would be to

![Diagram](image-url)

Fig. 4 Schematic diagram for a storage system with a third electrode (counter electrode) in the photoelectrode compartment. P = Photoelectrode, A = Counter electrode, M = Membrane, S = Storage electrode, EL = Electrolyte, E, F = Electrical switch, and L = Load.
have both switches closed all the time. In this case, electric current flows from the photoelectrode to both counter and storage electrodes. The system is energetically tuned such that when insolation is available, a significant fraction of the converted energy flows to the storage electrode. In the dark or diminished insolation, the storage electrode begins to discharge, driving continued current through the load. In this system, a proper balance should be maintained between the potential of the solar energy-conversion process and the electrochemical potential of the storage process. There may be residual electric flow through the photoelectrode during dark cell discharge, as the photoelectrode is sluggish, but not entirely passive, to a reduction process. This can be corrected by inserting a diode between the photoelectrode and the outer circuit.

4.2.4 Optimization of Photoelectrochemical Storage

The power obtained is the product of voltage and current, and consideration of the photocurrent is as important as the photovoltage. If the band-bending is sufficiently large, then the minority carrier redox reaction, which is essential to maintain the photocurrent, can compete effectively with the recombination of photogenerated electron hole pairs. This recombination represents a loss of absorbed photo energy. Therefore, an objective is to maintain a high band-bending and at the same time a significant photovoltage. A photoanode creates a negative photovoltage under illumination, which results in reducing the band-bending. In principal, one way to accomplish high band-bending is to choose a very positive redox couple in the electrolyte. The converse is true for a photoanode. Improvements relating to its stability and conversion efficiency are of paramount importance.

4.2.4.1 Improvements of the Photoresponse of a Photoelectrode

To improve the solar response of a photoelectrode, a proper match between the solar spectrum and the band gap of the semiconductor should be maintained. When a single band gap semiconductor is used, a band gap in the vicinity of 1.4 eV is most desirable from the standpoint of optimum solar-conversion efficiency. An important criterion is that the minority carrier that is driven toward the semiconductor–electrolyte interface should not participate in a photocorrosion reaction that is detrimental to the long-term stability of the photoelectrode. Photocorrosion can be viewed in terms of either kinetic or thermodynamic considerations and the real cause may be a mixture of both. From thermodynamic perspective, a photoanode is susceptible to corrosion if the fermi level for holes is at a positive potential with respect to the semiconductor corrosion potential [21]. The corrosion can be prevented or at least inhibited by choosing a redox couple that has its $E_{\text{redox}}$ more negative than that for the corrosion process [22, 23]. The kinetic approach has been to allow another desired redox process to occur at a much faster rate than the photocorrosion reaction [13]. Other attempts to minimize the photocorrosion has been to coat the photoelectrode surface with layers such as Se [24] and protective conductive polymer films [25], and to search for alternate low band gap semiconductors [26]. Extensive reviews on the performance and stability of cadmium chalcogenides include those by Cahen and coworkers, 1980 [27] and Hodes, 1983 [28]. Etching of photoelectrode surface has been recognized and...
widely used as an important treatment to achieve high-conversion efficiency [29]. This effect is mostly attributed to removal of surface states that may act as trapping centers for photogenerated carriers. A related procedure called photoetching, initially developed for CdS and then applied to a wide variety of semiconductors, improves the photoelectrode performance and preferentially removes the surface defects acting as recombination centers [30].

In addition to the variety of etching procedures, several other surface treatments have been used to improve photoelectrode performance. Examples include a Ga ion dip on CdSe [31], ZnCl₂ dip on thin film CdSe [32], Ru on GaAs [33], Ru on InP [34], and Cu on CdSe [34]. Reasons explaining the effectiveness of these dips range from a decrease of dark current to electrocatalysis by surface-deposited metal atoms. Solution phase chemistry of the electrolyte is an important parameter that has been shown to dramatically influence photoeffects. The equilibrium position of the redox couple will affect equilibrium band-bending. A photoanodic system with a solution containing a more positive potential redox couple causes a greater band-bending, which in turn leads to a higher photovoltage and efficient carrier separation under normal experimental conditions.

4.2.4.2 Effect of the Electrolyte

Semiconductor photoeffects in a complex redox electrolyte are largely affected by the solution properties such as solution redox level, interfacial kinetics (adsorption), conductivity, viscosity, overall ionic activity, solution stability, and transparency within a crucial wavelength region. Redox electrolytes are known to inhibit unfavorable phenomena such as surface recombination and trapping [35]. In addition, solution redox couple may develop a favorable influence on the PEC system by improved charge-transfer kinetics leading to improved stability of the photoelectrode [36]. Additives incorporated in redox electrolytes are known to enhance the performance of PEC systems. Addition of small concentrations of Se in polysulfide electrolyte is known to improve the stability of CdSe (single crystal)/polysulfide system [22]. In this case, Se improves the PEC performance by reducing S/Se exchange and by increasing the dissolution of the photooxidized product S, which is the rate-determining step in the oxidation of sulfide at the anode. Addition of Cu²⁺ into the I⁻/I₃⁻ electrolyte is known to improve the stability of CuInX₂ photoelectrode considerably [37], and in the same electrolyte, tungsten and molybdenum dichalcogenide photoelectrochemistry can be substantially improved by addition of Ag⁺, or other metal cations, and shift of the I⁻/I₃⁻ E_{redox} [38].

In the case of CdSe/polysulfide system, solution activity, conductivity, efficiency of the photoanode (fill factor), charge-transfer kinetics at the interface, and the stability of the photoelectrode are known to exhibit improvements in the trend Li > Na > K > Cs > for alkali polysulfide electrolyte. This trend is explained in terms of the secondary cation effect on electrochemical anion oxidation in concentrated aqueous polysulfide electrolytes [39]. In the case of Cd(Se,Te)/polysulfide system, the efficiency of light energy conversion is improved by using a polysulfide electrolyte without added hydroxide because of the combined effect of increasing the solution transparency, relative increase of S₄²⁻, and decrease in S₃²⁻ in solution. For the same photoelectrode–electrolyte system, an optimum photoeffect was observed for a solution containing a sulfur–sulfide ratio of 1.5 : 2.1 with 1 : 2 molar
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potassium sulfide concentrations because of the combined effect of optimized solution viscosity, transparency, activity, and shift in solution redox level [40]. Stability of the polysulfide redox electrolyte, which is another parameter that determines the long-term performance of a PEC cell, has been shown to increase with sulfur and alkali metal sulfide concentration and to decrease with either increasing –OH concentration or at high ratio of added sulfur to alkali metal sulfide [39, 41]. The combined polysulfide electrolyte optimization can substantially enhance cadmium chalcogenide photoelectrochemical conversion.

Chemical composition of the electrolyte is a particularly important parameter in PEC systems based on complex electrolytes, such as polysulfide or ferro/ferricyanide. In the latter redox couple, replacement of a single hexacyano ligand strongly changes the photoelectrochemical response of illuminated n-CdSe [42], and addition of the KCN to the electrolyte can increase n-CdSe and n-CdTe photovoltage by 200 mV [43].

4.2.4.3 Effect of the Counter Electrode

In a photoanodic system, even at moderate current densities, the occurrence of sluggish counter electrode kinetics for the cathodic process will cause significant polarization losses and diminish the photovoltage. Minimization of these kinetic limitations necessitates a counter electrode with good catalytic properties. For example, as shown by [34], CoS on stainless steel or brass electrodes exhibits electrocatalytic properties toward polysulfide reduction and overpotentials as low as 1 mV cm² mA⁻¹ has been realized. Composition of a particular redox electrolyte may have a bearing on the extent of counter electrode polarization [32, 39].

In PEC systems, a compromise is maintained to simultaneously optimize the photoelectrode efficiency, stability, and electrolytic properties of the electrolyte. Practical PEC systems often require large working and counter electrodes and their geometric configuration within the PEC system will effect mass transport and effective cell current. In some cases, advantageous use has been made of selective sluggish counter electrode kinetics toward certain cathodic processes. For example, carbon is a poor cathode for H₂ evolution compared to Pt, and the direct hydrogenation of anthraquinone at a PEC cathode has been avoided by using a carbon anode [44]. In this case, such hydrogenation represents an undesirable side reaction.

4.2.4.4 Combined Optimization of Storage and Photoconversion

An efficient photoelectrochemical conversion and storage system requires not only an efficient functional performance of the separate cell components but also a system compatibility. In the combined photoelectrochemical storage system, simultaneous parameters to be optimized include

1. minimization of light losses reaching the photoelectrode,
2. high photoelectrode–conversion efficiency of solar energy,
3. close potential match between the photopotential and the required storage-charging potential,
4. high current and potential efficiency of the redox storage process,
5. high energy capacity of the redox storage,
6. reversibility (large number of charge–discharge cycles of the redox storage),
7. stability of the photoelectrode,
8. stability of the electrolyte,
9. stability of the counter electrode,
A photoelectrochemical solar cell implicitly contains an electrolytic medium. In the majority of laboratory PEC configurations, incident light travels through the electrolytic medium before illuminating the photoelectrode. The resultant light absorbance by the electrolyte is a significant loss, which is avoided by use of a back cell configuration. For example, the substantial absorptivity of dissolved polyselenide species has been avoided in a n-GaAs photoelectrochemistry through the use of the back wall cell configuration presented in Fig. 5 [45].

The photoelectrochemical system shown in Fig. 4 is a combination of a photoelectrode, electrolyte, membrane, storage, and a counter electrode. As an example of challenges that may arise in the combined photoconversion and storage system, consider an n–CdSe/polysulfide/tin sulfide version of Fig. 4 and consisting of Cell 1.

**Cell:** 1. CdSe | HS\(^{-}\), OH\(^{-}\), S\(_x\)\(^{2-}\) | Membrane | HS\(^{-}\), OH\(^{-}\) | SnS | Sn

With illumination, the cell exhibits simultaneous photoelectrode, counter electrode and storage reactions, and equilibria including

- **Photoanode:**
  \[
  \text{HS}^{-} + \text{OH}^{-} \rightarrow S + 2\text{e}^{-} + \text{H}_2\text{O} 
  \]
  (9)

- **Photocompartment equilibria:**
  \[
  S + S_x^{2-} \rightarrow S(x + 1)^{2-} \quad (10)
  \]

- **Counter electrode:**
  \[
  S + 2\text{e}^{-} \rightarrow \text{HS}^{-} + \text{OH}^{-} \quad (11)
  \]

**Fig. 5** A back wall n-GaAs/aqueous polyselenide photoelectrochemical cell.
Storage electrode:

\[
\text{SnS} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Sn} + \text{HS}^- + \text{OH}^- \quad (12)
\]

Unlike the case of the analogous regenerative PEC system, in the preceding equations, sulfur formed at the photoanode (and dissolved as polysulfide species, \(\text{S}_{(x+1)}^{2-}\) for \(x = 1\) to 4) is not balanced by the reduction that is taking place at the counter electrode because of the simultaneous reduction process taking place at the storage electrode. As a result, sulfur is accumulated in the photoelectrode compartment and is removed only in the subsequent discharge process. This dynamic variation in electrolyte composition may have a profound influence on the stability of the photoelectrode and electrolyte and on cell potential. Hence, to minimize these effects, either excess polysulfide must be included in the photocompartment or a limit must be set to the maximum depth of cell charge and discharge.

Another important consideration is the energy compatibility between the photoconversion and the storage processes. This compatibility is referred to as the voltage optimization. Figure 6 presents the combined IV characteristics for an ideal photoelectrode and current–voltage curves for two potential redox processes; process A and process B. \(V_{\text{ph}}\) is the maximum potential corresponding to the point of maximum power, \(P_{\text{max}}\), and \(I_{\text{sc}}\) and \(V_{\text{ph}}\) are the short-circuit current and open-circuit photopotentials, respectively. \(E_A\) and \(E_B\) refer to the redox potentials for storage processes, respectively.
photovoltage that can be generated. $I_{sc}$ is the short-circuit photocurrent corresponding to maximum band-bending. In Fig. 6, consider the electrochemical process represented by curve B. This process is located outside the region of potentials generated by the photoelectrode; it does not represent a potential storage system to be driven by a single photoelectrode. In such a case, a serial combination of more than one photoelectrode would be necessary. For a redox process to be a potential candidate for a redox storage system, the storage and photodriven current–voltage curves should intersect. Whereas $V_{ph}$ and $I_{sc}$ correspond to zero power, the point $P_{max}$ shown in Fig. 6 corresponds to the maximum power point. Solar energy conversion is accomplished at its maximum efficiency only during operation in the potential vicinity of $P_{max}$.

By adjusting the electrical load $L$, shown in Fig. 4, the system can be constrained to operate near its maximum power efficiency. In this case, if the counter electrode is not polarized, the potential difference between photoelectrode and the counter electrode will be close to $V_{max}$. If one chooses a facile redox process for the storage electrode, as indicated by the sharply rising IV curve for process A in Fig. 6, with $E_{redox}$ in the vicinity of $V_{max}$, then the potential during charge and discharge of the storage process will remain near $V_{max}$. As a result, the potential will be a highly invariant current that would be maintained through the load $L$, regardless of insolation intensity. This situation represents an ideal match between solar energy conversion and storage processes within a PESC. Non-ideality occurs with poor voltage-matching or kinetic limitations and polarization losses associated with the counter, storage, or photoelectrodes.

Ideally, the membrane used to separate the two-cell compartments, as indicated in Fig. 4, must be permeable only to ions that will transport charge, but that will not chemically react or otherwise impair any electrode. The permeability of membranes is generally less than ideal. Different membranes permit other ions and water to permeate to a varying degree [46, 47]. Gross mixing of active materials across the membrane causes them to combine chemically and in the process loose energy. Favorable qualities that a membrane should exhibit are low permeability toward chemically reactive ions, low resistivity, mechanical integrity, and cost effectiveness.

4.2.5 High Efficiency Solar Cells with Storage

4.2.5.1 Multiple Band Gap Cells with Storage

A limited fraction of incident solar photons have sufficient (greater than band gap) energy to initiate charge excitation within a semiconductor. Because of the low fraction of short wavelength solar light, wide band gap solar cells generate a high photovoltage but have low photocurrent. Smaller band gap cells can use a larger fraction of the incident photons, but generate lower photovoltage. Multiple band gap devices can overcome these limitations. In stacked multijunction systems, the topmost cell absorbs (and converts) energetic photons, but it is transparent to lower energy photons. Subsequent layer(s) absorb the lower energy photons. Conversion efficiencies can be enhanced, and calculations predict that a 1.64-eV and 0.96-eV two–band gap system has an ideal efficiency of 38% and 50%, for 1 and 1000 suns concentration, respectively. The ideal efficiency increases to a limit of 72% for a 36–band gap solar cell [48].
Recently, high solar conversion and storage efficiencies have been attained with a system that combines efficient multiple band gap semiconductors, with a simultaneous high capacity electrochemical storage [49, 50]. The energy diagram for one of several multiple band gap cells is presented in Fig. 7, and several other configurations are also feasible [1, 2a, b]. In the figure, storage occurs at a potential of $E_{\text{redox}} = E_{A^{+}/A} - E_{B^{+}/B}$. On illumination, two photons generate each electron, a fraction of which drives a load, whereas the remainder ($1/xe^{-}$) charges the storage redox couple. Without light – the potential falls below $E_{\text{redox}}$ – the storage couple spontaneously discharges. This dark discharge is directed through the load rather than through the multijunction semiconductor’s high dark resistance.

**Cell:** In Fig. 8, an operational form of the solar conversion is presented and a storage cell described by the Fig. 7 energy diagram. The single cell contains both multiple band gap and electrochemical storage, which unlike conventional photovoltaics, provides a nearly constant energetic output in illuminated or dark conditions. The cell combines bipolar AlGaAs ($E_g = 1.6$ eV) and Si ($E_g = 1.0$ eV) and AB$_5$ metal hydride/NiOOH storage. Appropriate lattice-matching between AlGaAs and Si is critical to minimize dark current, provide ohmic contact without absorption loss, and maximize cell efficiency. The NiOOH/MH metal hydride storage process is near ideal for the AlGaAs/Si because of the excellent match of the storage and photocharging potentials. The electrochemical storage processes utilizes MH oxidation and nickel oxyhydroxide reduction:

$$\text{MH} + \text{OH}^– \rightarrow \text{M} + \text{H}_2\text{O} + e^-;$$

$$E_{\text{M/MH}} = -0.8 \text{ V vs SHE} \quad (13)$$

**Fig. 7** Energy diagram for a bipolar band gap indirect ohmic storage multiple band gap photoelectrochemical solar cell (MBPEC).
NiOOH + H₂O + e⁻ → Ni(OH)₂ + OH⁻;

\[ E_{\text{NiOOH/Ni(OH)₂}} = 0.4 \text{ V vs SHE} \quad (14) \]

As reported [49] and as shown in Fig. 9, the cell generates a light variation insensitive potential of 1.2–1.3 V at total (including storage losses) solar-electrical energy conversion efficiency of over 18%.

A long-term indoor cycling experiment was conducted to probe the stability of the AlGaAs/Si metal hydride storage solar cell [50]. Unlike the variable insolations of Fig. 9, in each 24-hour cycle, a constant simulated AM0 (135.3 mW cm⁻²) illumination was applied for 12 hours, followed by 12 hours of darkness, and the cell potential, and storage (charge and discharge) currents monitored as a function of time over approximately an eight-month period. Figure 10 presents representative results for two-day periods occurring 0, 40, 140, and 240 days into the experiment. As summarized in the lower curves of the figure, the load potential is again nearly constant, despite a 100% variation in illumination (AM0/dark) conditions. Over a 24-hour period, the load potential increases by ~2% as the cell charges with illumination, followed by a similar decrease in potential as stored energy is spontaneously released in the dark. The cycles exhibited in Fig. 4 are representative, and as observed exhibit little variation on the order of weeks, and exhibit a variation of ~1% over a period of months. In this figure, photopower is determined as the product of the measured cell potential and measured photocurrent. Power over load is determined as the product of
4.2 Photoelectrochemical Solar Energy Storage Cells

The measured cell potential and measured load current.

Under constant 12-hour (AM0) illumination, the long-term indoor cycling cell generated a nearly constant photocurrent density of 21.2 (constant to within 1% or ±0.2 mA cm$^{-2}$), and as seen in the top curves of Fig. 10, a photopower that varied by ±3%. The cell’s storage component exhibits the expected increase in charging potential with cumulative charging, which moves the system to a higher photopotential. The observed increase in photopower during 12 hours of illumination is because of this increase in photopotential with cumulative charging. A majority of the photogenerated power drives the redox cell, and the remainder consists of the power over load during illumination, as illustrated in Fig. 10. In the dark, inclusive of storage losses, the stored energy is spontaneously released and this power over load during both 12-hour illumination and 12-hour dark periods is also summarized. The cell is a single physical–chemical device generating load current without any external switching.

4.2.5.2 PECS Driving an External Fuel Cell

In the early 1980s, Texas Instruments, Inc. developed an innovative program based on a hybrid photovoltaic storage that used imbedded multilayer photoanode and photocathode silicon spheres and was...
designed to provide a close match between their maximum power point voltage and a solution phase bromine oxidation process in acidic solution. The program was discontinued, but the system has several attractive features.

**Cell:** 3 [51]. In the bromine-imbedded Si sphere system, energy stored as bromine is recovered in an external hydrogen bromine fuel cell. The conversion and storage reaction and cell configuration are summarized by

\[
2\text{HBr} + \text{H}_2\text{O} + \text{hv} \rightarrow \text{H}_2 + \text{Br}_2 + \text{H}_2\text{O} \quad (15)
\]

**Photo anode:**
Contact metal | Ohmic contact | n-Si | p-Si | Surface metal | Solution

**Photo cathode:**
Contact metal | Ohmic contact | p-Si | n-Si | Surface metal | Solution

A description of the Texas Instrument cell action is provided in Fig. 11.

### 4.2.6 Other Examples of Photoelectrochemical Storage Cells

Photoelectrochemical storage cells of different configurations have been suggested, designed, and tested for their performance, under sunlight or artificial illumination. Although none of these configurations has attained the high solar to electrical conversion and storage efficiency of the system in the earlier sections, they are of significant
scientific interest and form a solid basis for further development toward future systems. The following three sections, covering PECS with either a solution, solid, or intercalation storage redox processes, provide a brief summary of many of these investigations, with a particular emphasis on their performance.

4.2.6.1 PECS Cells with Solution Phase Storage

Cell: 4 [52]. This is an example of the use of photoexcitable absorbers to promote a redox process using the following reaction sequence:

\[
\text{TH}^+ + 2\text{Fe}^{3+} + 3\text{H}^+ \longrightarrow \text{TH}_4^{2+} + 2\text{Fe}^{2+}
\]

\((\text{TH}^+ = \text{Thionene acetate})\)  

(16)

The back reaction between Leucothionene (\(\text{TH}_4^{2+}\)) and \(\text{Fe}^{3+}\) is slow. Leucothionene is oxidized at the \(\text{SnO}_2\) electrode.

\[
\text{TH}_4^{2+} \longrightarrow \text{TH}^+ + 2e^- + 3\text{H}^+ \quad (17)
\]

Ferric cation is reduced at a Pt electrode in a second compartment.

As a result, the concentration ratio of \(\text{Fe}^{3+}/\text{Fe}^{2+}\) is increased in the first compartment and decreases in the second compartment, which is equivalent to a difference in chemical potential. The system returns to its original uncharged state by discharging in the dark. Only 60 mV of potential difference is equivalent to a decade change of the \(\text{Fe}^{3+}/\text{Fe}^{2+}\) concentration ratio. Hence, this concentration cell does not generate a significant potential and the power density is low. The cell has the configuration.
SnO$_2$ | 0.0001 M Thionene Acetate, 0.01 M FeSO$_4$, 0.001 M Fe$_2$(SO$_4$)$_3$ H$_2$SO$_4$, pH = 1.7–2 | Ion-exchange membrane | 0.01 M FeSO$_4$ 0.001 M Fe$_2$(SO$_4$)$_3$ | Pt

Studied cell characteristics: Polycrystalline photoelectrode, Pt counter electrode, $E_{\text{redox}}$ of Fe$^{3+}$/Fe$^{2+}$ = 0.77 V vs SHE, illumination 40–50 mW cm$^{-2}$ by a tungsten lamp, initial current during discharge = 9.1 $\mu$A, and initial voltage = 10.9 mV.

Cell: 6 [54]. In this cell, a wide gap semiconductor ($E_g$ = 3.3), BaTiO$_3$ is used, capable of absorbing only near UV radiation and comprising less than 5% of available solar energy. This limits its practical use for solar energy conversion. The following storage couple is used:

$$\text{Ce}^{3+} + \text{Fe}^{3+} \xrightarrow{\text{Light}} \text{Ce}^{4+} + \text{Fe}^{2+}$$ (19)

The storage system operates well away from the maximum power point of the semiconductor device, and therefore storage and discharge efficiency is poor. The cell uses a salt bridge between the two compartments and is of the form

Single crystal | n-BaTiO$_3$ | 0.1 M Ce$_2$(SO$_4$)$_3$, 0.005 M Ce(SO$_4$)$_2$ | Salt bridge | 0.1 M Fe$_2$(SO$_4$)$_3$, 0.005 M FeSO$_4$ | Pt

Studied cell characteristics: Pt counter electrodes, three-electrode configuration as in Fig. 4., $E_{\text{redox}}$ of Ce$^{4+}$/Ce$^{3+}$ = 1.45 V vs SHE, $E_{\text{redox}}$ of Fe$^{3+}$/Fe$^{2+}$ = 0.77 V vs SHE, illumination sunlight, conversion efficiency = 0.01%, FF = 0.26, photopotential = 730 mV, $V_{\text{max}}$ = 0.33 V, charge efficiency 15%, potential across two Pt terminals of the charged cell = 0.60, and short-circuit current = 0.12 mA.

Cell: 7 [55]. In this study, attempts have been made to improve the behavior of a MoS$_2$ electrode in HBr electrolyte. Equilibration between the electrode and HBr has been improved by subjecting the electrode to a dark anodic potential. A ratio of 10 between the areas of counter and working electrode is another favorable feature in this study to minimize the polarization resistance at the counter electrode. Nafion-315 membrane contributes only a
4.2 Photoelectrochemical Solar Energy Storage Cells

moderate resistance of 20 ohm cm$^2$. The storage reaction and cell configuration are

\[
\begin{align*}
\text{Light:} & \quad 2\text{Br}^- + 3\text{I}_2 & \rightleftharpoons & \text{Br}_2 + 2\text{I}_3^- \\
\text{Dark:} & \quad \text{Br}_2 & \triangleleft & \text{C} & \text{2I}_3^- \quad (20)
\end{align*}
\]

$n$-MoSe$_2$ | 0.1 M HBr, 0.01 M Br$_2$ | Nafion 315 | 1 M KI, 0.18 M I$_2$ | Pt

Studied cell characteristics: Single crystal photoelectrode, Pt counter electrodes, cell configuration as in Fig. 4. \(E_{\text{redox}}\) of Br$^-$/Br$_2$ = 1.087 vs SHE, \(E_{\text{redox}}\) of I$_3^-$/I$^-$ = 0.534 V vs SHE. Illumination 200 mW cm$^{-2}$ Xe lamp, conversion efficiency = 6.2%, potential across two Pt terminals of the charged cell = 0.49, and short-circuit current = 0.5 mA.

Cell: 8 [55]. The next cell also uses a Nafion membrane, but makes use of $n$-CdSe to drive a polysulfide–polyselenide storage couple. Low-output power density is the biggest drawback in this cell. The storage reaction and cell configuration are

\[
\begin{align*}
\text{Light:} & \quad \text{S}^0 + \text{Se}_2^2^- & \rightleftharpoons & \text{S}_2^2- + \text{Se}^0 \\
\text{Dark:} & \quad \text{S}_2^2- & \triangleleft & \text{C} & \text{Se}^0 \quad (21)
\end{align*}
\]

$n$-CdSe | 1 M in Na$_2$S, S, NaOH | Nafion 315 | 1 M in Na$_2$Se, Se, NaOH | Pt

Studied cell characteristics: Polycrystalline photoelectrode, Pt counter electrodes, cell configuration as in Fig. 4. \(E_{\text{redox}}\) of polysulfide electrolyte = −700 mV vsa SCE• \(E_{\text{redox}}\) of Se$_2^2-$/Se$^-$ = −800 mV vs SEC, illumination 100 mW cm$^{-2}$ Xenon lamp, conversion efficiency 4%, FF = 0.45, photovoltage = −400 mV, charged cell has an open-circuit voltage of 60 mV, and initial current across a 100 ohm across Pt electrode = 0.5 mA.

Cell: 9 [44]. This study uses organic redox species for energy-storage purposes. Stability of the $n$-WSe$_2$ photoanode in iodine electrolyte and the stability of anthraquinone redox couple have been demonstrated in this study. Any H$_2$ evolution would carry out direct hydrogenation of AQ and associated side reactions, and therefore a carbon electrode has been selected because of the H$_2$ over potential on this electrode. The cell underwent several deep charge and discharge cycles with reproducible performance. The storage reaction and cell form are

\[
\begin{align*}
\text{Light:} & \quad 2\text{AQ} + 2\text{H}^+ & \rightleftharpoons & \text{AQH}_2 + \text{I}_2 \\
\text{Dark:} & \quad \text{AQH}_2 & \triangleleft & \text{C} & \text{I}_2 \quad (22)
\end{align*}
\]

$n$-WSe$_2$ | 1 M KI, 0.1 M Na$_3$SO$_4$, 0.5 M H$_2$SO$_4$ | Saturated KCl bridge | 5 \times 10$^{-2}$ M AQ, 0.5 M H$_2$SO$_4$ | C

Studied cell characteristics: Single-crystal photoelectrode, C counter electrode during charging, Pt during discharging. The cell configuration is similar to that in Fig. 4. \(E_{\text{redox}}\) of I$_3^-$/I$^-$ = 0.534 V vs SHE, \(E_{\text{redox}}\) of AQ/AQH$_2$, illumination 150 mW cm$^{-2}$ He–Ne laser (632.8 nm), conversion efficiency = 9%, discharge across a 10 ohm produce a current 1 mA cm$^{-2}$, and open-circuit voltage 200 mV.

Cell: 10 [44]. This study uses a p-WSe$_2$ photocathode rather than $n$-WSe$_2$. During the cell discharge, oxidation of AQH$_2$ at the surface of p-WSe$_2$ indicates that the electrode has the dual role of being a cathode during the charging and being the anode during the discharge. As discussed earlier, this limits the activity and low-current densities were observed. The storage reaction and cell configuration are

\[
\begin{align*}
\text{Light:} & \quad \text{AQ} + 2\text{H}^+ & \rightleftharpoons & \text{AQH}_2 + \text{I}_2 \\
\text{Dark:} & \quad \text{AQH}_2 & \triangleleft & \text{C} & \text{I}_2 \quad (23)
\end{align*}
\]

p-WSe$_2$ | 5 \times 10$^{-2}$ M AQ | Saturated | 1 M KI, 0.5 M H$_2$SO$_4$ | Pt

Single crystal | 0.5 M H$_2$SO$_4$ | Salt bridge | 0.5 M Na$_2$SO$_4$ |
Solar Energy Conversion without Dye Sensitization

Cell: 11 [55]. The theoretical band gap of WSe₂ provides a near ideal single band gap match for the solar spectrum. But the following cell has some disadvantages. These include the low solubility of the storage redox couple employed, MV²⁺ and MV⁴⁺ and the possibility of undesirable side reactions of the radical ion MV⁴⁺. Using dual (n-type and p-type) photoelectrodes expands the potential regime one can access for the redox-storage couple. The storage reaction and cell configuration are

\[
21^- + 2MV^{2+} \xrightarrow{\text{Light}} 2MV^{4+} + I_2 \quad (24)
\]

\[
n-WSe_2 | I^- | MV^{2+} | p-WSe_2
\]

4.2.6.2 PECS Cells Including a Solid Phase–Storage Couple

The earlier experimental investigations, Cells 2–9, use only solution phase redox couples. However, as indicated in the following examples, a solid phase–storage couple may also be employed, which in principle tends to increase the cell's storage capacity.

Cell: 12 [57]. Having at least one component in insoluble form may add compactness into the cell configuration, although low conductivity of the insoluble active component may cause significant polarization losses associated with the storage electrode, as exemplified by the low conductivity of silver (chloride) in one of the next cells. The next four cells use a TiO₂ polycrystalline photoelectrode. In the first cell, the storage reaction and cell configuration are

\[
2H_2O + 4Ag^+ \xrightarrow{\text{Light}} 4H^+ + 4Ag + O_2 \quad (25)
\]

\[
TiO_2 | 1 \text{ M HNO}_3, 1 \text{ M KNO}_3 | \text{Anion Specific Membrane} | 1 \text{ M AgNO}_3, 1 \text{ M KNO}_3 | Ag
\]

Studied cell characteristics: Polycrystalline photoelectrode, Pt counter electrodes, cell configuration is similar to Fig. 4, \(E_{\text{redox}}\) of O₂, H⁺/H₂O couple = 1.23 V vs NHE at pH = 1, \(E_{\text{redox}}\) of Ag/Ag⁺ = 0.80 V vs NHE, illumination = 500 W Hg lamp, conversion efficiency = 1%, photopotential = 0.28 V vs NHE, open-circuit voltage of the charged cell = 0.28 V, and short-circuit current = 0.3 mA cm⁻².

Cell: 13 [57]. Of the four TiO₂ Cells 10–13, the following cell 3.2 exhibited the highest short-circuit discharge current and voltage. However, during the charging process, a stationary concentration of Ce⁴⁺ was observed in the photoanode compartment. This suggests the existence of competing process that consumes the oxidized species Ce⁴⁺. The later is known to participate in photochemical reactions under illumination [10]. Considering the low concentration of the reduced form of active materials used with the photoanode, there is a possibility that the water oxidation becomes the dominant process during charging. In this study, it was observed that with a passage of a charge of 10 coulomb during charging, Ce⁴⁺ present in the photoanode compartment accounted for only 22% of the charge. In this second TiO₂ photoelectrode cell, the storage reaction and cell configuration are

\[
Ce^{3+} + Ag^+ \xrightarrow{\text{Light}} Ce^{4+} + Ag \quad (26)
\]

\[
TiO_2 | 1 \text{ M HNO}_3, 0.05 \text{ M Ce}_2(\text{SO}_4)_3, 0.1 \text{ M Ce(SO}_4)_2, \text{ Anion Specific Membrane} | 1 \text{ M AgNO}_3, 1 \text{ M KNO}_3 | Ag
\]

Studied cell characteristics: Polycrystalline photoelectrode, Pt counter electrode, cell configuration illumination etc. are similar to the earlier cell, \(E_{\text{redox}}\).
of Ce$^{4+}$/Ce$^{3+}$ vs SHE, charge efficiency of the cell without stirring = 18%, open-circuit voltage of the charged cell = 0.76, and initial short-circuit current 1.3 mA cm$^{-2}$.

**Cell: 14 [57].** In this third TiO$_2$ photoelectrode cell, the storage reaction and cell configuration are

$$2\text{Fe}^{2+} + \text{Cu}^{2+} \xrightleftharpoons{\text{Light}}^{\text{Dark}} 2\text{Fe}^{3+} + \text{Cu}$$

TiO$_2$ | 1 M KNO$_3$, 0.01 M FeSO$_4$ | Anion Specific Membrane | 0.025 M CuSO$_4$, 1 M KNO$_3$ | Cu

Studied cell characteristics: Polycrystalline photoelectrode, $E_{\text{redox}}$ of Cu$^{2+}$/Cu = 0.34 V vs NHE, $E_{\text{redox}}$ of Fe$^{3+}$/Fe$^{2+}$ = 0.77 vs NHE, open-circuit voltage of the charged cell = 0.3, and short-circuit current 1.5 mA cm$^{-2}$.

**Cell: 15 [57].** The wide band gap of TiO$_2$ is not an appropriate match to the solar spectrum. In this fourth TiO$_2$ photoelectrode cell, the storage reaction and cell configuration are

$$\text{Fe}^{2+} + \text{AgCl} \xrightleftharpoons{\text{Light}}^{\text{Dark}} \text{Fe}^{3+} + \text{Ag} + \text{Cl}^-$$

TiO$_2$ | 0.2 M KCl, 0.01 M FeCl$_2$ | Anion Specific Membrane | 0.2 M KCl | AgCl | Pt

Studied cell characteristics: Single crystalline photoelectrode, Pt counter electrodes, cell configuration is similar to Fig. 4. $E_{\text{redox}}$ of Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ is 0.36 V vs NHE, $E_{\text{redox}}$ of Ni$^{2+}$/Ni = -0.25 V vs NHE, illumination 500 W Hg lamp, conversion efficiency 13% for 450–540-nm region, photovoltage = 0.63 V, open-circuit voltage of the charged cell = 0.75 V, short-circuit current = 4.3 mA cm$^{-2}$, and charge efficiency = 55%.

**Cell: 16 [58].** In this next cell, Ni is deposited during charge at 80% charge efficiency. Losses may be because of the competing reaction of H$_2$ evolution. Cell voltage of the charged cell is higher than the photovoltage available, which indicates the possible influence of another redox couple Ni(OH)$_2$/NiOH occurring at a higher redox potential. Only about 55% of the charge stored can be recovered during discharge. The possibility of self-discharge reactions because of imperfect permeability of the membrane has been cited as a possible cause, and is further complicated by the complex ferro/ferricyanide equilibria that is known to occur (Licht, 1995). In this cell, the storage reaction and cell configuration are

$$2\text{Fe}^{2+} + \text{Ni}^{2+} \xrightleftharpoons{\text{Light}}^{\text{Dark}} \text{Fe}^{3+} + \text{Ni}$$

n-GaP | 0.2 M K$_2$SO$_4$, pH = 6.7, 0.05 M K$_3$Fe(CN)$_6$, 0.05 M K$_4$Fe(CN)$_6$ | Anion Specific Membrane | 0.05 M K$_2$SO$_4$, 0.2 M NiSO$_4$, 0.06 M NiCl$_2$ | Pt

Studied cell characteristics: Single crystalline photoelectrode, Pt counter electrodes, cell configuration is similar to Fig. 4. $E_{\text{redox}}$ of Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ is 0.36 V vs NHE, $E_{\text{redox}}$ of Ni$^{2+}$/Ni = -0.25 V vs NHE, illumination 500 W Hg lamp, conversion efficiency 13% for 450–540-nm region, photovoltage = 0.63 V, open-circuit voltage of the charged cell = 0.75 V, short-circuit current = 4.3 mA cm$^{-2}$, and charge efficiency = 55%.

**Cell: 17 [55].** The conversion efficiency data in the following cell reflect the poor quality of the GaAs material that was used, although in other studies, there has been higher efficiency GaAs PEC (without storage). In this study, significant polarization was observed and performance data of the storage cell was not reported. The storage reaction and cell
configuration are

\[
\begin{align*}
\text{Dark} & \quad \text{Light} \\
\text{Cd} + \text{Se}_2^{2-} + 2\text{OH}^- & \rightleftharpoons \text{Cd(OH)}_2 + 2\text{Se}^{2-} \\
\end{align*}
\]

(30)

\[n\text{-GaAs} | 0.1 \text{M Na}_2\text{Se}, 0.1 \text{M Se}, 1 \text{M NaOH} | \text{Nafion} | 2 \text{M NaOH} | \text{Cd}\]

Studied cell characteristics: Single crystalline photoelectrode, Pt counter electrode, cell configuration is similar to Fig. 4. \(E_{\text{redox}}\) of \(\text{Se}^{2-}/\text{Se}_2^{2-}\) = -800 mV vs SCE, \(E_{\text{redox}}\) of \(\text{Cd}/\text{Cd(OH)}_2\) = -1050 mV vs SCE. Illumination 100 mW cm\(^{-2}\) Xe lamp, conversion efficiency = 4\%, FF = 0.53, photopotential = -500 mV, and short-circuit discharge current of the storage cell in the dark using Pt electrodes = 14.6 mA cm\(^{-2}\).

**Cell: 19** [59]. In this study, the possibility of using organic semiconductors to drive storage processes is demonstrated. The process is in principle similar to a concentration cell. During photocorrosion, Prussian Blue (PB, Fe\(_4\)[Fe\(_{II}\)(CN)\(_6\)]\(_3\)) is reduced at the photocathode and PB is oxidized at the anode. In the dark, the redox process involving PB is reversed producing an electron flow. Process ability, stability, and lack of photo-corrosion make these low band gap organic materials very attractive for photoelectrochemical applications. However, they are defect-based systems, and the very low conversion efficiencies and self-discharge appear to outweigh these benefits. The storage reaction and cell configuration are

\[
\begin{align*}
\text{Light} & \quad \text{Dark} \\
\text{Fe}^{II}_4[\text{Fe}^{II}(\text{CN})_6]_3^{4-} & \rightleftharpoons 4\text{h}^+ \\
\text{Fe}^{III}_4[\text{Fe}^{II}(\text{CN})_6]_3^{4-} + 4\text{e}^- \\
\end{align*}
\]

(32)

\[
\begin{align*}
\text{Light} & \quad \text{Dark} \\
\text{Fe}^{II}_4[\text{Fe}^{II}(\text{CN})_6]_3^{4-} & \rightleftharpoons 4\text{e}^- \\
\text{Fe}^{IV}_4[\text{Fe}^{IV}(\text{CN})_6]_3^{4-} \\
\end{align*}
\]

(33)

\[\text{ITO} | \text{P3MT} | \text{PB} | 0.2 \text{M KCl}, 0.1 \text{M HCl} | \text{PB} | \text{ITO}\]

Studied cell characteristics: Illumination 500 W Xenon lamp, the ITO/P3MT electrode has open-circuit voltage = 0.44 V, short-circuit photocurrent 0.09 \(\mu\)A cm\(^{-2}\), and charge efficiency of the storage cell = 40\%.

**Cell: 20** [60]. Metal ions introduced into a solid \(\beta\)-alumina lattice behave like ions in solution. This study illustrates a compact solid-state storage cell that can be charged using solar energy. During charging, Fe
and Ti change their oxidation state and the charge balance is maintained by the migration of Na\(^+\) ions from one phase to the other. In the actual cell design, an n-type semiconductor is connected to the alumina phase containing Ti and p-material is connected to the phase containing Fe. Limitations are the comparatively slow diffusion of ions in the solid electrolyte and resistance to ionic movement at various phase boundaries, and lower the energy output during discharge. In this device, back wall illumination demands the use of very thin semiconductor layers to minimize absorption losses and has the general form

\[ n\text{-semiconductor} \mid Na_2O.11(AlFeO_3) \mid Na_2O.11(Al_2O_3) \mid Na_2O.11(AlTiO_3) \mid p\text{-semiconductor} \]

**Cell: 21** [47]. In this detailed study, selection of a Nafion-315 membrane was done on the basis of (1) stability in high alkaline sulfide solutions, (2) low IR drop, and (3) low permeability to sulfide. Maintaining an area ratio of 1:8 between photo and storage electrodes has minimized polarization at the storage electrode. The storage system was driven by three semiconductor PEC devices connected in series. Charging was done up to 90% of the capacity followed by complete discharge. Overall observed charge efficiency was 83%. Although the system was not fully optimized with respect to photoelectrode, electrolyte, and storage, voltage efficiency of 75% was obtained during discharge. Discharge curves were flat until the stored active material was fully consumed. The storage reaction and cell configuration are

\[
\text{CdSe} + 2\text{h}^+ \xrightarrow{\text{Light}} \text{Se}^0 + \text{Cd}^{2+} \quad (35)
\]

and the other electrode in photoelectroplated by Cd

\[
\text{CdTe} + 2\text{e}^- \xrightarrow{\text{Light}} \text{Cd}^0 + \text{Te}^{2-} \quad (36)
\]

\[ n\text{-CdSe} \mid 1 \text{ M in NaOH, Na}_2\text{S, S Nafion-315} \mid 0.1 \text{ M ZnO, 1 M NaOH} \mid C \]

Studied cell characteristics: Polycrystalline photoelectrode, Ni counter electrode, basic cell configuration is based on Fig. 4, \( E_{\text{redox}} \) of \( S_2^2/\text{S}^2^- = 0.500 \text{ V vs SHE} \), \( E_{\text{redox}} \) of \( \text{Zn/Zn(OH)}_4^{2-} = -1.25 \text{ V vs SHE} \), artificial illumination, conversion efficiency = 3%, photovoltage = -0.50 V, during discharge through 75-ohm load between C and Ni discharge current = 10 mA, and voltage = 0.6 V.

**Cell: 22** [61]. This cell takes advantage of photocorrosion to drive a storage cell. Under illumination, n-CdSe is decomposed and p-CdSe is electroplated, and the reverse occurs during cell discharge. However, photoactivity depends on an optimized semiconductor surface, and in an environment where the surface is changed constantly, the surface optimization is lost. This and the poor kinetics of the p-type photoreduction result in a continual deterioration of the photoactivity and cause low photoefficiency and low-discharge power density. The storage reaction and cell configuration are

\[
\text{CdSe} + 2\text{h}^+ \xrightarrow{\text{Light}} \text{Se}^0 + \text{Cd}^{2+} \quad (35)
\]

and the other electrode in photoelectroplated by Cd

\[
\text{CdTe} + 2\text{e}^- \xrightarrow{\text{Light}} \text{Cd}^0 + \text{Te}^{2-} \quad (36)
\]

\[ n\text{-CdSe} \mid 0.1 \text{ M CdSO}_4 \mid p\text{-CdTe} \]

**Cell: 23** [46]. This is a detailed study of a thin film cell with moderately high outdoor solar efficiency, high storage efficiency, and an output that is highly invariant despite changing illumination. This study provides extensive details of the choice
of photoelectrode, membrane, and electrochemistry of the tin–tin sulfide redox storage. Cd(Se,Te) electrodes, compared to CdSe, improve the band gap match and increase solar-conversion efficiency. Two photoelectrodes in series were used to provide a voltage match to the storage redox couple in a cell of the form of Fig. 12.

The conversion and storage reactions and cell configuration are presented as

\[
\text{SnS} + 2e^- \rightarrow S^{2-} + \text{Sn Storage} \quad (37)
\]

\[
S^{2-} \rightarrow S + 2e^- \text{ Photo electrode} \quad (38)
\]

\[
n-\text{Cd(Se,Te)} | 2 \text{ M in NaOH, Na}_2\text{S, S} | \text{Red cad Membrane} | 2 \text{ M in NaOH, Na}_2\text{S} | \text{SnS} | \text{Sn}
\]

Studied cell characteristics: Bipolar series polycrystalline photoelectrode, CoS counter electrodes, cell configuration is as shown in Fig. 4 without the need of switches \( E \) or \( F \). \( E_{\text{redox}} \) of \( S/S^{2-} = -0.48 \text{ V vs NHE} \), \( E_{\text{redox}} \) of \( \text{SnS}/\text{Sn}, S^{2-} = -0.94 \text{ V vs NHE} \). Illumination sunlight, 500 mW hr cm\(^{-2}\) per day, conversion efficiency 6–7\%, photovoltage \(-600 \text{ mV} \), and storage efficiency >90\%. After two weeks of continuous operation the overall solar to electrical efficiency (including conversion and storage losses) is 2–7\%.

**Cell:** 24 [4]. The earlier cell is improved by a series of solution phase optimizations (cesium electrolyte with low hydroxide and optimized polysulfide), to provide a higher photopotential and improved stability and also the use of a single crystal, rather than thin film, Cd(Se,Te) to also improve photopotential and cell efficiency, as described earlier in Fig. 12. Because of the higher photopotential, only a single photoelectrode is required to match the storage potential and high overall efficiencies are observed. The cell has the design as shown in beginning of the chapter (Fig. 2) and uses conversion and storage reactions described in the earlier cell and a configuration

\[
n-\text{Cd(Se,Te)} | 0.8 \text{ M Cs}_2\text{S}, 1 \text{ M Cs}_2\text{S}_4 | \text{Red cad Membrane} | 1.8 \text{ M Cs}_2\text{S} | \text{SnS} | \text{Sn}
\]

Studied cell characteristics: The PEC had a power conversion efficiency of 12.7\% under 96.5 mW cm\(^{-2}\) insolation and voltage at maximum power point was of \(-1.1 \text{ V vs SHE} \), sufficient to drive the SnS/Sn storage system. Under direct illumination, the 0.08 cm\(^2\) single crystal photoelectrode generated more than 1.5 mA through the 3 cm\(^3\) SnS electrode driving SnS reduction while supporting 0.33 mA through a 1500 load simultaneously at a photogenerated 0.495 V. In the dark spontaneous oxidation drive, the load with storage efficiency over 95\%. The total conversion efficiency, including conversion and storage losses, was 11.8\%.

### 4.2.6.3 PECSCells Incorporating Intercalation

In photointercalation, illumination drives insertion storage into layer type compounds [62]. The photointercalation process can be characterized as

\[
\text{TX}_2 + e^- (h) + p^+ (h) + \text{M}^{\text{sol}} \rightarrow \text{TM}_{\text{L}} \text{X}_2 + p^+ \quad (39)
\]

where TX\(_2\) is generally a nonintercalated transition metal dichalcogenide. For this process to occur without the assistance of an external power source, a counter electrode is driven at an electrode potential negative to that of the layer type intercalating electrode. The process is generally restricted to \( p \)-type materials. The development of this concept has been slow because of dearth of materials that are stable semiconductors and at the same time behave as
intercalating compounds that are able to exchange guest ions and molecules with an electrolyte in a reversible manner, and yet that is not disruptive to photon absorption.

Cell: 25 [63]. In this cell, $E_{\text{redox}}$ of copper thiophosphate is variable depending on the degree of intercalation. A limitation of this system is poor-discharge kinetics and low-energy density of the discharge. The cell configuration is given by

$$\text{Cu}_3\text{PS}_4 | 0.02 \text{ M CuCl} | \text{CH}_3\text{CN} | \text{Cu}_2\text{S}$$

Studied cell characteristics: $E_{\text{redox}}$ of Cu$^{+}$/Cu$^0 = -0.344$ vs NHE, illumination 117 mW cm$^{-2}$ Xe lamp, photopotential = 100 mV, charging current $< 50 \mu$A cm$^{-2}$, and discharge current $< 10 \mu$A cm$^{-2}$.

Cell: 26 [64]. This cell illustrates another all solid state design for a thin storage cell. p-Cu$_x$S changes its electrode potential with changes in its composition. During charging, Cu is oxidized at n-CdS surface while it is reduced at the Cu electrode. Between the two electrodes Cu$^+$ ion transport process takes place in the solid state electrolyte. The cell configuration is given by

$$\text{Cu} | \text{n-CdS} | p-\text{Cu}_x\text{S} | \text{RuCl}_4\text{I}_3\text{Cl}_{3.5} | \text{Cu}$$

Cell: 27 [64]. As with the earlier cell, this final cell requires a very thin design because to reach the junction, light has to travel several layers. The cell functions in the same manner as the earlier cell, and the configuration is given by

Conductive Glass | Cu | Cu$^+$ Conducting solid electrolyte | p-Cu$_2$Te | n-CdTe | Mo

4.2.7 Summary

Conversion and storage of solar energy is of growing importance as fossil fuel energy sources are depleted and stricter environmental legislation is implemented. Although society’s electrical needs are largely continuous, clouds and darkness dictate that photovoltaic solar cells have an intermittent output. Photoelectrochemical systems have the potential to not only convert but also store incident solar energy. Design component and system considerations and a number of photoelectrochemical solar cells with storage have been reviewed in this chapter.

Acknowledgment

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References

2. (a) S. Licht, O. Khaselev, T. Soga et al., J. Phys. Chem. 1998, 102, 2536; (b) ibid, 2546.
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4.2 Photoelectrochemical Solar Energy Storage Cells

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