Solar water splitting to generate hydrogen fuel—a photothermal electrochemical analysis

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Abstract

Theory and experiment are derived for highly efficient photothermal electrochemical solar water splitting to provide clean, renewable sources of hydrogen fuel. The theory derives semiconductor band-gap-restricted, thermal enhanced, solar water splitting efficiencies, combining photodriven charge transfer, with excess sub-band-gap insolation to lower the water potential. Fundamental water thermodynamics and solar photosensitizer constraints determine solar to hydrogen fuel conversion efficiencies in the 50% range over a wide range of insolation, temperature, pressure and photosensitizer band-gap conditions. Experimentally, a novel physical chemical process within molten NaOH is demonstrated, in which an external single, small band-gap photosensitizer, such as Si, can drive the energetics of water cleavage. This is accomplished by tuning (decreasing) the water splitting electrochemical potential, $E_{\text{H}_2\text{O}}$, rather than tuning the photosensitizer band gap; this diminished potential is due to (i) thermodynamic temperature induced decrease of $E_{\text{H}_2\text{O}}$ with increasing temperature, and (ii) partial recombination of the cleavage products.

Keywords: Solar energy; Hydrogen fuel; Water electrolysis; Water splitting; Solar hydrogen

1. Introduction

Hydrogen fuel to drive transportation and other societal energy needs is receiving increasing attention [1], but what is to be the H2 source? Solar water splitting can provide clean, renewable sources of hydrogen fuel [2]. A variety of approaches have been studied to achieve this important goal including indirect or direct or thermochemical [3,4], photosynthetic [5] or photoelectrochemical [2,6–10] solar water splitting. Each of these previous approaches has limitations, and as summarized in Scheme 1 has exhibited a limited conversion of solar energy to H2. The highest efficiencies had been observed with multiple band-gap semiconductor electrolysis cells sustaining over 18% solar energy conversion efficiency to H2 [10]. This paper combines a novel derivation of band-gap-restricted thermal enhanced solar water splitting efficiencies [11], along with recent experimental evidence of thermal electrochemical solar water splitting processes by semiconductor materials support of that model [12]. The model provides a theoretical basis for solar energy to hydrogen conversion efficiencies in the 50% range, by combing excess sub-band-gap insolation with efficient solar driven water electrolysis at elevated temperatures.

The UV and visible energy rich portion of the solar spectrum is transmitted through H2O. Therefore sensitization, such as via semiconductors, is required to drive the water-splitting process. Solar photoelectrochemical attempts to split water utilized TiO2 [6,7] and InP [8] and also multiple band-gap semiconductors [9,10]. Photoelectrochemical water splitting studies have generally focused on diminishing the high band gap apparently required for...
solar water splitting [6,7]. Semiconductors, such as TiO$_2$ can split water, but their wide band-gap limits the photo response to a small fraction of the incident solar energy. Studies sought to improve the solar water splitting by tuning (decreasing) the band-gap of the photosensitizers, $E_g$, to better match the water splitting potential, $E_{H_2O}$. Here, we take an alternate approach: instead of tuning $E_g$ to fit $E_{H_2O}$, we tune $E_{H_2O}$ to fit $E_g$. Early photoelectrochemical models had incorrectly predicted only low solar water splitting conversion efficiencies, with a maximum of $\sim 15\%$, would be attainable [9]. This was recently shown to be improved to $\sim 30\%$ solar water splitting modeled conversion efficiency by eliminating (i) the linkage of photo to electrolysis surface area, (ii) non-ideal matching of photo and electrolysis potentials, and incorporating the effectiveness of contemporary (iii) electrolysis catalysts and (iv) efficient multiple band-gap photosensitizers [10]. However, both the early and improved models either did not incorporate heat effects on (semiconductor) charge utilization, or semiconductor effects on heat utilization.

At high temperatures water ($\gg 2000^\circ C$) chemically disproportionates without electrolysis. However, catalysis, gas recombination and containment materials limitations above 2000$^\circ$C have led to very low efficiencies [4]. Electrochemical water splitting, generating H$_2$ and O$_2$ at separate electrodes, largely circumvents the gas recombination limitations, and a hybrid of photothermal electrochemistry will be shown to provide a pathway for efficient solar energy utilization. Utilizing heat to facilitate water electrolysis had been suggested [13], although no rigorous analysis from the fundamentals of solar energy, thermodynamics and electrochemical processes had been developed. One schematic representation for this solar thermal water electrolysis assisted (photothermal electrochemical water splitting) is presented in Scheme 2, and rather than a field of concentrators, similar systems may use individual solar concentrators. Thermally assisted solar electrolysis consists of (i) light harvesting, (ii) spectral resolution of thermal (sub-band-gap) and electronic (super-band-gap) radiation, the latter of which (iii) drives photovoltaic or photoelectrochemical charge transfer $V(i_{H_2O})$, while the former (iiib) elevates water to temperature $T$, and pressure, $p$; finally (iv) $V(i_{H_2O})$ driven electrolysis of H$_2$O($T, p$) as schematized in Scheme 2.

2. Elevated temperature results

Fletcher, repeating the fascinating suggestion of Brown that saturated aqueous NaOH will never boil, hypothesised that a useful medium for water electrolysis might be very high temperature NaOH saturated, aqueous solutions. These do not reach a temperature at which they boil at 1 atm due to the high salt solubility, binding solvent, and changing saturation vapour pressure, as reflected in their phase diagram [14]. We measure this domain, and also electrolysis in an even higher temperature domain above which NaOH melts ($318^\circ$C) creating a molten electrolyte with dissolved water, resulting in unexpected $V_{i_{H_2O}}$.

Fig. 1 summarizes measured $V_{i_{H_2O}}$ in aqueous saturated and molten NaOH electrolytes. As seen in the inset, Pt exhibits low over potentials to H$_2$ evolution, and is used
Scheme 2. Schematic representations of solar water electrolysis improvement through excess solar heat utilization.

Fig. 1. $V_{H_2O}$ measured in aq. saturated or molten NaOH, at 1 atm. CO$_2$ is excluded by argon purge. The molten electrolyte is prepared from heated, solid NaOH with steam injection. O$_2$ anode is 0.6 cm$^2$ Pt foil. IR and polarization losses are minimized by sandwiching 5 mm from each side of the anode, two interconnected Pt gauze (200 mesh, 50 cm$^2$ = 5 cm × 5 cm × 2 sides) cathodes. Fig. inset: At 25$^\circ$C, 3 electrode values at 5 mV/s versus Ag/AgCl, with either 0.6 cm$^2$ Pt or Ni foil, and again separated 5 mm from two 50 cm$^2$ Pt gauze acting as counter electrodes.

As seen in the Fig. 2, the observed value at high temperature of $V_{H_2O}$ approaches that calculated for a thermodynamic system of 500 bar, rather than 1 bar, H$_2$O.

A source of the nominally less than thermodynamic water splitting potentials is described in Scheme 3. Shown on the left hand is the single compartment cell utilized here. Cathodically generated H$_2$ is in close proximity to the anode, while anodic O$_2$ is generated near the cathode. Their presence will facilitate the water forming back reaction, and at the electrodes this recombination will diminish the potential. In addition to the observed low potentials, two observations support this recombination effect. The generated H$_2$ and O$_2$ is collected, but is consistent with a coulombic efficiency of $\approx$ 50% (varying with $T$, $j$, and interelectrode separation). Consistent with the right-hand side of Scheme 1, when conducted in separated anode/cathode compartments, this observed efficiency is 98–100%. Here, however, all 0.4 V decrease in the O$_2$ activation potential at a Pt surface. Through 300$^\circ$C in Fig. 1, measured $V_{H_2O}$ remains greater than the calculated thermodynamic rest potential. Unexpectedly, $V_{H_2O}$ at 400$^\circ$C and 500$^\circ$C in molten NaOH occurs at values substantially smaller than that predicted. These measured values include voltage increases due to IR and hydrogen overpotentials and hence provide an upper bound to the unusually small electrochemical potential. This phenomena is summarized in Fig. 2, in which even at relatively large rates of water splitting (30 mA cm$^{-2}$) at 1 atm, a measured $V_{H_2O}$ below that predicted by theory is observed at temperatures above the NaOH melting point. The theoretical calculations over an expanded temperature range will be presented in Fig. 4, with calculations described in that section. As seen in the Fig. 2, the observed value at high temperature of $V_{H_2O}$ approaches that calculated for a thermodynamic system of 500 bar, rather than 1 bar, H$_2$O.
cell open circuit potentials increase to beyond the thermodynamic potential, and at $j = 100 \text{ mA cm}^{-2}$ yields measured $V_{\text{H}_2\text{O}}$ values of 1.45, 1.60, 1.78 V at 500°C, 400°C, and 300°C, which are approximately 450 mV higher than the equivalent Fig. 1 values for the single configuration cell.

The recombination phenomenon offers advantages (low $V_{\text{H}_2\text{O}}$), but also disadvantages ($\text{H}_2$ losses), requiring study to balance these competing effects to optimize energy efficiency. In molten NaOH, the effects of temperature variation of $\Delta G^0_{\text{f}}(\text{H}_2\text{O})$ and the recombination of the water splitting products can have a pronounced effect on solar driven electrolysis. As compared to 25°C, in Fig. 1 only half the potential is required to split water at 500°C, over a wide range of current densities.

The unused thermal photons which are not required in semiconductor photodriven charge generation, can contribute to heating water to facilitate electrolysis at an elevated temperature. The characteristics of one, two, or three series interconnected solar visible efficient photosensitizers, in accord with the manufacturer’s calibrated standards, are presented in Fig. 3. These silicon photovoltaics are designed for efficient photovoltage under concentrated insolation ($h_{\text{solar}} = 26.3\%$ at 50 sun). Superimposed on the photovoltaic response curves in the figure are the water electrolysis current densities for one, or two series interconnected, 500°C molten NaOH single compartment cell configuration electrolyzers.

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3. Theory of electrochemical thermal solar/H₂ energy conversion

Photodriven charge transfer through a semiconductor junction does not utilize photons which have energy below the semiconductor band gap. Hence a silicon photovoltaic device does not utilize radiation below its band gap of \( \sim 1.1 \) eV, while a AlGaAs/GaAs multiple band-gap photovoltaic does not utilize radiation of energy less than the 1.43 eV band gap of GaAs. As will be shown, this utilized, available long wavelength insolation represents a significant fraction of the solar spectrum. This long wavelength insolation can be filtered and used to heat water prior to electrolysis. The thermodynamics of heated water dissociation are more favorable than that room temperature. This is expressed by a free energy chemical shift and a decrease in the requisite water electrolysis potential, which can considerably enhance solar water splitting efficiencies.

The spontaneity of the H₂ generating water splitting reaction is given by the free energy of formation, \( \Delta G_f^\circ \), of water and with the Faraday constant, \( F \), the potential for water electrolysis:

\[
\begin{align*}
H_2O & \rightarrow H_2 + \frac{1}{2} O_2, \quad (1) \\
-\Delta G_{\text{split}}^\circ & = \Delta G_f^\circ (H_2O); \\
\Delta G_f^\circ (25^\circ C, \text{1 bar, } H_2O_{\text{liq}}) & = -237.1 \text{ kJ mol}^{-1}, \quad (2)
\end{align*}
\]

\[
E_{H_2O}^\circ = \Delta G_f^\circ (H_2O)/2F;
\]

\[
E_{H_2O}(25^\circ C, \text{1 bar, } H_2O_{\text{liq}}) = 1.229 \text{ V.} \quad (3)
\]

Reaction 1 is endothermic, and electrolyzed water will cool unless external heat is supplied. The enthalpy balance and its related thermoneutral potential, \( E_{\text{meut}} \), are given by

\[
\begin{align*}
\Delta H_{\text{split}} & = \Delta H_f(H_2O_{\text{liq}}); \\
\Delta H_f^\circ (25^\circ C, \text{1 bar, } H_2O_{\text{liq}}) & = -285.8 \text{ kJ mol}^{-1}, \quad (4)
\end{align*}
\]

\[
E_{\text{meut}} \equiv -\Delta H_f(H_2O_{\text{liq}})/2F;
\]

\[
E_{\text{meut}}(25^\circ C, \text{1 bar, } H_2O_{\text{liq}}) = 1.481 \text{ V.} \quad (5)
\]

The water electrolysis rest potential, Eq. (3), is determined from extrapolation to ideal conditions. Variations of the concentration, \( c \), and pressure, \( p \), from ideality are, respectively, expressed by the activity (or fugacity for a gas), as \( a = \gamma c \) (or \( \gamma p \) for a gas), with the ideal state defined at 1 atm for a pure liquid (or solid), and extrapolated from \( p = 0 \) or for a gas or infinite dilution for a dissolved species.

As noted in Table 1, the critical point of water is 374°C and 221 bar. Below the boiling point, \( E_{H_2O}^\circ \) is similar for 1 bar and high water pressure, but diverges sharply above these conditions. Values of \( E_{H_2O}^\circ \) include at \( p_{H_2O} = 1 \) bar: 1.229 V(25°C), 1.167 V(100°C), 1.116 V(300°C), 1.034 V(600°C), 0.919 V(1000°C), 0.771 V(1500°C), and at \( p_{H_2O} = 500 \) bar: 1.224 V (25°C), 1.163 V(100°C); 1.007 V(300°C); 0.809 V(600°C); 0.580 V(1000°C). Due to overpotential losses, \( \zeta \), the necessary applied electrolysis potential is

\[
V_{H_2O}(T) = E_{H_2O}^\circ (T) + \zeta_{\text{anode}} + \zeta_{\text{cathode}} \\
\equiv (1 + \zeta)E_{H_2O}^\circ (T). \quad (8)
\]
The table of thermodynamic free energy and enthalpy of water formation for (a) all constituents at 1 bar, and (b) 500 bar water and 1 bar H2 and O2.

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The 1 bar values are calculated from data in Ref. [15] and the 500 bar values are from Ref. [16].

The water electrolysis potential energy conversion efficiency occurring at temperature, \(T\), is \(\eta_{echem}(T) = E_{f H_2O}(T)/V_{H_2O}(T)\). Solar water splitting processes utilize ambient temperature water as a reactant. An interesting case occurs if heat is introduced to the system; that is when electrolysis occurs at an elevated temperature, \(T\), using water heated from 25°C. The ratio of the standard potential of water at 25°C and \(T\), is \(r = E_{f H_2O}(25°C)/E_{f H_2O}(T)\). As shown in Fig. 4, \(E_{f H_2O}(T)\) diminishes with increasing temperature, as calculated using contemporary thermodynamic values summarized in Table 1 [18,19]. In this case, an effective water splitting energy conversion efficiency of \(\eta'_{echem} > 1\) can occur, to convert 25°C water to H2 by electrolysis at \(T\):

\[
\eta'_{echem} = r\eta_{echem}(T) = rE_{f H_2O}(T)/V_{H_2O}(T) = E_{f H_2O}(25°C)/V_{H_2O}(T). \tag{9}
\]

For low overpotential electrolysis, \(V_{H_2O}(T > 25°C)\) can be less than \(E_{f H_2O}(25°C)\), resulting in \(\eta_{echem} > 1\) from Eq. (9). Whether formed with pn or Schottky type junctions, the limiting, energetic constraints on photovoltaic (solid state) driven electrolysis are identical to those for photo-electrochemical water splitting, although the latter poses additional challenges of semiconductor/electrolyte interfacial instability, area limitations, catalyst restrictions, and electrolyte light blockage. The overall solar energy conversion efficiency of water splitting is constrained by the product of the available solar energy electronic conversion efficiency, \(\eta_{phot}\), with the water electrolysis energy conversion efficiency [9]. For solar photothermal water electrolysis, a portion of the solar spectrum will be used to drive charge transfer, and an unused, separate portion of the insolation will be used as a thermal source to raise ambient water to a temperature \(T\):

\[
\eta_{solar} = \eta_{phot}\eta_{echem} = \eta_{phot}[E_{f H_2O}(25°C)/E_{f H_2O}(T)][E_{f H_2O}(T)/V_{H_2O}(T)] = \eta_{phot}1.229/V_{H_2O}(T). \tag{10}
\]

Conditions of \(\eta_{solar} > \eta_{phot}\) will be shown to place specific restrictions on the photosensitizer. When \(V_{H_2O} < E_{neut}\), heat must flow to compensate cooling which occurs at the electrolysis rate, that is, for an enthalpy balanced system any additional required heat must flow in a flux.
photoelectrolysis system can contain multiple photo harvesting units and electrolysis units, where the ratio of electrolysis to photovoltaic units is defined as $R$. Efficient water splitting occurs with the system configured to match the water electrolysis and photopower maximum power point. This is illustrated in Fig. 5 representing the photosensitizers as power supplies driving electrolysis with a photodriven charge from a photon flux to generate a current compared to Cases I, III and IV, splitting the same equivalents of water. For solar driven charge transfer, this maximum power is described by the product of the insolation power, $P_{\text{sun}}$, with $\eta_{\text{phot}}$, which is then applied to electrolysis, $\eta_{\text{phot}}P_{\text{sun}} = P_{\text{chem}} = \eta_{\text{chem}}H_2O$. Rearranging for $H_2O$, and substitution into Eq. (11), yields for heat balanced solar electrolysis at conditions of $T$ and $p$, initiating with $25^\circ C$, 1 bar water:

$$E_{\text{net}} = 1.481 \text{ V}$$

$$= V_{H_2O}(T, p)(1 + P_{\text{heat}}/\eta_{\text{phot}}P_{\text{sun}}).$$

Fig. 6 presents the available insolation power, $P_{\text{sun}}$ (mW cm$^{-2}$) of the integrated solar spectrum up to a minimum electronic excitation frequency, $\nu_{\text{min}}$(eV), determined by integrating the solar spectral irradiance, $S$(mW cm$^{-2}$ nm$^{-1}$), as a function of a maximum insolation wavelength, $\lambda_{\text{max}}$(nm). This $P_{\text{sun}}$ is calculated for the conventional terrestrial insolation spectrum either above the atmosphere, AM0, or through a 1.5 atm pathway, AM1.5. Relative to the total power, $P_{\text{sun}}$, of either the AM0 or AM1.5 insolation, the fraction of this power available through the insolation edge is designated $P_{\text{rel}} = P_{\text{sun}}/P_{\text{sun}}$. In solar energy balanced electrolysis, excess heat is available primarily as photons without sufficient energy for electronic excitation. The fraction these sub-band-gap photons in insulation is $\eta_{\text{heat}} = 1 - P_{\text{rel}}$, and comprises an incident power of $\eta_{\text{heat}}P_{\text{sun}}$.

Fig. 7 presents the variation of the minimum electronic excitation frequency, $\nu_{\text{min}}$ with $\eta_{\text{heat}}$, determined from $P_{\text{rel}}$ using the values of $P_{\text{sun}}$ summarized in Fig. 6. A semiconductor sensitizer is constrained not to utilize incident energy below the band gap. As seen in Fig. 7 by the intersection of the solid line with $\nu_{\text{min}}$, over one third of insolation power occurs at $\nu_{\text{min}} < 1.43$ eV (867 nm), equivalent to the IR not absorbed by GaAs or wider band-gap materials. The calculations include both the AM0 and AM1.5 spectra. In the relevant visible and IR range from 0.5 to 3.1 eV ($\pm 0.03$ eV) for both the AM0 and AM1 insolation spectra, $\nu_{\text{min}}(\eta_{\text{heat}})$ in the figure are well represented ($R^2 \geq 0.999$) by the polynomial fits:

$$\nu_{\text{AM0}, \text{eV}} = 0.53008 + 3.1405z_{\text{heat}}$$

$$- 3.0687z_{\text{heat}}^2 + 2.9103z_{\text{heat}}^3,$$
When captured at a thermal efficiency of $\eta_{\text{heat}}$, the sub-band-gap insolation power is $\eta_{\text{heat}}\Delta\eta_{\text{heat}}P_{\text{sun}}$. Other available system heating sources include absorbed super-band-gap photons which do not effectuate charge separation, $P_{\text{recomb}}$, and non-insolation sources, $P_{\text{amb}}$, such as heat available from the ambient environment heat sink, and $P_{\text{recov}}$, such as heat recovered from process cycling or subsequent $H_2$ fuel utilization. The power equivalent for losses, such as the low power consumed in delivering the heated water to electrolysis, $P_{\text{pump}}$, can also be incorporated. Together these comprise the power for heat balanced electrolysis, which with $P_{\text{heat}}$ from Eq. (12) yields $\alpha_{\text{heat}}$:

$$P_{\text{heat}} = \eta_{\text{heat}}\Delta\eta_{\text{heat}}P_{\text{sun}} + \beta;$$

$$\beta = P_{\text{recomb}} + P_{\text{amb}} + P_{\text{recov}} - P_{\text{pump}},$$

$$\alpha_{\text{heat}} = \left[\frac{\eta_{\text{photon}}}{\eta_{\text{heat}}}\right]\left\{1.481 \frac{V}{(1 + \zeta)}E_{\text{H}_2O}^{\Delta h} - 1\right\} - \frac{\beta}{(\eta_{\text{heat}}P_{\text{sun}})}.$$

For solar electrolysis at $T$ and $p$, a minimum insolation energy, $v_{\text{min}}$, leaves available for transmittance the requisite thermal energy. This constrains the minimum electronic excitation energy and the band gap, $E_{g_{\min}}$, which is determined from Eqs. (13) and (14) using $\alpha_{\text{heat}}$ values estimated.
Fig. 6. The solar irradiance (mW cm$^{-2}$ nm$^{-1}$) in the figure inset, and the total insolation power (mW cm$^{-2}$) in the main figure of the solar spectrum.

Fig. 7. $\eta_{\text{heat}}$, the fraction of solar energy available below the minimum sensitizer insolation frequency used to drive charge transfer, $v_{\text{min}}$. $\eta_{\text{heat}}$ is determined as $1-P_{\text{rel}}$, with $P_{\text{rel}} = P_{\text{max}}/P_{\text{sun}}$, and using values of $P_{\text{max}}$ summarized in Fig. 3. The available incident power below $v_{\text{min}}$ will be $\eta_{\text{heat}} P_{\text{sun}}$. The band gaps of various semiconductors are superimposed as vertical lines in the figure.

From Eq. (16):

$$E_{g-\text{min}} = v_{\text{min}}(P_{\text{sun}}, \eta_{\text{heat}}),$$

$$\eta_{\text{heat}}(T, p) \approx (\eta_{\text{phot}}/\eta_{\text{heat}})((1.481 \text{ V}/E_{H_{2}O}(T, p)) - 1),$$

$$E_{g-\text{min}}(\text{AM0}), \text{eV} = 0.53008 + 3.1405 \eta_{\text{heat}} - 3.0687 \eta_{\text{heat}}^2 + 2.9103 \eta_{\text{heat}}^3 - 5.1286 \eta_{\text{heat}}^2 + 3.8980 \eta_{\text{heat}}^3.$$  \hspace{1cm} (17)

A value of $\zeta = 0$ will overestimate, and $\beta = 0$ will underestimate, $\eta_{\text{heat}}$ in Eq. (16) as presented in Eq. (17). Contemporary commercial alkaline water electrolysis cells exhibit overall $\zeta \approx 0.15$ [20], and large surface areas alkaline electrolysis cells sustain $\zeta < 0.05$ [9]. Furthermore, $\zeta$ tends to diminish with increasing $T$, facilitating $H_{2}O$ which approach $E_{H_{2}O}$ at elevated temperatures, and consistent with the rigorous upper limit for the solar electrolysis efficiency from Eq. (10):

$$\eta_{\text{solar-max}}(T, p) = 1.229 \eta_{\text{phot}}/E_{H_{2}O}(T, p).$$  \hspace{1cm} (18)

In Figs. 8–11, determinations of the solar water splitting energy conversion are summarized, as calculated from Eq. (18) using the $E_{H_{2}O}(T, p)$ data in Fig. 4, and for various
Fig. 9. The energy conversion efficiency of solar driven water splitting to generate H2 as a function of temperature at AM1.5 insolation, with the system minimum band-gap determined at \( p_{H_2O} = 500 \) bar. The maximum photoelectrolysis efficiency is determined from Eq. (18) for various indicated values of \( \eta_{\text{phot}} \). The system minimum band-gap is determined from Eq. (17) for various indicated values of \( \eta_{\text{phot}} \) and \( \eta_{\text{heat}} \).

Solar water splitting system’s minimum allowed band gap, \( E_{g}\text{min}(T, p) \) from Eq. (17) for a wide temperature range. Figs. 8 and 9, or 7 and 10, are, respectively, modeled based on AM1.5, or AM0, insolation. Figs. 8 and 10 are calculated, at various temperatures for \( p_{H_2O} = 1 \) bar; while Figs. 9 and 11 repeat these calculations for \( p_{H_2O} = 500 \) bar. In Fig. 9, compared to Fig. 8, the rate of increase in temperature of \( \eta_{\text{solar-max}} \) is significantly greater for higher pressure photoelectrolysis (\( p_{H_2O} = 500 \) bar). However as seen comparing the minimum band-gap in these figures (or in Figs. 10 and 11 in the analogous AM0 models), at these higher pressures this higher rate of efficiency increase with temperature is offset by lower accessible temperatures (for a given band gap). Larger \( \zeta \) in \( V_{H_2O} \) will diminish \( \eta_{\text{solar}} \), but will extend the usable small band-gap range. Together, Figs. 8–11, determine the constraints on \( \eta_{\text{solar}} \) from various values of \( \eta_{\text{phot}} \). The high end of contemporary experimental high solar conversion efficiencies ranges from 100% \( \eta_{\text{phot}} = 19.8\% \) for multicrystalline single junction photovoltaics, to 27.6% and 32.6% for single-junction and multiple-junction photovoltaics [21]. The efficiency of solar thermal conversion tends to be higher, than solar electrical conversion, \( \eta_{\text{phot}} \), particularly in the case of the restricted spectral range absorption used here; and values of \( \eta_{\text{heat}} = 0.5, 0.7 \) or 1 are utilized for Eq. (17). While a small band gap, \( E_g < 1.23 \) eV, is insufficient for water cleavage at 25°C, its inclusion in Figs. 8–11 is of relevance in two cases, (i) where high temperature decreases \( V_{H_2O}(T) \) below \( E_g \) and (ii) where this \( E_g \) is part of a multiple band-gap sensitization contributing a portion of a larger overall photopotential. It is also noted that \( E_g > 3.0 \) eV is inadequate for an efficient use of the solar spectrum.

4. Solar/H₂ electrochemical thermal conversion efficiencies

Representative results from Fig. 11 for solar water splitting to H₂ systems from AM1.5 insolation include a 50% solar energy conversion for a photoelectrolysis system at 638°C with \( p_{H_2O} = 500 \) bar; \( p_{H_2} = 1 \) bar and \( \eta_{\text{phot}} = 0.32 \).
5. Available solar/H₂ electrochemical thermal components

Without inclusion of high temperature effects, we had already experimentally achieved η_{solar} > 0.18, using an η_{phot} = 0.20 AlGaAs/Si system [10]. Existing, higher η_{phot} (=0.28–0.33) systems should achieve proportionally higher results, and inclusion of heat effects and the elevated temperature decrease of the water electrolysis potential will lead to even higher values of solar energy to H₂ fuel conversion efficiencies.

Experimental components, for example as described in Scheme 2, of efficient solar driven generation of H₂ fuel at 40–50% solar energy conversion efficiencies appear to be technologically available. In the 50% range efficiencies photoelectrochemical cells tend to be unstable, which is likely to be exacerbated at elevated temperatures, and the model system will be particularly conducive to photovoltaic, rather than photoelectrochemical, driven electrolysis. The photovoltaic component is used for photodriven charge into the electrolysis component, but does not contact the heated electrolyte. In this case the high efficiencies appear accessible, stable photovoltaics are commonly driven with concentrated insolation [20] and specific to the system model here, heat will be purposely filtered from the insolation prior to incidence on the photovoltaic component.

Dielectric filters used in laser optics split insolation without absorption losses. For example, in a system based on a parabolic concentrator, a casegrain configuration may be used, with a mirror made from fused silica glass with a dielectric coating acting as band pass filter. The system will form two focal spots with different spectral configuration, one at the focus of the parabola and the other at focus of the casegrain. The thermodynamic limit of concentration is 46.000 suns, the brightness of the surface of the sun. In a medium with refractive index greater than one, the upper limit is increased by two times the refractive index, although this value is reduced by reflective losses and surface errors of the reflective surfaces, the tracking errors of the mirrors and dilution of the mirror field. Specifically designed optical absorbers, such as parabolic concentrators or solar towers, can efficiently generate a solar flux with concentrations of ~2000 suns, generating temperatures in excess of 1000°C [23,24].

Commercial alkaline electrolysis occurs at temperatures up to 150°C and pressures to 30 bar [20], and super-critical electrolysis to 350°C and 250 bar [25]. Although less developed than their fuel cell counterparts which have 100 kW systems in operation and developed from the same oxides [26], zirconia and related solid oxide based electrolytes for high temperature steam electrolysis can operate efficiently at 1000°C [27,28], and approach the operational parameters necessary for efficient solar driven water splitting. Efficient multiple band-gap solar cells absorb light up to the band gap of the smallest band-gap component. Thermal radiation is assumed to be split off (removed and utilized for water
heating) prior to incidence on the semiconductor and hence will not substantially affect the band gap. Highly efficient photovoltaics have been demonstrated at a solar flux with a concentration of several hundred sun. AlGaAs/GaAs has yielded at $\eta_{\text{phot}}$ efficiency of 27.6%, and a GaInP/GaAs cell 30.3% at 180 suns concentration, while GaAs/Si has reached 29.6% at 350 suns, InP/GaInAs 31.8%, and GaAs/GaSb 32.6% with concentrated insolation [21].

Solar energy driven water splitting combines several attractive features for energy utilization.

6. Summary

The energy source (sun) and reactive media (water) for solar water splitting are readily available and are renewable, and the resultant fuel (generated $\text{H}_2$) and its discharge product (water) are each environmentally benign. The model presented here provides theoretical evidence that the combination of contemporary efficient multiple band-gap photovoltaics and concentrated excess sub-band-gap heat will combine into highly efficient elevated temperature solar electrolysis of $\text{H}_2$ fuel. Efficiency will be further enhanced by excess super-band-gap and non-solar sources of heat, but diminished by losses in polarization and photo-electrolysis power matching. Solar concentration can provide the high temperature and diminish the requisite surface area of efficient electrical energy conversion components, and high temperature electrolysis components are available. The theory and initial results presented provide evidence their combination into highly efficient solar generation of $\text{H}_2$ will be attainable.

References