A comparison of PV/electrolyser and photoelectrolytic technologies for use in solar to hydrogen energy storage systems

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Abstract

The approach of using hydrogen for an energy store to offset seasonal variations in solar energy is one very much at the periphery of current renewable energy system design. Nonetheless, its inherent advantages for long term storage in stand alone power systems warrant further detailed investigation. This paper provides a comparative overview of the very disparate technologies within two generic approaches to achieving this goal. These are: photovoltaic (PV) powered electrolysis of water and direct photoelectrolytic (PE) generation of hydrogen from water. Comparison of these is difficult, however, the paper compares devices of similar material system and structure within each generic scheme. PV/electrolysis is the more mature technology but there is still a wide range of potential 'solar to hydrogen' efficiencies. A figure of about 9% is estimated for comparison, with justification given. The comparative figure for PE is more difficult to judge because of even more disparate approaches to specific problems of sufficient photovoltage and stability, but an approximate comparative figure of 5% is estimated. Thus making PV/electrolysis more appropriate at present. Nonetheless, inherent advantages of simplicity of system design and potential robustness mean that PE may become more appropriate as the technology develops.

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1. Introduction

The amount of solar energy that strikes the Earth in a period of a few days is greater than the amount of fuel burnt over the whole course of human history [1]. However, one of the barriers to widespread implementation is that the solar resource is variable and this leads to problems when matching to approximately constant electricity demand in a stand alone power system (SAPS). The diurnal and weather variability can be met by short term battery storage, but this is only sufficient for up to several days of bad weather. In order to cope with long term seasonal variations, an energy storage medium with greater longevity is required. The splitting of water (H₂O) to generate hydrogen (H₂) can be used as such a medium, with potential for very low

greenhouse gas and particulate emissions both on generation and re-use.¹

Solar hydrogen is described as a potential energy storage medium to offset the seasonal variability of solar energy (e.g. [3–5]). Currently, photovoltaic (PV) systems for SAPS in a remote area rely on batteries for storage of electrical energy. While there are several disadvantages to using batteries [6], there is often no alternative in an off-grid application. In a SAPS system with no backup generator, perhaps the greatest disadvantage of batteries is their requirement to be sized for the month with the lowest solar radiation in order to have a loss of load probability of close to zero. This month is typically, but not always, in winter, and the resulting system is oversized for the majority of the year, thereby increasing system costs significantly.

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¹ This is only true if the hydrogen is generated by a primary energy source that is non-greenhouse gas emitting, such as renewable energy [2].

A system that can store energy generated in excess of the requirement of the load in summer and release this energy for use when the system is insufficient to supply the load in the winter, would allow system sizing for the *average* rather than the *worst* month and hence could significantly reduce system size and hence cost. This effect is particularly apparent for systems at high latitudes where the difference in solar insolation between summer and winter months is most marked [7].

Hydrogen storage systems can in principle achieve the required long term seasonal energy storage for such a scheme. The key aspect is the mechanism for conversion of incident solar radiation into molecular hydrogen for storage. This paper compares the technologies available to achieve. These technologies are considered in two generic approaches: PV cells used to electrolyse water and photoelectrolytic (PE) cells used to directly generate hydrogen from water using sunlight.

The work does not discuss hydrogen storage technologies themselves as these are many and varied and beyond the scope of the paper. Instead a generic efficiency of 50% is assigned for the efficiency of re-extraction of energy from such storage. This figure is a generally accepted one in the literature and is discussed in a little more detail, with references, in Section 3.3.

2. System comparisons

For the purposes of comparison, the two generic technologies are considered as two systems as shown in Figs. 1 and 2.

The two generic approaches considered cover technologies that differ markedly. They share hydrogen as the energy store but differ in the way it is produced—PV/electrolysis and direct photoelectrolysis production, respectively. These technologies vary in their levels of maturity; hence it is difficult both to choose appropriate technologies for comparison and to compare these technologies with very different characteristics. With these caveats in mind and with the goal of achieving a reasonable, at least approximately quantitative comparison, certain

Fig. 2. Case B: schematic of PE/H₂ storage system.

common properties for the systems have been assumed. These include:

- The sole primary energy source for each system is solar power.
- The same and a constant electrical load is used for each system. For this work a figure of 10.7 kWh/day was used from the literature [8], although the value is not critical for the comparison.
- The hydrogen storage and re-use technologies are considered to be the same for each generic system for comparison. Detailed discussion of the collection, storage and re-use technologies is beyond the scope of this paper. A generic efficiency for all these processes of 50% is used in calculations, see Section 3.3.
- The hydrogen system is required to supply the same number of days of autonomy for each system. This includes coverage due to short term fluctuations such as cloud cover and variations in energy collected due to seasonal variation. The latter will depend primarily on latitude.

The following sections consider each of the two generic approaches in turn with descriptions of the technologies involved, including reasons for the particular choices made in light of the above considerations.

3. Case A: PV/electrolyser with H₂ storage

The system envisaged here uses the electricity from PV modules coupled to an electrolyser to generate hydrogen (H₂) and oxygen (O₂) from water. This scenario requires a PV module array, an electrolyser, a H₂ storage facility and plant for re-conversion of the H₂ into electricity.

3.1. Summary of PV technologies

There is a large range of technologies that could be considered. These technologies vary significantly in production volume, efficiency, and price. A partial list of these is shown in Table 1.

3.1.1. Crystalline silicon solar cells [13,14]

Silicon is a benign material which is sourced from abundant raw materials. However, processing of very high purity single crystal and multicrystalline material is energy and time intensive. The technology currently faces a feedstock problem as its

Fig. 1. Case A: schematic of PV/electrolyser system.

Table 1
Photovoltaic cell types and one-sun efficiencies (at air mass 1.5 global) [9]

PV technology	Efficiency, η (%)	
	Laboratory-grade cells (%)	Production ^a /max module
<i>Crystalline silicon technologies</i>		
Monocrystalline (c-Si)	24.7	13–17.7% [10]/22.7%
Multicrystalline (mc-Si)	20.3	12–13.5%/15.3%
<i>Some examples of thin film solar cells</i>		
Amorphous (a-Si)	9.5	~ 5%
Crystalline thin film silicon	16.6	~8.2%
Cadmium telluride (CdTe)	16.5	9.6% [11]/10.7%
Copper indium gallium diselenide (CIGS)	18.4	11.0% [12]/13.4%
Dye-sensitised titanium dioxide (TiO ₂)	10.4	4.7% (sub-module)
<i>Multijunction tandem solar cells</i>		
III–V multijunction (236× concentration) (low aerosol optical depth direct spectrum)	39.0	~27% (sub-module, 10×)
Amorphous (a-Si) multijunction	12.1	~ 6%/10.4%

^aSeveral technologies are not in full production and only module/submodule efficiencies are available.

volume increase means that it is emerging from its prior position as a by-product of the silicon electronics industry. However, this feedstock problem is expected to be short lived as the industry matures further. The most extensively produced and used PV modules are standard multicrystalline silicon (mc-Si) modules, which represent a significant fraction of the world PV market (52% in 2005). Monocrystalline silicon (c-Si) modules are the next most extensively used technology (38% in 2005). Defect density for c-Si is low and hence efficiency is high. For mc-Si defect densities are higher and hence efficiency lower.

3.1.2. Thin film technologies [13,15]

These technologies aim to use low temperature, and hence low energy intensive, processes for deposition of thin semiconductor layers. The processes include evaporation, chemical vapour deposition and sputtering and have relatively low embodied energy and economic costs. The processes are also able to scale for large scale production and as they deposit on foreign cheap substrates (often glass), offer the potential for large savings in semiconductor material usage and hence cost. However, the low temperatures of deposition result in imperfect crystallisation or indeed amorphous materials. These have high defect densities and efficiencies are lower than for bulk crystalline silicon solar cells. It also tends to be more difficult to translate laboratory-scale efficiencies to production because of the less well characterised device structures and lack of off-the-shelf equipment from the silicon semiconductor industry.

Amorphous silicon (a-Si) cells have low efficiencies but are cheap to produce and have the largest market share for thin films, 4.7% in 2005. It is necessary to alloy the a-Si with hydrogen to reduce defects densities. Ribbon silicon crystalline techniques have a market share of about 2.9% in 2005. Thin film crystalline silicon cells on glass are just coming into full production and offer much lower potential costs at moderate efficiencies. Other non-silicon thin film crystalline materials include compounds of the group II and group IV elements, such

as cadmium telluride (CdTe), (1.6% market share in 2005). These have higher efficiencies but use toxic Cd compounds. The chalcopyrite analogues of II–VI compounds such as copper indium gallium diselenide (Cu(InGa)Se₂, where a Cu(In,Ga) alloy replaces the group II element), avoid this problem to a large extent, (although a thin window layer of CdS is still used in most designs). Cu(InGa)Se₂ cells produce the highest efficiencies of the thin film approaches (0.2% market share in 2005).

The dye sensitised solar cell (DSC) based on titania is also a thin film technology but is in a rather different category. This is because it is a photoelectrochemical PV technology (see Section 4.1) and uses very cheap material and solution casting techniques at room temperature and pressure. Efficiencies are still low for this technology and it is not yet in full production. However, there are reports of laboratory-scale devices with almost 11% efficiency [16].

3.1.3. Multijunction tandem solar cells [14,15]

All of the devices discussed above use a single PV p–n junction and thus have to compromise their photon absorption edge (or energy band gap) to maximise the product of voltage and current in their absorption of the broad solar spectrum. Multijunction or tandem cells avoid this problem by using two or more p–n junctions, of different energy band gaps, arranged on top of each other. Thus each junction absorbs a different narrower ‘slice’ of the solar spectrum more optimally. The addition of outputs from the two junctions for the same area then gives a higher power and hence higher efficiency.

The most efficient devices are those based on two or three separate p–n junction solar cells connected in series but grown in a monolithic structure from lattice matched III–V compounds such that the whole tandem cell is a single crystal. For example the structure could be a triple junction gallium indium phosphide (GaInP)/gallium arsenide (GaAs)/germanium (Ge) cell. Such devices have very low defect densities and hence very high efficiencies but are very expensive as they use relatively

exotic materials and expensive epitaxial growth techniques. For this reason, these devices are most commonly used either in space or in concentrator applications, where cost of the solar cell is a smaller proportion of the system cost.

An alternative approach is still to use a tandem solar cell but to use thin film a-Si and amorphous Si:Ge alloys. Both double and triple junction devices are made, such as the a-Si/a-Si:Ge cell. As the materials are deposited by thin film techniques the cells are much cheaper than III–V cells but also the overall cell is much less efficient because of much higher defect densities.

In summary, the range of PV technologies is very wide but as the most widely used technology is multicrystalline Si cells at a production efficiency of about 13.5%, these are assumed for the generic discussion for the rest of Section 3 and the comparisons in Sections 5 and 6.

3.2. Electrolysis

A generic electrolyser efficiency is calculated by a standard potential used of 1.9 V. This ‘voltage efficiency’ being the ratio of the water redox potential at 1.23 V to the standard potential =65%.^{2,3} This is in agreement with quoted values of ~ 67% for electrolysis [20].

The advantages of electrolysis at elevated temperature should also be mentioned. With increasing temperature the voltage required to split water decreases from 1.23 V at 300 K to 0 V at greater than 2000 K where water dissociates spontaneously without need for an applied voltage. For instance, conventional or alkaline water electrolysis proceeds at typically 80 °C whilst solid polymer electrolysis can proceed at up to 120 °C. At these temperatures there is not any significant reduction to the voltage required at room temperature and efficiencies are around 65–70%.⁴ However, for high temperature steam electrolysis at 800–900 °C, using solid electrolytes based on zirconia and yttria, the voltage can be reduced significantly and the efficiency should increase to over 90% [4,17,18,21,22, p. 210].

3.3. H₂ storage

The hydrogen is assumed to be collected, stored and re-used at a later date but no discussion of these details is attempted, as this is beyond the scope of the paper. A generic efficiency for all these processes of 50% is used in calculations. This is thought to be reasonable from the literature, there are differences in compression, liquification or other compacting efficiencies but these tend to be balanced by differences in boil off or other storage loss mechanism efficiencies or differences in efficiencies from the various combustion, fuel cell or other

re-use technologies [4,5,14,21]. Even if the 50% figure is open to some doubt, the question applies equally to PV/electrolysis as to PE. This figure of 50% is likely to improve in the future.

Since hydrogen storage can smooth out seasonal fluctuations, the PV panels can be tilted at the latitude angle for the best year-round performance. Therefore, the PV array is sized using the *yearly average* peak sunshine hours (PSH_{yearly}) rather than the *worst month* PSH_{worst} values that would have to be used in a system without seasonal storage such as a PV/battery system. The former can be significantly greater. For instance, PSH_{yearly} is 49% and 83% higher than PSH_{worst} for latitudes of 38°S and 55°S, respectively [23]. (The latitudes of Melbourne in Australia and Macquarie Island in the Southern Ocean, respectively.⁵) Thus reducing the number of PV modules required at each latitude by 33% and 45%, respectively—a significant saving.

3.4. PV/electrolysis system based SAPS

Currently there would appear to be several advantages for a SAPS based on PV generation, whether the energy is stored as electrical energy or as hydrogen including:

- PV is a developed technology with module efficiencies ranging from 5 to almost 18% (or even higher for technologies currently at the laboratory stage) depending on the exact technology chosen.
- PV modules contain no moving parts and are sold with a warranty that guarantees the power generation for typically 25 years.
- PV modules are an ideal power supply for an electrolyser. The output voltage of a PV array is DC and is roughly constant with illumination level, it is mainly the current that varies with illumination. This is a good match to the electrolyser, which requires a constant voltage of at least 1.9 V_{DC} (for the generic electrolyser considered). Increasing PV current would increase the overall volume of hydrogen produced, although it would also slightly lower the production efficiency [18].
- PV modules can be mounted on roofs, incurring much lower installation costs (termed balance of system (BOS) costs).
- Depending on the amount of maintenance required for the electrolyser, it may be practical to place the zero-maintenance PV modules out of the way on the roof, whilst keeping the electrolyser readily accessible for maintenance.
- This separation could also be used to exploit the lower voltage required for electrolysis at higher temperatures discussed above, by keeping the electrolyser at a high temperature. PV module efficiency decreases with temperature, hence they would benefit from cooling rather than heating. (Modules on the roof are difficult to keep cool but nonetheless the physical separation from the electrolyser can be an advantage.)

² The standard potential for a noble metal electrode is around 1.8–1.9 V, e.g. Pt = 1.8 V. For base metals the potential increases to 2.1 V. The unavoidable thermodynamic loss is ~ 0.37 V giving a limit of 1.6 V, and an in principle limiting efficiency of 77% [17, Bolton p. 200; 18].

³ Non-unity electrolysis ‘current efficiency’ is not considered here as it depends on a large number of factors [17,18]. This is not too gross an assumption as ‘current efficiency’ can be > 90% [19].

⁴ These efficiencies are ‘lower heating values’, i.e. they do not count the heat energy in the hot water used or produced.

⁵ Or roughly equivalent to Washington (38°N) and southern Hudson Bay (55°N) in the northern Americas or to Athens or Lisbon (38°N) and Belfast or Moscow (55°N) in Europe.

- Since the sizing of the PV panels is relatively independent of the amount of storage required, once the electrolyser, hydrogen storage and re-use technology is sufficiently developed these could be used to replace the batteries in existing SAPS. As batteries need to be replaced every 5–10 years on average, there is great potential for retrofitting existing systems, although the greatest cost advantage would be achieved by installing the electrolyser in the beginning.⁶

4. Case B: PE (photoelectrolysis) for direct solar to H₂ production

The concept in this case is to use PE cells that are able to use sunlight to directly disassociate water into H₂ and O₂, thus avoiding the intermediary electrical energy conversion stage of the PV-electrolyser system. Thus this route replaces the PV modules and electrolyser of Case A with a PE array.

The same H₂ storage and re-conversion facility is required as in Case A, Section 3.3.

Because of the earlier state of maturity of photoelectrochemical as compared to PV cells, the following sections review the generic approaches to direct solar to hydrogen conversion. There is a summary of PE efficiencies roughly comparable with PV technologies in Section 4.2.

4.1. Photoelectrochemical cells

Photoelectrochemical (PEC) cells absorb photons of light in a semiconductor and use the energy to enable a redox chemical reaction in an electrolyte. If the net products and reactants of the reaction are unchanged the device is termed PV and generates electricity just as does its solid state analogue. If there is a net change in reactants/products the device is termed either: photoelectrolytic (PE) for an endothermic reaction requiring energy input; or photocatalytic where the energy is just used to overcome an activation energy in an exothermic reaction [17, Nozik A p. 272; 15, p. 531]. Here we are concerned with splitting H₂O into H₂ and $\frac{1}{2}$ O₂. This is an endothermic reaction in which solar energy is 'stored' in the more energetic H₂ that is produced. Hence we are concerned with PE cells. There are two redox couples involved in the reaction: $\text{H}_2\text{O} + 2\text{h}^+ \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2$ at the anode and $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ at the cathode [15, p. 533; 24]. PE technology is at a very early stage so it is difficult to predict which is likely to be the most appropriate, therefore various types of PE cell are considered below.

4.2. Photoelectrolysis (PE)

Only a very few materials generate sufficient photovoltage to split water. These include strontium titanate (SrTiO₃) and potassium tantalate (KTaO₃), however, the band gap of these materials is very high ($E_g > 3.2$ eV) and hence the efficiency of

the PE process in sunlight is very low, on the order of about ~1% [3,15,19,24,17, p. 184]. Other materials with lower band gaps have higher efficiencies but produce lower voltages than the 1.23 V+ overvoltage required to split water. For instance, gallium arsenide (GaAs) has a high efficiency but only produces 1 V, while TiO₂ and Si similarly only produce 0.7 V. These voltages can be boosted by one of the three schemes shown in Fig. 3.

The external bias source (Fig. 3a) is the most straightforward. If this is provided by a PV cell the system retains its advantageous properties of only using renewable energy and stand alone operation. But the PV cell has to be illuminated in addition to the PE cell, and this adds to the overall area required for collection of solar radiation. However, as the PE cell is low efficiency and the PV cell high efficiency in comparison (even for a low efficiency PV cell) this area increase is not large. The chemical bias option (Fig. 3b) is another workable solution, but the pH on each side of the membrane seeks to equalise, so the bias needs replenishing and this requires an external power source [24–26].

The tandem cell approach (Fig. 3c) is the most elegant solution, as it provides the extra bias in the PE cell itself. This cell is more complex, requiring a PV cell of lower band gap under the PE cell and connected to it in series most usually by a tunnel junction. Sunlight of wavelengths too long to be absorbed in the PE cell is transmitted through to the PV cell where it provides a photovoltage that boosts the voltage available for electrolysis. More than one extra tandem cell element may be required to provide this voltage boost. The device is electrically similar to the cell with the externally biased PV cell in Fig. 3a; however, it does require two extra properties. First, the PE cell must be thin enough such that it is transparent to long wavelength light with which to illuminate the PV cell. Second, the current through the whole device (that available for electrolysis) is limited to the smaller of the two currents from the PV tandem cell and the PE cell. Thus the device is best if these currents are equal. Unlike Fig. 3a this current matching cannot be achieved simply by varying the respective areas of the PV and PE cells. Hence the performance of the two cells must be more closely matched than the simple bias situation in Fig. 3a [25,27].

Nonetheless a tandem device is inherently more efficient at collecting the energy of the solar spectrum, also in comparison to a simple bias there are no external wires, thus the system configuration is simpler and potentially more robust. Similarly to the discussion of multijunction cells in Section 3.1.3, the choice of a tandem cell for this tandem PV/PE configuration in Fig. 3c is a compromise between efficiency and cost. A tandem PV/PE cell based on III–V compounds would be similar to the III–V multijunction device described in Section 3.1.3, such as GaInP/GaAs/Ge, with a similar high cost but also high efficiency. Alternatively a thin film device fabricated from amorphous Si and Si:Ge alloys could be used. The structure could be a double or triple junction cell, such as a-Si/a-Si:Ge and would be similar to the amorphous Si based multijunction device described in section 3.1.3, in terms of a lower efficiency but also lower cost. In each case the structure would be such that the

⁶ The drop in re-use efficiency from 85% to 50% on replacing batteries with H₂ storage would be approximately offset by the fact that sizing would be based on PSH_{yearly} rather than PSH_{worst} [7].

Fig. 3. Methods for boosting photovoltage so as to exceed 1.23 V and thus allow water splitting.

Table 2
Photoelectrolytic cell efficiencies

	PE technology	Solar to H ₂ efficiency (%)	Ref.
1	III–V high eff. multijunction system, capable of direct splitting of water	15	[25]
2	Amorphous silicon multijunction system, capable of direct splitting	7	[25]
3	TiO ₂ system requiring biasing, either external by a PV cell or internal as a chemical bias	~ 1.5	[24]
4	TiO ₂ with modified properties not requiring a bias: either by dye sensitisation [16]; perhaps with an additional WO ₃ cell [31]; or by modification of the titania surface to reduce its band gap, either non-stoichiometrically or by alloying [30]	~ 4.6	[16,31,30]

high band gap material forms the PE part of the cell in contact with water with the band gap of the materials decreasing for the PV cells connected in series underneath it [25,27,28]. (Hence, in these cases either GaInP/GaAs/Ge or a-Si/a-Si:Ge.)

The other, perhaps critical factor, is that the lower band gap materials for PE cells that give high efficiencies, such as GaAs and amorphous silicon, are not stable under sunlight and photo-degrade, or at best are metastable. They dissolve in the electrolyte via parasitic reactions that are more energetically favourable than photoelectrolysis of water. Increasing the band gap also increases the split in decomposition potentials such that photocorrosion is less favourable than photoelectrolysis thus stopping this photodegradation. Unfortunately the only materials that are stable have large band gaps. These include TiO₂ ($E_g = 3.0$ eV for rutile, $E_g = 3.2$ eV for anatase); SrTiO₄ or KTaO₃ at between 3.2 and 3.6 eV and hence have low photoelectrolysis efficiency. (A large band gap and stability both being due to high ionic bond strength.) In addition, despite its high band gap, the particular line up of the flat band potential for TiO₂ means that the photovoltage it produces is only 0.7 V and hence insufficient to split water [19,24,29]. Nonetheless TiO₂ is very photostable, cheap, and readily deposited as a thin film. Hence, it is often the material of choice in PE cells. Work is continuing to boost both the current it can generate and hence its efficiency and the voltage it can produce [24,30].

4.3. Summary of PE efficiencies

Based on the points in the discussion above four types of PE system are considered as being most appropriate for comparison, as they are deemed the most likely to be developed further. Approximate published efficiencies for each of these are given in Table 2. Because of the immature nature of this technology,

it is likely that these will increase significantly over the next several years.

4.4. PE systems

While it is difficult to predict the most successful materials that will be used for PE H₂ generation, there would seem to be scope for developing the PE technology from a systems perspective as well. In particular, there would appear to be aspects of solar hot water (SHW) and PV technology that could be used to enhance the performance of PE systems. The first consideration here is the optimum angle for solar collection. As previously discussed, the aim of H₂ storage is to smooth out seasonal fluctuations in the solar resource, thereby enabling the collector to be mounted at the latitude angle. There would appear to be no insurmountable barrier to be overcome in order to achieve gas separation if the PE system is operating at an angle. In addition, an estimated 30% boost in total energy collected could be achieved by allowing the collector to track the sun's path across the sky [15], either single-axis (east-west) with a seasonal tilt adjustment, or full two-axis (east-west and azimuth) tracking. One challenge may be with the use of rigid tubing from the PE collector that would restrict the movement of a solar tracker.

Secondly, we can consider that a large area of PE material protected from the environment via a glass cover plate could be similar in appearance to today's flat-plate SHW systems. The SHW manufacturing and field experience may prove extremely valuable in getting the PE technology deployed quickly and more successfully.

Finally, the increased efficiency of electrolysis at elevated temperatures, discussed in Section 3.4, should also be applicable to PE systems [17,18]. Hence, PE cells operated at high

Table 3
Comparison of the two generic system technologies [9]

	PV (%)	Solar to H ₂ (%)	H ₂ system (%)	Comments and Refs.
<i>PV/electrolyser</i>		$PV \times 0.65$	50	
III–V multijunction (1 sun)	32.0	20.8		[14,15]
a-Si multijunction	12.1	7.8		[14,15]
Dye sensitised TiO ₂	8.2	5.3		[9,16,31]
c-Si modules	13.5	8.8		[13]
<i>PE</i>			50	
III–V multijunction		15		[25]
a-Si multijunction		7		[25]
TiO ₂ + bias		1.5		[24]
Modified TiO ₂		4.6		[30,16]

temperatures are an alternative way of avoiding the problem of insufficient photovoltage. However, operation at high temperatures brings with it various material problems in addition to the loss of heat and thus energy, which will decrease efficiency. Nonetheless operation at the moderately higher temperatures experienced in a solar illuminated system is an advantage for such PE cells rather than being the disadvantage it is for PV cells.

5. Comparison: PV/electrolyser with PE for H generation

As can be seen from Table 3 it is difficult to compare like with like because of the range of technologies involved. Nonetheless a few general conclusions can be drawn. The PV and PE technologies presented in Table 3 are selected from Sections 3.1 and 4.3, respectively, on the basis of approximate similarity in material type or cell structure. Thus high quality III–V multijunction PV is compared to III–V multijunction PE, similarly a-Si multijunction or titania based cells for both PV and PE are compared. However, the technologies are often not directly comparable, hence c-Si production PV modules and other types of titania PE device are also included. The former of these is the most likely PV technology to be used in a PV/electrolysis system. A comparable statement cannot be made for the PE technologies because they are all at too early a stage of development.

The relevant parameter is ‘solar to hydrogen’ efficiency within each material type comparison and this is shown for each of the PV/electrolysis and PE approaches.

It can be seen from Table 3 that, within a given material type, the PV/electrolysis technologies tend to give higher ‘solar to hydrogen’ efficiencies than the PE technologies. Whilst there are many assumptions in this result it is an important one and indicates that at present PV/electrolysis is the slightly more successful approach.⁷ The reason for this is that at present PV technology has greater flexibility, uses more stable materials and is more mature. However, the PE approach has aspects that make it attractive as a longer term solution: it is a direct and

hence more elegant approach and it employs systems that are simpler and have fewer components.

6. Discussion

Two generic approaches are considered for the concept of using hydrogen as an energy store for primary solar energy. This is a possible solution to the problem of supplying a constant load using seasonally variable solar energy. The two generic systems are PV modules used to electrolyse water and PE modules used to convert water to hydrogen using solar energy directly.

Several assumptions and caveats are necessary to compare the wide range of possible technologies within the two generic approaches but with this in mind the results of the comparison in Section 5 indicate that PV/electrolysis presently gives higher ‘solar to hydrogen’ efficiencies than photoelectrolytic cells, when comparing cells of similar material and structure.

This varies from 21% (for PV/electrolysis) compared to 15% (for PE) for high quality (and hence expensive) III–V based multijunction designs to about 5% (PV) as compared to about 1.5% or 4% (PE) for titanium dioxide based devices.

For the purposes of comparison of the generic system approaches, Section 5 also shows that at present the best compromise of expense and efficiency for a PV/electrolysis system would use a multicrystalline Si technology and would give a ‘solar to hydrogen’ efficiency of about 9%, and this is likely to be the most appropriate figure to use. If this is coupled to the generic hydrogen re-use efficiency of 50%, the overall efficiency of solar energy collection in the summer and re-use in the winter months is about 4.5%.

An appropriate single efficiency figure for the PE generic approach is much more difficult to pick, because of the lower state of maturity of the technologies, but something around 5% for ‘solar to hydrogen’ efficiency seems approximately comparable—giving about 2.5% for overall efficiency.

There is no other system for solar generation with long term energy storage with which to directly compare these figures. Existing PV systems use the electricity grid as a pseudo-store but to calculate the comparable efficiency for this would be very complex and not very meaningful. Another approach, also often used, is for a PV system with backup diesel generator

⁷ One of these assumptions is the generic electrolysis efficiency of 65%. If this is actually as low as 50% the advantage of PV/electrolysis over PE disappears.

to charge a battery bank in periods of low solar insolation, but calculation of efficiency would again be difficult. A PV system with battery storage only—also not uncommon—would be the most directly comparable technically. The re-use efficiency of such battery storage is about 85% [32]. Coupled to the same PV technology efficiency as above, i.e. 13.5%, this would give an overall efficiency of 11.5%. But although this is a much higher figure than the 4.5% for the PV/electrolysis/hydrogen storage or the 2.5% for PE/hydrogen storage figures calculated above, the battery storage is only applicable over a period of a few weeks at best. Over the seasonal storage periods for which the hydrogen system is appropriate the battery re-use efficiency would drop to 0%. This comparison is explored in greater detail in another paper in this issue by the current authors [7].

This partially quantitative assessment only gives part of the picture. The following is a list of some of the qualitative advantages of each of the two generic systems considered:

PV electrolyser.

- PV is a much more mature technology and hence more easily integrated into systems.
- The electrolyser and PV can be sized independently and located separately.
- Electrolyser and hydrogen storage equipment could be retrofitted to existing PV/battery or even in principle to grid connected PV systems.

Although in the early stages of development, the PE system has potential advantages:

- A PE system comprises fewer parts and is thus theoretically less likely to fail, as long as those parts are reliable.
- A PE H-generation system is conceptually more elegant in its design, requiring no external or internal wiring.
- PE systems could potentially be similar in appearance to today's SHW systems, being mounted on the roof of a residential dwelling. This would require the PE (and more specifically, the separation of gases) to function at angles other than the horizontal.

Finally, it is worth mentioning that this paper does not discuss any economic factors for the systems. This would be difficult enough for the PV with electrolyser technology, which although relatively mature is still at a very early stage in the market place. It would be impossible for PE as all the technologies are at the laboratory stage. There is only scope for two general comments. Firstly that final system costs for either approach will be higher for the higher efficiency approaches that use more exotic materials and structures.⁸ Secondly the fact that a hydrogen seasonal storage system allows system sizing for the *average* month of solar insolation rather than the *worst* month, can allow significant savings in the size of solar array required, whether PV/electrolysis or PE is used, especially at

higher latitudes. An overview analysis of the PV/electrolyser costs compared with PV/battery costs is presented in the other paper in this issue by the current authors [7]. It concludes with an approximate figure that PE systems would need to approach to be comparable.

7. Conclusions

At present PV/electrolysis, as compared to direct photoelectrolysis, is the more appropriate technology with higher efficiency for a 'solar to hydrogen' storage system. This is because of the greater maturity of the former and because the latter has significant challenges to overcome in terms of achieving sufficient PE photovoltage to split water at a high efficiency whilst also being stable. Nonetheless, these problems are likely to be solved in the future and given the greater simplicity, potential robustness and elegance of PE systems, they may overtake PV/electrolysis at some stage. However, whether this can become economically viable will depend on many other factors.

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⁸ Although this does not preclude the actual cost per unit of hydrogen generated being *lower* because of the higher efficiency.

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