Exploiting Sun's Energy Effectively as a Source of Renewable Energy

Deepa Khushalani

Using Sun's energy effectively to drive important, industrially relevant chemical reactions is currently an area of research that is attracting a large attention. This route circumvents our reliance on non-renewable sources of energy and more importantly prevents the release of hazardous pollutants as a byproduct. One such reaction that has a large industrial relevance is the splitting of water to release hydrogen and oxygen. This is a thermodynamically energy intensive reaction, and the most relevant aspect is that hydrogen gas is the product which is being touted as a fuel of the future. Its energy density value is higher than other commercially relevant fuels, and its combustion only produces water as a byproduct with zero carbon footprint. Presented here are the current routes being considered for effective water splitting and the fundamental principles that need to be considered when pursuing new directions in this area.

It is well accepted now that concurrent with the increase in population, India's rapid economic growth has forced us to recognize the challenge of energy supply as nation's top priority. Over the last two centuries, most of our energy needs have been fulfilled by fossil fuel sources – initially coal and then natural gas and petroleum [1]. However, the adverse environmental effects arising from carbon dioxide and other pollutants that are released due to fossil fuel combustion necessitates the search for environmentally clean, renewable energy fuel sources. Several alternate sources of energy such as wind, solar, hydro, and biomass have been explored over the last several decades [2]. Among all these unconventional energy sources, solar energy has emerged as one



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Keywords

Renewable energy, solar energy, photosynthesis, electrolysis, photocatalysis, photovoltaic cell.



It is imperative that we as a society actively engage and make alternative sources of energy the primary thrust. This is vital in order to protect the current and future generations from the adverse health ramifications associated with higher pollution levels.

of the most practical alternatives to conventional non-renewable sources. This is mainly due to the fact that solar energy reaching the Earth from the Sun is massive, i.e., 3×10^{24} J per year or ca. This is 10^4 times more than what the entire human population currently consumes annually [3]. Most importantly, the source of energy is in principle, free and readily available throughout the planet. In fact, the mammoth potential of this energy reservoir has been known and acknowledged by scientists for a very long time. But somehow, even though the fundamental principles by which this energy can be 'harvested' have been known and readily accepted, the practical implementation of those principles in viable devices has not really come to complete fruition. One main reason is the addiction of the human population to easy and wellfounded sources of energy - namely the non-renewables. However, in light of the current situation regarding pollution world over and most importantly, closer to home, with the pollution levels of Delhi and other major Indian cities being touted on local media on almost a daily basis [4], it is high time that Indian scientists, and just as importantly the Indian Government, realize that it is imperative that we as a society actively engage and make alternative sources of energy the primary thrust. In order to protect the current and future generations from the adverse health ramifications associated with higher pollution levels while at the same time endeavouring to improve our quality of life, it is important to be aware of the type and potential of alternative sources of energy (and their limitations), and devise ways of implementing them sooner rather than later.

In terms of effectively exploiting solar energy, there are in fact two main, industrially applicable routes available through which this solar energy can be converted into viable forms of energy suitable for human consumption¹. The easiest way of looking at this problem is to think of it as an energy conversion problem. One option is to approach this problem as converting solar energy to an electrical impulse (i.e., electricity) using devices referred to as 'solar cells' [5]. This allows for immediate use of the solar energy in a manner that is conventional and familiar to society at

¹There are other ways that are however still in the nascent stage of research and will not be highlighted here, such as thermoelectric behaviour.

large. Solar cells are devices comprising multiple chemical layers and the main functioning is based on the photovoltaic effect which is closely related to the photoelectric effect. The principle driving all the solar cells (1st, 2nd, and 3rd generation of these devices) stem from absorption of a photon of energy to obtain an excited electron and a hole (charge carriers). The sole aim of the solar cell is to ensure that these excited species do not recombine but instead are separated effectively without loss of energy and are viably extracted from the device (via opposite electrodes) generating electricity [6].

Another popular direction is converting solar energy into some form of stored energy [7]. This stored energy is very commonly thought of being stored inside chemical bonds. As such, a molecule is synthesized using the solar energy and this energy therefore is effectively converted into chemical energy yielding 'solar fuels'. The molecule can subsequently be combusted (or participate in another chemical reaction) at a later date to release the energy. One of the main advantages of such route is that the captured energy is stored, and can be used at will and perhaps at a different location from where it was captured. Currently, the formation of some of the most common types of solar fuels being researched are hydrogen, methane, and methanol [8]. Furthermore, these molecules can not only be used for transport and electricity generation, but also as feedstock in (the chemical) industry.

Considering that the last few issues of this journal have covered the topic of photovoltaics (solar cells) [9] very comprehensively, for this particular article, I will concentrate on utilizing solar energy to generate solar fuels, specifically hydrogen. The reason why hydrogen is being focused on is simply because generating energy from methane and/or methanol produce CO_2 as a byproduct. Moreover, in terms of approaching this aspect scientifically, the concepts of photosynthesis can be used as an inspiration, and its principles can be used as a rough guide to hypothesising new routes to forming solar fuels. Briefly, photosynthesis is a ubiquitous process that in principle, converts CO_2 , in presence of H_2O , to glucose and O_2 . This aspect is universally known and ac-

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cepted. The reason that it is used as a benchmark for all solar fuel generation is because photosynthesis drives a thermodynamically energy intensive, non-spontaneous reaction using sun's energy to form solar fuel of its own i.e., biomass – glucose. It is well accepted that this is an endothermic process and free energy of the system (ΔG) is known to be positive [10]. This basically means that energy needs to be absorbed to drive the reaction given below (1):

$$6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$$
 (1)

In reality, the simplicity of the above equation hides a process that is far from trivial and comprise myriad of sequential steps involving both energy and electron transfer. Briefly, the process can be outlined, for the plant system, to occur inside the thylakoid region of chloroplasts [11]. Light is absorbed first in a subunit called PSII (Photosystem two) by a variety of pigments that absorb at different wavelengths. Nature has exploited these pigments in a cascading manner to efficiently transfer energy to the main light harvester. Chlorophyll a is such an intriguing molecule where the energy absorption results in the formation of an excited electron that is guickly transferred to the 'primary electron-acceptor'. This relocation of the excited electron from its host to another molecule is crucial as this process prevents a common problem namely, recombination. As such, separation of charges are effectively ensured. Subsequently, this electron is then transferred to PSI (Photosystem I) where the electron is used to reduce NADP⁺ to NADPH (in presence of H⁺). Considering that Chlorophyll a in PSII was used to form the excited extractable electron, for the photosynthesis process to be cyclical, the electron in Chlorophyll a has to be replenished and is done so by an electron derived from a chemical reaction involving water oxidation. It is this aspect, i.e., water oxidation, that has generated the most interest from chemists and physicists as the species inside chloroplasts that perform this herculean task efficiently is a unique active site inside PSII. The water-splitting site, more specifically the water oxidizing site (or cluster) – WOC, has been revealed as a cluster of an inorganic active site consisting of four Mn ions and one Ca ion (Mn₄Ca) surrounded by amino-acid side chains. Seven of these

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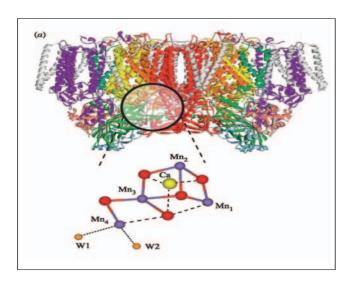


Figure 1. The structure of Mn₄C active site inside PSII [13].

unique amino acids side chains are used as ligands to stabilize the metals to create an catalytic active site. The metal cluster is organized as a cubane composed of three Mn ions and the one Ca²⁺ ion linked by oxo bonds. The fourth Mn is attached via a bridging oxygen together with another oxo bridge to an Mn ion of the cubane, *Figure* 1 [12]. It needs to be clearly stated that this active site serves as the catalyst and it allows the following reaction (2) to take place effectively:

$$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$$
 (2)

Even though this structure has been now known since 2011, either synthesizing it in the lab or mimicking it in a variety of *in vitro* conditions has yet to be done efficiently, and most importantly, to date, there are no viable routes available that exactly replicate this active site for water oxidation. More importantly, the aim of studying photosynthesis has been to derive inspiration to find ways of perhaps making analogous synthetic paradigms that fulfill the ultimate task (a holy grail for many researchers) – using solely sun's energy to drive a chemical reaction that produces a product that stores energy effectively. As alluded to earlier, one such molecule of great interest is hydrogen. It is touted



Table 1. Specific energy density of a variety of common fuels [14].

Storage Material	Specific Energy (MJ/kg)
Hydrogen (compressed) at 70 MP _a	142
Diesel/Fuel oil	48
Jet fuel	46
Gasoline (petrol)	44.4
Ethanol fuel (E100)	26.4
Coal	24
Methanol fuel (M100)	19.7
Wood	16.2
TNT	4.6
Lithium-ion battery	0.36-0.875
Alkaline battery	0.67
Lead-acid battery	0.17

²The amount of energy stored per unit weight of the material.

as the ultimate solar fuel simply because of the energy density capability² of this molecule. Do note that in comparison, photosynthesis yields glucose, not H₂. *Table* 1 gives a brief comparison between a variety of materials, and the enormous potential of hydrogen molecule as a viable fuel material can be easily appreciated. It can be seen that the specific energy density of compressed hydrogen gas is approximately three times that of what is stored in gasoline. This is a massive amount of energy that if harnessed carefully, can provide a dramatic turning point in the way world's energy requirements are met.

Most importantly, not only is the energy density of hydrogen immensely high, the aerobic combustion of hydrogen produces innocuous water as the reaction product. This is a highly exothermic reaction, and there is zero carbon footprint associated with the reaction (3):

$$2H_2 + O_2 \rightarrow 2H_2O$$
 $\Delta G = -237kJ/mol$ (3)

Although these advantages of utilizing hydrogen molecule have

been known for a long time, it however is a troubling fact that even as of 2018, the limiting factor that has prevented large scale use of this material has been the generation of hydrogen required to sustain the global demand [15]. There are several routes available through which hydrogen can be produced as the main or a side product. However, if only the non-polluting or viable from an energy cycle perspective routes are considered, there are only two chemical processes from which hydrogen molecule can be synthesized in sufficient quantities. These are (a) the electrolysis (electrocatalysis) of water and (b) the photocatalysis of water. Either of these routes, from a theoretical viewpoint would be ideal. However, it is their practical capability that is still a hindrance from making them industrially applicable. These methods will be discussed in the following two sections.

Electrolysis of Water to Generate Hydrogen Gas

The easiest and perhaps the most well-known route for hydrogen production is electrolysis. Electrolysis implies that a redox reaction is initiated in an electrochemical cell whereby an external potential is applied to an electrolyte containing water. At the anode, an oxidation reaction is carried out while at the cathode, the analogous reduction reaction is observed. The overall reaction can be split into two half reactions as follows:

Oxidation half reaction:
$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 (4)

Reduction half reaction:
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 (5)

Overall reaction:
$$2H_2O \rightarrow 2H_2 + 2O_2$$
 (6)

In terms of the potential of these two reactions, electrochemically, the standard reduction potential of the oxidation reaction



In reality, the potential at which the electrolysis is observed is much higher than +1.23 V, and this value that is above the expected potential is referred to as the overpotential.

is +1.23 V while that of the reduction reaction is 0 V. Hence the minimum total energy or potential required to split water into its constituents, hydrogen and oxygen is 1.23 V [16]. However, this benign depiction of the electrolysis of water is quite naive and an oversimplification in many ways. It hides several crucial aspects which are paramount to water splitting. Therefore, in practice, this thermodynamic potential is not realized due to variety of factors that need to be optimized. In reality, the potential at which the electrolysis is observed is much higher than +1.23 V, and this value that is above the expected potential is referred to as the 'overpotential'.

When considering the aforementioned two reactions at a fundamental level, it is imperative to realize that the processes occur at the electrode-electrolyte interface. As such, the chemical and physical properties of both the electrode and electrolyte play a pivotal role in redox reactions. The electrode surface is commonly referred to as the catalytic active site, and the electrode is the electrocatalyst. In order to reduce the overpotential, a variety of factors can be manipulated which lower the internal resistance of the electrochemical cell. This can be done by relatively trivial experimental variations such as decreasing the distance between two electrodes, or by more complicated and more relevant rate determining parameters such as improving the conductivity of the electrolyte or by employing better electrocatalysts. The latter parameter is perhaps the most researched aspect in electrochemistry. In order to understand the role of the electrode surface, it is important to realize what are the kinetic aspects that drive the hydrogen evolution reaction (HER) [17]. The HER is a classic example of a two-electron transfer reaction with one catalytic intermediate. Although there is still some conjecture regarding the exact mechanism, the overall consensus is that the reaction can proceed via first the Volmer step, followed by either the Heyrovsky or Tafel step. The '*' denotes a catalytic site on the electrode surface. Therefore, reaction may occur through either the Volmer–Heyrovsky or the Volmer–Tafel mechanism:

Volmer step:
$$H^+ + e^- + * \rightarrow H^*$$
 (7)

Heyrovsky step:
$$H^* + H^+ + e^- \rightarrow H_2 + *$$
 (8)

Tafel step:
$$2H^* \rightarrow H_2 + 2^*$$
 (9)

When observing these reactions, the rate of the overall reaction is largely purported to be determined by the hydrogen adsorption free energy, ΔG_H . If hydrogen binds to the surface too weakly, the adsorption (Volmer) step will limit the overall reaction rate, whereas if the binding is too strong, the desorption (Heyrovsky/Tafel) step will limit the rate. Thus, a necessary but definitely not the sole condition for an active HER catalyst is ΔG_H . This parameter can obviously not be easily obtained experimentally. Therefore, in the absence of a comprehensive theoretical study, experimentalists resort to other practically achievable parameters to manipulate such as pH, the conductivity of the catalyst, its reactivity/inertness in a variety of electrolytes (solid/liquid/aqueous), nature and amount of defects present on the catalyst, exact stoichiometry, crystallinity (particle size, shape, and facets exposed), three dimensional architecture (particles, films, porous reticulated structures, etc.), BET and electrochemical surface area, and porosity, which are all part of a myriad of factors that influence the kinetic aspects of the hydrogen evolution reaction.

Of all the aforementioned aspects mentioned, perhaps the most sought after aspect is the stoichiometry of the catalyst. For specifically the HER reaction, the chemical nature of the catalyst is perhaps the most studied aspect, and the reader is referred to other resources [18] for a comprehensive list of catalysts that have been exploited for HER reaction so far.

Despite the fact that it is the reduction half reaction of the water splitting process that provides for the key fuel of the future, the actual overall water splitting rate is not dictated by this two electron process. It is in fact the counter electrode oxidation reaction Although there is still some conjecture regarding the exact mechanism of the hydrogen evolution reaction, the overall consensus is that the reaction can proceed via first the Volmer step, followed by either the Heyrovsky or Tafel step.



that has so far provided the greatest challenge to researchers. At this juncture, it needs to be highlighted that both the two half reactions need to proceed at the same rate for the overall water splitting to occur on a reasonable time scale and potential. If this does not happen, then charging at one of the electrodes occurs (anomalous augmentation of charge) which then impedes the overall water splitting reaction. Considering that oxidation half reaction is a four electron process, it is this formidable process that is the most challenging, as kinetically, this needs to proceed at the same rate as the two electron reduction process. Closer analysis of the mechanism of the oxidation reaction (OER – oxygen evolution reaction) yields the following hypothesised reactions [19]:

$$2H_2 + * \rightarrow OH^* + H_2O + H^+ + e^-$$
 (10)

$$OH^* + H_2O + H^+ + e^- \rightarrow O^* + H_2O + 2H^+ + 2e^-$$
 (11)

$$O^* + H_2O + 2H^+ + 2e^- \rightarrow OOH^* + 3H^+ + 3e^-$$
 (12)

$$OOH^* + 3H^+ + 3e^- \rightarrow O_2 + 4H^+ + 4e^- + *$$
 (13)

Closer examination of these reactions yields information such as – the activation barrier for each reaction is different, and the nature of the catalyst, i.e., '*' will govern the rates dramatically. Again, just as in the case for HER reactions mentioned above, these catalysts are predominantly inorganic materials that have surface properties that lend themselves to improved adsorption of the intermediate species involved with OER and allow efficient electron transfer to occur. The activation energies of the various intermediates displayed above are reduced, and the reaction proceeds in a more kinetically unhindered way. Properties such as stoichiometry, defects, surface area, facets exposed, phases, interfacial interaction with electrolytes, etc., are used to optimize the properties of these inorganic catalysts. The reader is referred to [20] for a comprehensive list of stoichiometries that have thus far been evaluated for efficient OER behaviour.

Photocatalysis

The inspiration of this system comes from the fact that in photosynthesis, the energy is supplied by sun, whereas in electrolysis, the energy (even a small amount of overpotential) is supplied by an external electrical source. As such, the holy grail of water splitting is to not use any electrical source and to simply directly employ sun's energy. Again a catalyst has to be used. But now the additional requirement is that the catalyst has to be activated by sunlight. Such catalysts are referred to as 'photocatalysts'. The reader is to observe the similarities in the reactions given in equations (2) and (4) above – these similarities are what drive the research into photocatalysis.

As the name intimates, a photocatalyst is a material that is able to increase the rate of a reaction, however, only when specifically activated by either UV or visible electromagnetic radiation. Two important aspects underlay the central tenet in photocatalysis. The catalyst must be able to absorb photons (preferably with a large range of energies), and also must be able to adsorb reactants onto its surface. As such, all photocatalysts are solid structures whose functioning is inspired by Chlorophyll a and PSII. Therefore, light absorbing structures such porphyrins, dyes, semiconductors, conjugated polymers, etc., have been exploited for this purpose. The rationale behind this is that when light absorbing molecules or a large band-gap semi-conductor absorbs photon, the system undergoes a transition, whereby electrons from a filled valence band (or HOMO) are promoted to an empty conduction band (or LUMO). Although this is applicable to a large variety of materials, the crux of the principle lays in the fact that (a) the carriers generated (electrons and holes) must not recombine, (b) the chemical potential of these carriers must be commensurate with the chemical reactions that are to be eventually initiated (excited electrons participate in reduction and excited holes participate in the oxidation reactions), and (c) as such, the carriers must be prevented from recombining (usually a fast process), and instead be allowed to diffuse to the surface (usually a slower process) where a subsequent generation of crucial reactive radicals are formed.

Light absorbing structures such porphyrins, dyes, semiconductors, conjugated polymers, etc., have been used as photocatalysts to split water.

Figure 2. Use of a solid state semi-conductor for photocatalytic splitting of water [21].

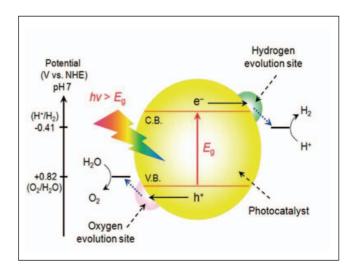


Figure 2 displays the preferred parameters in the splitting of water when a solid-state semi-conductor is used.

Again, the reader is referred to review articles [23] which provide more details and a comprehensive list of stoichiometries that have been evaluated for photocatalytic splitting of water.

Current Impediments and Future Directions

The processes briefly outlined above showcase the relatively simple scientific concepts that are to be undertaken for viable water splitting to occur. Despite the relative simplicity of these processes, the practical viability has still not been achieved. The reasons for this are many and reside mostly with the chemical and physical properties of the catalysts thus far studied. As illustrated in *Figure* 2, the main approach is to split water into H₂ and O₂ using a single visible-light-responsive photocatalyst with a sufficient potential to achieve overall water splitting. In this system, the photocatalyst should have a suitable thermodynamic potential for water splitting, a sufficiently narrow band gap to harvest visible photons, the diffusion of the excited carriers (electrons and holes) must be substantial and commensurate with each other,

recombination or trapping of these species must not occur, and stability against photocorrosion is necessary. These are stringent requirements that are not easily met in one material, and as such, the number of reliable, reproducible photocatalysts suitable for one-step water splitting is limited. Therefore, there are many deviations that are currently being pursued, two such aspects are (a) photoelectrocatalysis whereby concepts of photo and electrocatalysis are combined (electrocatalysts in presence of light) [22], and (b) application of a two-step excitation mechanism using two different photocatalysts [23]. This is referred to as the Z-scheme and the advantages of a Z-scheme are that a wider range of visible light is available as there are multiple catalysts employed, and the Gibbs free energy required to drive each photocatalyst can be reduced as compared to the one-step water splitting system. More importantly, the separation of evolved H_2 and O_2 is possible.

Conclusion

In summary, regardless of the directions that researchers are currently pursuing, it behoves us, the society, to at least realize and appreciate that the creation of a clean and affordable energy supply is paramount to the survival of our species and in this direction, the development of photocatalytic water splitting under solar light is a worthwhile endeavour to undertake. This method of sustainable hydrogen production is a major objective for the current and future generations, and to do this under ambient conditions is one of the greatest challenges facing scientists in the twenty-first century.

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