**HYDROGEN – IS AN IDEAL ENERGY SOURCE?**

B. Viswanathan National Centre for Catalysis Research, Department of chemistry, Indian Institute of technology, Madras, India

**1.Introduction**

The energy source is an essential ingredient for live process on earth. This being the case, the available sources are not equally-distributed sa as easily available to all or and the cost is manipulated by those who have access to these resources. Essentially, the conflicts arising among life processes are mainly in sharing the available energy sources otherwise the world will be a peaceful place for life process. To acquire the available energy sources, all living beings have to compete and in this process annihilate others thus causing sufferings to fellow creatures. If the energy sources were to be equally available to all without much labour, then life on this earth will be comfortable for all living beings. From time to time, the search for new and sustainable energy sources have been the main assignment to human beings. Without going through the history, let us consider what the situation in the last few decades in this endeavour.

The energy source that can be sustainable is the one which has large quantity of convertible energy for a given mass or quantity. This has been identified by a parameter, namely the heating value. Among the available chemical sources, hydrogen seems to be the choice and this energy source is bound on earth in combined form mostly with oxygen or carbon, in the form of water or hydrocarbons respectively. Hydrocarbon source for hydrogen is not desirable since it gives rise to oxides of carbon simultaneously and these are in one form or other harmful for living beings. Water source for hydrogen appears to be most ideal choice since it is available to all live processes even though it may not be as desirable equality.

Hydrogen can be harnessed from water by a number of ways. However, many of these processes are not economical since the input energy is far greater than the output energy that can be harnessed from the decomposition of water to get hydrogen and oxygen. In the last few decades, the photoelectrochemical decomposition of water (originally proposed by Fujishima and Honda in 1972 [1]) appears to be an attractive methodology for generation of hydrogen from water probably with the input energy coming from light or solar source the cost of which can be affordable. The direct electrochemical process (though practiced for pure hydrogen production for special use) is not economical because of the higher overvoltage required for the reaction. Photoelectrochemical process is similar to electrochemical process but the input energy is solar energy or light energy and the in-built potential generated in the cell. Even after nearly 50 years or so, the efficiency of this process has not reached a commercially viable level, probably the materials so far tried are not generating enough excitons or sustain them without recombination and effectively transport them to the surface to carry out the reduction and oxidation reactions.[2].

The proposition of hydrogen as the fuel source was made as early as 1874 by Jules Verne. Let us quote his words from the source, The Mysterious Island. “ **Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable Water will be the coal of the future”** [3] . This prophecy appears (?) to come true.

The basic principle and the process taking place in a photoelectrochemical cell for water decomposition can be stated as follows. The semiconductor electrode absorptions appropriate wavelength photons and creates excitons (e- and h+) and transports these charge carriers to the surface to carryout the reduction reaction ( H2 evolution) at the cathode usually a metal counter electrode and oxidation reaction (O2 evolution) at the semiconductor anode electrode.[4,5]. The choice of the semiconductor is based on the energy position of conduction band minimum and valence band maximum which decide the driving force for the reduction (H~~2~~) and oxidation (O~~2~~) evolution reactions.

If hydrogen has to become an energy source, the conversion devices like fuel cells (hydrogen fuel converted to electricity) or other conversion devices including direct combustion should be developed for various applications like transport, stationary applications and the se deevices must ensure safety condition.

The thermodynamic reversible potential for waster decomposition is 1.229 V but in practice it requires nearly 2 V due to overvoltage of the order of 0.6 to 0.8 V.

**2.Hydrogen Generation**

There are various methods to generate from a variety of sources like electrolysis of water,, biomass, petroleum-based liquids, microbes, and biofuels [6]. Of these strategies which produce various coloured hydrogen, photo-electrolysis method has been threatening to become viable for the past decades. Initially, the material selection ( nearly almost all known semiconductors (elemental, binary, ternary and composite) have been examined for this reaction) has been the focus from the points of band gap engineering ( to utilize most part of the solar spectrum) Photo-corrosion resistant and easy availability. However, it has been already recognized that these factors may not be the cause of low efficiency of this process.

Photoelectrochemical decomposition process is in a way innovated from the Natural photosynthesis, but in a crude, simple manner. Of late heterojunction photocatalytic systems have been identified to decompose water better than by single semiconductors as seen from the limited data given in Table 1.

**Table 1 Selected data on heterojunctions for the decomposition of water**

|  |  |  |
| --- | --- | --- |
| **Photocatalytic system** | **Scheme** | **Activity** |
| **CeO2-ZnO**  **La2Ti2O7-In2S3**  **CdS/CoSx**  **BP/Bi2WO6**  **CdS-g-C3N4-graphene** | **Type II**  **Type II**  **z-scheme**  **Z-scheme**  **S-scheme** | * 1. **μmol cm−2 h−1 [7]**   **158.89 μmolg−1 h−1 [8]**  **9.47 mmol g−1 h−1 [9]**  **21042 μmolg−1 h−1[10}**  **86.38 μmolg−1 h−1 [11]** |

It is seen that rates up to 103 μ mole/g/h has been possible in these heterojunctions**.** In spite of these improvements in the yield of hydrogen from water, it is still not yet sufficient. This probably means that we have not yet fully learnt the process that nature practices even though we try to mimic nature [12}. Nature employs a ladder of redox couples for smooth transfer of reducing species.(electrons) and that type of configuration has to be built in the heterojunctions systems. In essence, the charge transport and transfer architecture appear to be the key for successful hydrogen generation from the decomposition of water and the knowledge from natural photosynthesis in the form of a series of redox couples simultaneously present for smooth transport and transfer of electrons to protons must be built in the heterojunction devices.[13]

**3. Hydrogen Storage**

The second component of hydrogen economy is the storage of hydrogen in easily transportable and quickly utilizable manner. Among various options available, solid state hydrogen storage appears to be the most convenient way from all points of view.

In normal solid state one void space is available for each of the constituting species (usually termed tetrahedral, square planar or octahedral) and in this condition if H/M were to be of the order of 6.5 Wt % (DOE standards), the atomic weight of the metal has to be `15 or less. This condition may be satisfied by few elements in the periodic table like Be, Mg etc. Carbon atom can sustain four hydrogen atoms in the form of methane.(CH4) but it means all the four valencies must be satisfied by bonding with hydrogen atoms. This means that carbon atom alone can hold 25 wt% hydrogen by chemical bonding. This condition may not hold good for bulk carbon materials. Possibly one-dimensional sheet of carbon architecture may be able to bind nearly 6.25wt% of hydrogen. In this layered configuration, we have to assume every carbon atom forming the sheet has one bonding valency free for bonding with hydrogen. Regarding porous solids, hydrogen can condense by capillary condensation forces (physical adsorption) and this requires sub-ambient conditions (low temperatures) for physical adsorption. It appears at present, it may not be possible to store hydrogen to the extent stipulated by DOE by chemical forces or chemical bonding scheme.

In Table 2 the essential data on hydrogen storage by solid state materials are assembled from literature. It is seen that ambient conditions ( room temperature and atmospheric pressure) the storage capacity is low compared with the DOE standards of 6.5 wt % but however under cryogenic conditions or at high pressures the storage capacity in solid state may change favourably.

**Table 2 Selected hydrogen storage capacity of typical solid-state materials**

|  |  |  |
| --- | --- | --- |
| **Material** | **Storage capacity in Wt%** | **Ref** |
| **SWNT**  **Fe Ti**  **Laves Phase (Ti ,ZR)**  **LaNi5 type systems**  **Mg2Ni** | **~2**  **~1.9**  **` 2.0**  **`1.2**  **3.62** | **14**  **15**  **16**  **17**  **18** |

It appears that at ambient conditions solid state materials may not store sufficient amount of hydrogen so as to be useful for mobile or stationary applications. However, further studies may resolve this issue unambiguously.

**4. Transfer and Transport**

Another component of Hydrogen Economy is the transfer and transport of hydrogen from the places of generation to places where it is utilized. This component aloo includes the distribution. All these activities have to be carried out in a safe manner and the cost of this component must be within the limits of affordability.

Hydrogen is stored in the form of metal hydrides, the material exhibits oxidation resistance and hence does not lead to degradation with time. Hydrogen can be transported safely at atmospheric pressure, without the need for high-pressure tanks, much like general cargo in these days.

Distribution is a commercial venture and it has to be in an appropriate place so that equi-distribution is possible. But transfer has to be scientifically controlled. The container device has to be strong but at the same light weight. Yhe consideration on these aspects will be mostly from the commercial point of view and hence this aspect has not been taken up for a detailed analysis.

5. **References**

[1] A. Fujishima and K. Honda, Electrochemical Photolysis of Water at A Semiconductor Electrode, Nature, **238,** 37--39 (1972).

[2] Prasant V Kamat and Kevin Sivula, *Celebrating 50 Years of Photocatalytic Hydrogen Generation, ACS Energy Letters***, .7,**3149−3150 (2023).

[3]<https://www.bing.com/search?EID=MBSC&form=BGGCDF&pc=U763&q=Jules+Verne+The+Mysterious+Island&PC=U316&FORM=CHROMN>;

[4] <http://catalysis.eprints.iitm.ac.in/2362/1/chapter3.pdf>

[5]Hans-Joachim Lewerenz and Laurence Peter (Editors) Photoelectrochemical Water Splitting Materials, Processes and Architectures The Royal Society of Chemistry 2013**.**

[6]Singh S, Kumar R, Setiabudi HD, Nanda S, Vo DVN. Advanced synthesis strategies of mesoporous SBA-15 supported catalysts for catalytic reforming applications: A state-of the art review. Applied Catalysis A: General. 2018;**559**:57-74. DOI: 10.1016/J .APCATA.2018.04.015.

[7]C.H. Zeng, S. Xie, M. Yu, Y. Yang, X. Lu, Y. Tong, Facile synthesis of large-area CeO2/ZnO nanotube arrays for enhanced photocatalytic hydrogen evolution J Power Sources, 247 (2014), pp. 545-550

[8] E. Hua, S. Jin, X. Wang, S. Ni, G. Liu, X. Xu, Ultrathin 2D type-II p-n heterojunctions La2Ti2O7/In2S3 with efficient charge separations and photocatalytic hydrogen evolution under visible light illumination, Appl Catal Environ, 245 (2019), pp. 733-742.

[9] Y.H. Liang, M.W. Liao, M. Mishra, T.P. Perng, Fabrication of Ta3N5ZnO direct Z-scheme photocatalyst for hydrogen generation, Int J Hydrogen Energy, 44 (35) (2019), pp. 19162-19167

[10] J. Hu, D. Chen, Z. Mo, N. Li, Q. Xu, H. Li, *et al.,* Z-Scheme 2D/2D heterojunction of black phosphorus/monolayer Bi2WO6 nanosheets with enhanced photocatalytic activities, Angewandte Chemie International Edition, 58 (7) (2019), pp. 2073-2077.

[11] J. Liu, X. Wei, W. Sun, X. Guan, X. Zheng, J. Li, Fabrication of S-scheme CdS-g-C3N4-graphene aerogel heterojunction for enhanced visible light driven photocatalysis, Environ Res, 197 (2021), Article 111136.

[12] <https://www.student-notes.net/photosynthesis-unveiling-the-z-scheme-and-light-reactions/#google_vignette>.

[13] <https://biologyinsights.com/what-is-the-z-scheme-in-photosynthesis/>?.

[14] [Hui-Ming Cheng](https://www.sciencedirect.com/author/7404285996/huiming-cheng), [Quan-Hong Yang](https://www.sciencedirect.com/author/35202365100/quan-hong-yang), [Chang Liu](https://www.sciencedirect.com/author/56271460200/chang-liu), Hydrogen storage in carbon nanotubes, [Carbon](https://www.sciencedirect.com/journal/carbon),  [39,(10](https://www.sciencedirect.com/journal/carbon/vol/39/issue/10)), 1447-1454 (2001).

[15] G.K.Sujan, Zengxi Pab, Huijun Li, Daniel Liang and Nazmul Alam, An overview on TiFe intermetallic for solid-state hydrogen storage:microstructure, hydrogenation and fabrication processes, Critical Reviews in Solid state and Materials Science, . 45, (5), 410–427 (2020). <https://doi.org/10.1080/10408436.2019.1652143>.

[16] Volodymyr A. Yartys, and Mykhaylo V. Lototskyy, Laves type intermetallic compounds as hydrogen storage materials: A review. Journal of Alloys and compounds,  [**916**](https://www.sciencedirect.com/journal/journal-of-alloys-and-compounds/vol/916/suppl/C), 165219 (2022).

[17] Yuchen Liu, Djafar Chabane and Omar Elkedim, Optimization of LaNi5 hydrogen storage properties by the combination of mechanical alloying and element substitution, International Journal of Hydrogen Energy, **53, 394-402 (2024).**

[18] Felipe Henrique Matheus, Guilherme Zepon, Verona Biancardi Oliveira, and  Daniel Rodrigo Leiva, Highly reactive hydrogen storage Mg2Ni alloy prepared by mechanochemistry and H-cycling, International Journal of Hydrogen Energy, **51**, 320-328 (2024).

[