

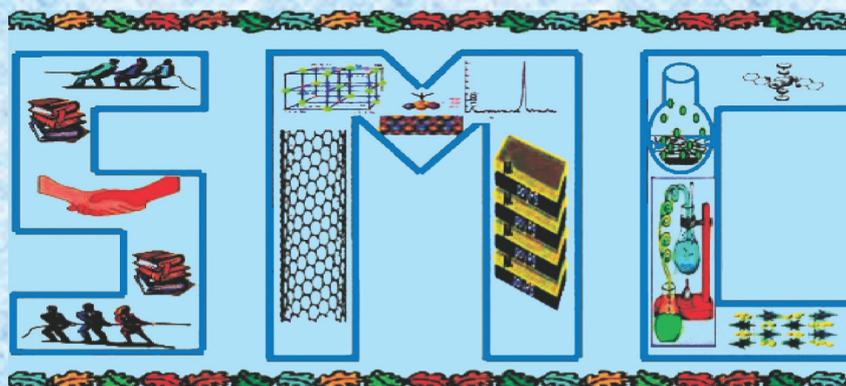
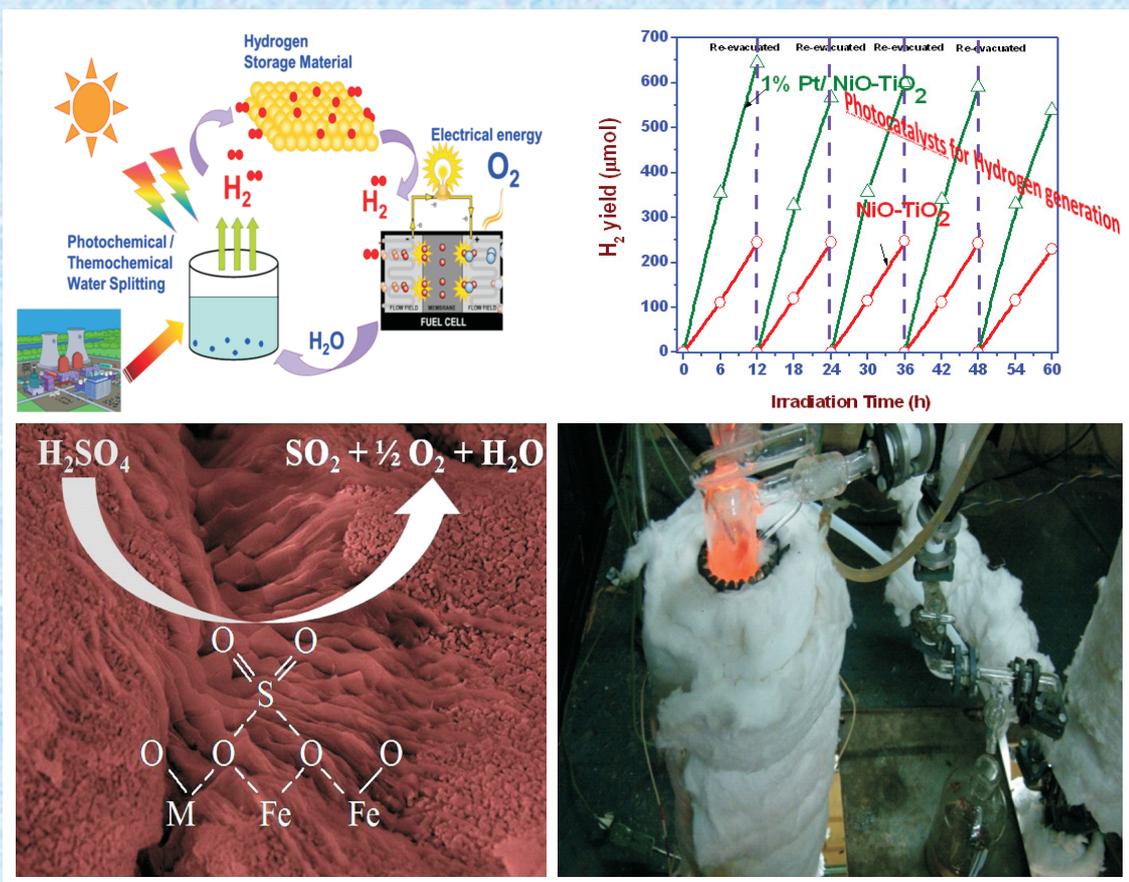
# SMC Bulletin

A Publication of the Society for Materials Chemistry

Volume 5

No. 2

August 2014



SOCIETY FOR MATERIALS CHEMISTRY

# Society for Materials Chemistry

Society for Materials Chemistry was mooted in 2007 with following aims and objectives:

- to help the advancement, dissemination and application of the knowledge in the field of materials chemistry,
- to promote active interaction among all material scientists, bodies, institutions and industries interested in achieving the advancement, dissemination and application of the knowledge of materials chemistry,
- to disseminate information in the field of materials chemistry by publication of bulletins, reports, newsletters, journals.
- to provide a common platform to young researchers and active scientists by arranging seminars, lectures, workshops, conferences on current research topics in the area of materials chemistry,
- to provide financial and other assistance to needy deserving researchers for participation to present their work in symposia, conference, etc.
- to provide an incentive by way of cash awards to researchers for best thesis, best paper published in journal/national/international conferences for the advancement of materials chemistry,
- to undertake and execute all other acts as mentioned in the constitution of SMC.

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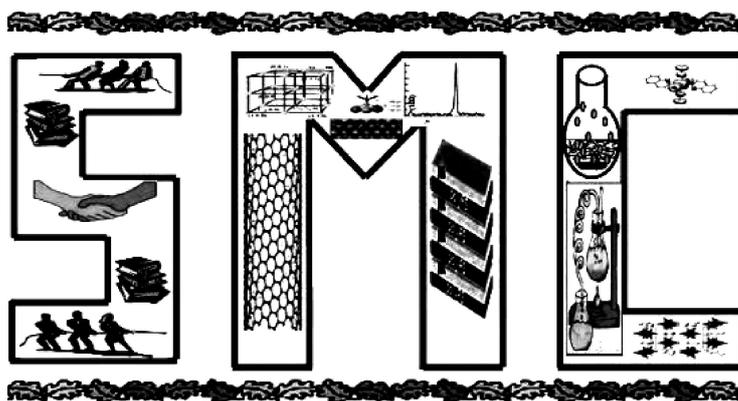
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*Please note that the authors of the paper are alone responsible for the technical contents of papers and references cited therein*

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*Front cover shows images from L-R clockwise 1. Schematic of hydrogen technology, 2. Photocatalytic hydrogen evolution, 3. Sulfuric acid decomposer in closed glass loop of I-S process and 4. SEM micrograph of oxide catalyst developed for I-S thermochemical cycle.*

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## *Guest Editorial*

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**Mrinal R. Pai**



**A. Shrinivas Rao**

It is our pleasure to be associated with SMC and particularly this issue of “Materials for Hydrogen Energy” as guest editors. We thank SMC for giving us this responsibility and hope that justice is done by us.

Beyond doubt, earth is getting warmer due to increasing carbon dioxide levels and definite climate change is being felt. According to IPCC, Intergovernmental Panel on Climate Change – a premier international scientific body established by United Nations, atmospheric concentration of carbon dioxide has crossed 400 ppm which is the highest in at least last 800,000 years. To limit and reduce CO<sub>2</sub> concentrations renewable energy source such as Hydrogen is to be extensively put to use.

Various options for generation and storage of hydrogen are available. But different ways of hydrogen production devoid of CO<sub>2</sub> generation are crucial and being researched world over, so also in our country. They are electrolytic, photolytic and thermal routes where energy source is either from renewable or from non-fossil fuel. Storage of hydrogen with high weight percent is being extensively researched though high pressure cylinders usage is prevalent.

Here in this bulletin we present articles on different approaches followed worldwide for hydrogen generation and storage. Topics ranging from hydrogen generation by S-I and Cu-Cl thermochemical cycles, photocatalytic, photoelectrochemical processes, hydrogen storage in carbon based as well as metal hydride systems and various other processes relevant to hydrogen energy are covered. We thank all authors from different institutes for sharing their knowledge, expertise and scientific data in form of contributed articles in the present bulletin.

The next issue of the Society of Materials Chemistry Bulletin is proposed to be on “Supramolecular Materials”.

Readers are encouraged to give their feedbacks at email id. [socmatchem@gmail.com](mailto:socmatchem@gmail.com)



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## From the desks of the President and Secretary, Society of Material Chemistry

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**Sisir K Sarkar**  
*President*



**P. A. Hassan**  
*Secretary*

Greetings for the festive season from the Executive Council of SMC.

Since its inception, SMC has been actively involved in publishing theme based bulletin issues which serve as a platform to highlight the advances made in the field of materials chemistry and also encourage young researchers/academicians to join our fast growing society having more than 800 members. During the past few months, our efforts have been focused on the preparation for conducting the fifth Interdisciplinary Symposium on Materials Chemistry (ISMC-2014) to be held at Anushaktinagar during December 9 - 13, 2014. It is really a pleasure to bring this special issue on "Materials for Hydrogen Energy" on the eve of ISMC-2014. We would like to put on record our sincere thanks to the Guest Editors Dr. Mrinal R. Pai, Chemistry Division and Sh. Shriniwas A. Rao, Chemical Technology Division for taking keen initiative and efforts to bring out this issue.

Providing an abundant, clean, and secure renewable energy source is one of the key technological challenges facing mankind. Resurgence in the chemistry and biochemistry of hydrogen, the world's simplest closed-shell molecule, has been spurred by recent scientific and technological interest in hydrogen as an energy carrier and potential transportation fuel. A number of key challenges must be overcome for hydrogen to be used broadly in a sustainable future energy infrastructure to solve the globe's energy problems. The current platforms for hydrogen production are largely based on fossil fuels, are relatively energy inefficient, and lead to the emission of significant quantities of greenhouse gases.

Scientific advances are needed to develop more energy efficient and cost-effective methods for purification and delivery, to design higher energy density hydrogen storage systems, especially for vehicular on-board storage, and to enable more durable fuel cells for converting hydrogen into electrical energy. Despite its high gravimetric energy density, hydrogen, even in liquid form, has a low volumetric energy density compared to other transportation fuels, so on-board storage of hydrogen remains a critical technical barrier for widespread hydrogen-based transportation. Governments and industries, particularly in the United States, Japan, and Europe, have been investing heavily in R & D to overcome the technical barriers for hydrogen production, storage, and utilization to enable a sustainable future energy infrastructure based on hydrogen. This thematic issue on Hydrogen aims to capture the excitement of recent advances in hydrogen production, storage, and utilization by providing a broad overview of the current state of our scientific understanding of the pertinent chemistry. It is simply not possible to capture all the advances and aspects of the scientific challenges in a single issue, but we believe that the cross section provided by the articles will be of interest to a broad audience. We hope that the excellent articles in this thematic issue will inspire many scientists, in particular the younger generation, to become involved with this important topic and energy related fields in general.



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# Hydrogen Storage Possibilities in Carbon Materials

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## Abstract

Reported results on hydrogen storage in carbon materials have been a subject of controversy. The central point of this controversy is the storage capacity and also the activation centres in equipotential carbon surfaces. Incorporation of hetero atoms like B, N, P, and S in carbon lattice can possibly provide the necessary centres for the activation of hydrogen in either dissociated or quasi molecular form with increased bond length. The proposed model may account for the predicted storage capacity and can possibly direct towards the design materials for this purpose.

## Introduction

The transition to hydrogen based economy depends on three essential factors, namely production, storage and distribution. There are many options available for each of these three factors. In this, the option for storage should at least satisfy two of the essential criteria namely the hydrogen storage density must be as high as possible and the accessibility of hydrogen must be as easier as possible. Taking these factors into consideration, the Department of Energy (DOE) has come out with some expected standards of hydrogen storage capacity and has been frequently modifying these figures based on the developments that have taken place. One of these DOE stipulated standards is given in Table 1. Whatever may be the expected figure, it appears that a minimum of 6.25 weight percent is required from the consideration of economic viability.

**Table.1. H<sub>2</sub> Storage - the grand challenge (US DOE targets (somewhat reasonable) for on board hydrogen storage materials)**

Storage Parameter	Units	2015	Ultimate
System Gravimetric Capacity	g H <sub>2</sub> /kg	55(5.5 wt.%)	75(7.5 wt%)
System Volumetric Capacity	g H <sub>2</sub> /L	40	70

(Solid H<sub>2</sub> density at zero K and zero pressure is 86 g/L).

Even though many solid state options for hydrogen storage like metal and intermetallic hydrides, Metal organic frameworks, isorecticular metal-organic frameworks (IRMOF) covalent-organic frameworks (COF) clathrates and carbon materials have been considered, carbon materials with the possibility of morphology variation

have been one of the contending candidates mainly because nature has stored hydrogen mostly in hydrocarbons and also in water. Essentially, the storage of hydrogen has been treated within the framework of molecular physical adsorption (weak binding energy of the order of meV and essentially low temperature process), dissociative chemisorption (with strong binding energy of the order of 2-4 eV and high temperature process) or quasi-molecular form wherein the molecule is not completely broken but the bond is weakened with binding energy in the range of ~ 1 eV. Each of these forms will have the capacity to store but all of them cannot satisfy the necessary reversibility for use as fuel without expanding additional energy. In atomic solid state materials, approximately each atom gives rise to a void space and hence even if we assume each of these voids can accommodate one hydrogen atom, it is clear that the storage capacity will be inversely proportional to the atomic weight of the metallic element involved in the storage. In the case of transition metal containing intermetallics like FeTi, LaNi<sub>5</sub> etc., the storage capacity can be in the range of 2-3 weight percent, while in the case of light elements like Mg, it can exceed the threshold value of 6.25 weight percent. Though the idea of quasi molecular form of hydrogen sorption appears to be the possible mode of hydrogen storage, the concept of bonding as proposed by Kubas [1] involving bonding and back bonding model has to be examined since the orbitals wherein the back bonding were to occur may not be energetically favourable. The other concept [2] of molecular electric field of the metal polarizing molecular hydrogen though may be feasible, complete reversibility cannot be ensured in these cases. Therefore it appears that hydrogen storage may have to be dissociative for use as a fuel in mobile and stationary applications with appropriate bond strength.

The storage capacity of complex metal hydrides has also received considerable attention from various view

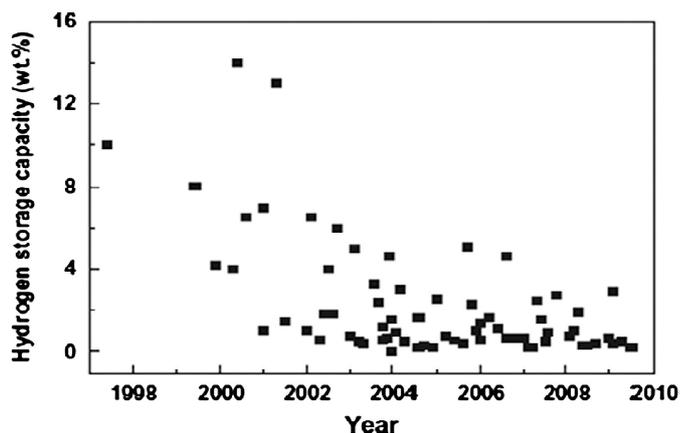


Figure 1. Hydrogen storage capacity in Weight % in carbon materials as a function of the year of the report of the study [reproduced from C. Liu, Y. Chen, C.Z. Wu, S.T. Xu and H.M. Chen, Carbon, 48,452-455 (2010)]

point. The essential point of these systems is that their storage capacity is in the desirable range and also there are considerable reprocessing possibilities available. The introduction of systems like  $\text{Li}_3\text{N}$  or  $\text{NH}_3\text{BH}_3$  has also possibly thrown new hope that chemical hydrides may be one of the appropriate candidates for solid state hydrogen storage applications.

Probably hydrogen storage in carbon materials under ambient conditions has seen more controversy than any other scientific endeavor due to various reasons in this time period. It is not our intention to examine this controversy. However, the fact remains that any value between 0 and 67 weight percent has been claimed to be the storage capacity in carbon materials (refer to the data given in Table 2, wherein the different measurements of hydrogen sorption on different carbon forms are assembled). The diversity of data of hydrogen storage in carbon materials is reflected

**Table 2: Selected data reported in literature on hydrogen storage in carbon nano materials.**

Nature of adsorbent	Temp range (K)	Pressure (MPa)	Wt % $\text{H}_2$ stored	Ref
SWNT	133	0.04	5-10	3
SWNT	298	0.67	3.5-4.5	4
SWNT	77-300	8	1-15	5
SWNT	80	7	8.25	6
SWNT	298	4.8	1.2	7
MWNT	298	12.16	56	8
MWNT	300-700	---	0.25	9
MWNT	298	10	0.68	10
MWNT	300	1	13.8	11
MWNT	300	7.0	0.7-0.8	12
SWNT	80	10	11	13
SWNT	80	10	2	14
SWNT	80	16	6.5	15
SWNT	300	0.04	10	16
SWNT	300	12	4	17
MWNT(Li doped)	200-400	0.1	20	11
MWNT (Li doped)	200-400	0.1	2.5	18
MWNT (K doped)	300	0.1	1.8	19
GNF	300	12	65	20
GNF	300	12	6.5	21
GNF	300	12	10	22

**Table.3.Weight percent Hydrogen stored in various possible materials as complex hydrides [21]**

Stored as ( storage ) Material	Weight percent stored
LiAlH <sub>4</sub>	10.54
MgH <sub>2</sub>	7.69
LiNH <sub>2</sub>	8.78
Mg(NH <sub>2</sub> ) <sub>2</sub>	7.15
NaBH <sub>3</sub>	10.57
Al(BH <sub>3</sub> ) <sub>3</sub>	16.78
NH <sub>3</sub> BH <sub>3</sub>	19.35
NaAlH <sub>4</sub>	7.41
Mg(AlH <sub>4</sub> ) <sub>2</sub>	9.27
LiBH <sub>4</sub>	18.36
Mg(BH <sub>4</sub> ) <sub>2</sub>	14.82
CH <sub>4</sub>	25.0
NH <sub>4</sub> BH <sub>4</sub>	24.24

in Fig.1. This unusual situation in scientific research has led to a spate of investigations on the hydrogen storage in carbon materials. In this presentation, focus has been given to analyze the reasons for this anomalous situation in scientific research and also to evaluate the storage capacity of hydrogen in carbon materials.

It has been stated that a minimum of 6.25 weight percent of hydrogen is necessary for commercial exploitation of this technology. It is therefore necessary that one considers all possible systems where hydrogen content can be higher than this threshold value. One such listing is given in Table 3. However, though it may be possible to store hydrogen above the threshold value of 6.25 weight percent, it must be kept in mind that the release of hydrogen requires expansion of energy and hence the net energy available is considerably reduced below the threshold value.

### Hetero atom Substituted Carbon Materials

Generally, good carbon materials are considered to be equi-potential surfaces and hence the dissociation of hydrogen molecule does not occur on this surface under ambient conditions. This deduction is also supported by the DFT calculations wherein it has been shown that the dissociation energy of molecular hydrogen is not altered on pure carbon surfaces, while heteroatom substituted carbon surfaces showed considerable decrease in hydrogen dissociation energy. For the details of the Density Functional Theory (DFT) calculations see references [23-26].

The data relevant to this statement are given in Table 4 for carbon surfaces substituted with hetero atoms like B, N, P and S. It has been shown in these studies that heteroatoms promote the dissociation of molecular hydrogen and the dissociated hydrogen is stored by spillover mechanism. A typical reaction profile shown in Fig.2 possibly demonstrates that the activation barrier reduction for the dissociation of hydrogen molecule is provided in the heteroatom substituted sites. The calculated activation barrier values for the multiple step activation of hydrogen on the substituted carbon surfaces as deduced from DFT calculations are given in Table 5. These calculated values possibly imply that the hydrogen storage possibly takes place by the dissociation of molecular hydrogen though not bound to a single specific site.

It is known that the hydrogen storage may involve the trapping of the dissociated hydrogen atoms (or other species) inside the geometrical volume constituting the solid. It is generally conceived that for solid state matrices, there will be approximately one void space (this can be octahedral, or tetrahedral or any other void space) for every atom constituting the solid matrix. If all these available void spaces in carbon lattice were to be occupied by dissociated or quasi-molecular hydrogen, then the maximum storage capacity can be in the range of 8 wt % which is of the same order of magnitude stipulated by DOE. If this were to be the mode of hydrogen storage in the interstitial positions, then the hydrogen atoms will be in the field of the neighbouring atoms (depending on the geometry of the interstitial site the hydrogen atom will be under the influence of n atoms). Therefore, this type of storage involving multiple sites bonding with no specific directional bonding may be able to store hydrogen for sufficient length of time and can release hydrogen with slight energy input which is essential for efficient storage purpose. This shows that the necessary hydrogen storage can be achieved only if the atomic weight of the element chosen for storage is 16 or near about it.

### Hydrogen storage on boron substituted carbon materials

To examine the postulate that heteroatoms may act as activation centres for hydrogen storage in carbon materials, boron substituted carbon material was examined in this study. It may be recalled from the results of DFT calculations shown above that boron substitution in adjacent and alternate positions may be the two possible centres and substitution at alternate positions is preferable for hydrogen storage. The boron substituted carbon material has been synthesized using Resorcinol and Triethylborate as carbon and boron sources. Boron

**Table 4. Bond length and dissociation energy of hydrogen on the carbon nanotube (CNT) calculated using B3LYP with 6-31g(p, d) basis set on the UFF optimized structure**

System	Total energy (Hartrees)	Bond length H <sub>1</sub> ....H <sub>2</sub> (Å)	Dissociation energy (eV)
Hydrogen	-1.175	0.708	4.76
CNT	-3686.5502	-	-
CNT + H <sub>2</sub>	-3687.7161	0.776	4.51
NCNT	-3703.5908	-	-
NCNT + H <sub>2</sub>	-3703.5989	0.835	0.22
PCNT	-3989.1694	-	-
PCNT + H <sub>2</sub>	-3990.5989	0.815	2.33
SCNT	-4046.0020	-	-
SCNT + H <sub>2</sub>	-4047.0067	0.817	0.13
BCNT	-3671.7254	-	-
BCNT + H <sub>2</sub>	-3672.9440	0.818	5.95
2B CNT(adjacent)	-3658.6666	-	-
2B CNT (adjacent)+ H <sub>2</sub>	-3659.8092	0.913	3.88
2B CNT (alternate)	-3659.3491	-	-
2B CNT(alternate) + H <sub>2</sub>	3660.3594	0.928	0.28

**Table 5. Transition state optimized parameters of the cluster and the value of the activation energy calculated by B3LXP with 6-31g (p,d) basis set**

System	E <sub>a</sub> I (eV)	E <sub>a</sub> II (eV)	H <sub>1</sub> -H <sub>2</sub> (Å)	X-H (Å)	C-H <sub>1</sub> <sup>b</sup> (Å)	C - H <sub>2</sub> <sup>b</sup> (Å)
CNT cluster	10.02	-	0.71	-	-	-
NCNT Cluster	3.84	4.58	1.45	1.11	1.70	1.94
P CNT cluster	3.81	3.99	1.51	1.61	1.27	2.33
S CNT Cluster	3.65	4.85	1.50	1.75	1.24	2.40
2B CNT Cluster (adjacent)	2.22	2.98	1.95	1.31	2.59	2.72
2B CNT cluster (alternate)	1.5	2.33	2.95	1.47	1.47	2.34

$$E_a = E(\text{transition state}) - E(\text{reactant})^b \text{ shortest C-H bond distance}$$

substituted carbon materials were synthesized by the following procedure: 11.2 g of resorcinol was taken in a beaker, 30 ml of formaldehyde solution was added stirred at room temperature for 1 hour, 15 ml of Triethylborate (TEB) solution was added stirred well then kept in an oven at 373 K for 24 hours. The final homogeneous mixture was transferred into a quartz tube then kept in a tubular furnace and calcined at two different (600 and 800 °C) temperatures for 6 hours under inert atmosphere. The heating rate employed for calcination is 10 °C/min.

For the carbon sample calcined at 600 °C, two broad x-ray diffraction reflections centered at 2θ values of 25° and 45° corresponding to reflections from (002) and (100)

planes and for the sample calcined at 800°C two reflections at 2θ values of 22° and 43° indicating that the synthesized materials possess carbon lattice, the broad reflections indicate the crystalline nature of the synthesized material. As the calcination temperature is increased, the intensity of the diffraction peaks increased. Since the amount of boron introduced is small, changes in 2θ value from that of pure carbon lattice is not significant though the diffraction peaks shift slightly to higher angle side. The average crystallite size of this carbon material was found to be ~0.8 nm. FT-IR Spectrum of the boron containing carbon material shows a broad absorption band in the region of 3200 – 3600 cm<sup>-1</sup> with the maximum around 3450 cm<sup>-1</sup>. This band can be

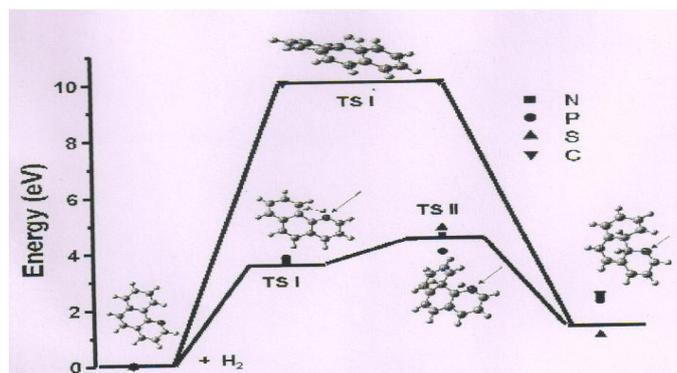


Figure 2a. The transition state energy profile of the heteroatom substituted CNTs cluster calculated by DFT method (B3LYP) with 6-31g (p,d) basis set the spheres indicated by arrows are heteroatoms like N, P, and S.

assigned to the O-H stretching mode vibration of adsorbed water. The position of this band and also the apparent asymmetry on the lower wave number side indicates the presence of hydrogen bonds. The absorption band at 2928 and 2857  $\text{cm}^{-1}$  can be due to the aliphatic character of the C-H bonds. It is clear that the C-OH and stretching mode of vibration can be found at 3742  $\text{cm}^{-1}$  and their bending mode of vibrations are in the range 1500 to 1650  $\text{cm}^{-1}$  with the maximum at 1536 and 1631  $\text{cm}^{-1}$ . The absorption band at 1424  $\text{cm}^{-1}$  is due to stretching vibration of C=C bond. The absorption in the range 1010  $\text{cm}^{-1}$  to 1200  $\text{cm}^{-1}$  with the maximum around 1092  $\text{cm}^{-1}$  can be assigned to the vibration of the B-C bond. These results also show that boron was incorporated in the carbon material [27-29]. The Raman spectrum of each of the two samples showed two broad peaks at 1304  $\text{cm}^{-1}$  and 1572  $\text{cm}^{-1}$  (600 °C calcined) and at 1320  $\text{cm}^{-1}$  D and 1575  $\text{cm}^{-1}$  G bands (for 800 °C calcined sample). These two bands showed the presence of defects and graphitic nature of the synthesized carbon material. The relative intensities ( $I_D/I_G$ ) of these peaks depend on the carbonization degree of the carbon materials. The ratio of integrated intensity ( $I_D/I_G$ ) of the D and G bands is = 1.04 (carbon prepared at 600 °C) and = 1.36 (carbon prepared at 800 °C). As the carbonization temperature is increased, the intensity of the D band and G band of the carbon material is increased and the two peaks slightly shifted to higher wave number side. Generally normal carbon materials show equal intensity for (D) and (G) bands. Furthermore, there was an increase in the intensity of the D band along with a decrease in its wave number position also increased with the boron substitution. The intensities of (D) and (G) bands are changed thus showing that boron substitution has taken place in the synthesized carbon material [30-32].

The high resolution scanning electron micrographs (SEM) of the boron containing carbon material are shown in Fig. 3. These images show the morphological aspects of the

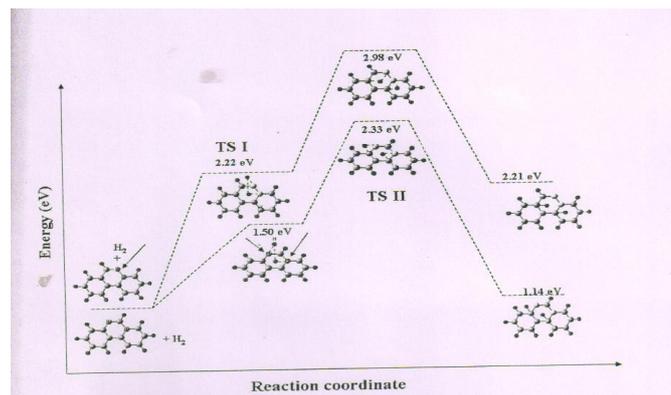


Figure 2b. The transition state energy profile of boron substituted CNT cluster calculated by DFT method (B3LYP) with 6-31g (p,d) basis set (the spheres indicated by arrows are boron atoms).

synthesized boron substituted carbon material, images (a), (b), (c) and (d) are obtained at different magnifications and images were recorded from the same area of the material. The images showed sphere like uniformed morphology.

The carbon 1s emission in X-ray photoelectron spectrum at 284.4 and 285.3 eV showed the presence of graphitic, and C-B type carbon environments. The presence of boron in this sample was ascertained from B 1s peak at 192.8 eV. The B 1s peak does not approach the value expected for a surface layer of boron oxide. In fact, it seems to approach lower binding energy value where B-C, or mixtures of B-C and B-O bonding are expected. Obviously, continued study of this effect is justified. However, there is no splitting or different peak for the boron in carbon materials has been seen to show the different chemical environment. However a clear peak broadening for boron has been observed at the lower binding energy region, which has been deconvoluted. The peak at (193.8  $\pm$  0.1 eV) can be assigned to the boron atom substituted in the graphitic structure as proposed by Jacques et. al. [33], and L. G. Jacobsohn et. al. [34]. The B1s peak value around 190.4-195.3 eV has been assigned to boron atoms with the local environment of  $\text{BC}_2\text{O}$ . From the deconvoluted B1s spectrum it is clear that the boron atom exists in two different chemical environments which are attributable to the presence of  $\text{B}_4\text{C}$  and  $\text{BC}_2\text{O}$  type chemical atmosphere [35-40]. The surface area determined by BET method was 215  $\text{m}^2/\text{g}$ . The hysteresis loop obtained in the adsorption desorption isotherms indicated the presence of both micro- and meso-pores in the sample.

The hydrogen adsorption capacity was determined at two different temperatures namely at 293 K and at 77 K. Before hydrogen absorption the synthesized carbon materials were degassed at 473 K for 6h. The carbon material calcined at 600 °C showed nearly 3.5 wt%

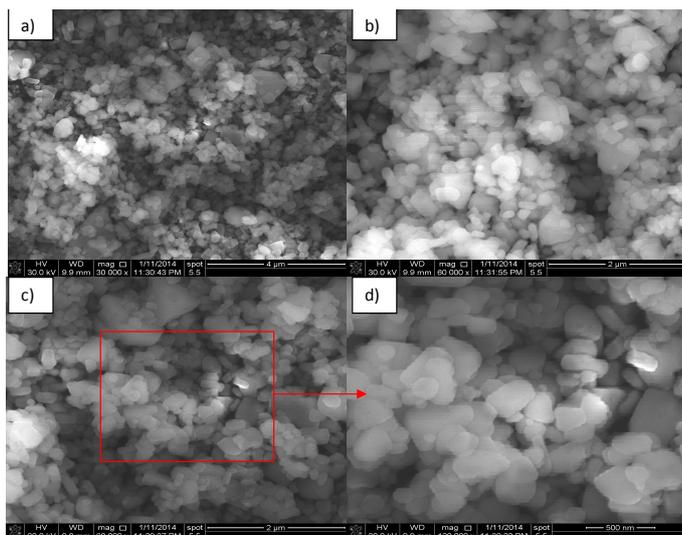


Figure 3: HRSEM images of the boron substituted carbon material for different magnification with same area of the material a) 60000x and b) 120000x.

hydrogen storage at room temperature and 0.5wt% at 77K. However, the carbon material calcined at 800 °C, showed 1wt% hydrogen storage at 18 bar pressure at room temperature and 0.15 wt% at 77K. Thus demonstrating that hetero atom substitution considerably alters the hydrogen sorption capacity of carbon materials. Work on other substituted carbon materials are in progress.

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	<p><b>A. Ariharan</b> is a research scholar in the National Centre for Catalysis Research. He has been working in the area of hydrogen storage by Carbon Materials especially Heteroatom substituted Carbon nanomaterials.</p>

# Application of Metal Hydride Systems for Hydrogen Storage

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## Abstract

The metal hydride systems have been investigated in detail for their hydrogen storage properties. Thermodynamic and kinetic studies carried out on the hydrogenation of alloys like FeTi, Ti<sub>2</sub>CrV, LaNi<sub>5</sub>, Ti<sub>2</sub>Nb, etc., have established different ways of optimizing their hydrogen storage properties. Suitable modification in the alloy composition by addition of metals like Fe, Co, Ni, Zr etc., significantly affects the hydrogen absorption/desorption properties.

## 1. Importance of Hydrogen Storage

In recent years, research in materials science has shown a rapid expansion towards discoveries of suitable materials for sustainable energy. A hydrogen economy is proposed to circumvent the ill effects of using hydrocarbon fuels in transportation and other end-use applications, where carbon is released to the atmosphere. In this context, the storage of hydrogen poses the biggest challenge in a new hydrogen economy because the storage medium must meet the requirements of high gravimetric and volumetric densities, fast kinetics and favorable thermodynamics [1-4]. Although molecular hydrogen has very high energy density on a mass basis, as a gas, at ambient conditions, it has very low energy density by volume. If it is to be used as fuel stored on board in the vehicles, pure hydrogen gas must be pressurized or liquefied, which in addition to being energy intensive also bring complications in terms of safety aspects. Considering all these issues, solid-state materials offer a practical alternative, and lot of efforts have been devoted in finding efficient solid state hydrogen storage materials.

There are different candidate materials for solid state hydrogen storage [5-11]. The most conventional and practical one is metal hydride, where different transition metal based and light weight alloys are being considered. The suitability of alloys for hydrogen storage applications can be judged from their hydrogen storage properties such as reversible hydrogen storage capacity, plateau pressure, plateau slope, hysteresis, sorption kinetics and thermodynamics of dissolved hydrogen [12]. Transition metal based alloys are quite promising for their good hydrogen absorption / desorption kinetics and favorable thermodynamics whereas light metal alloys show higher hydrogen absorption capacities but unfavorable kinetics and thermodynamics.

Other exclusively studied hydrogen storage materials include metal organic framework, carbon nanostructures

etc. Metal organic frameworks (MOF) can absorb hydrogen by physisorption, but it requires operating at cryogenic condition. Carbon nano structures are one of the most promising solid-state materials for hydrogen storage because of their porosity, high surface area and high gravimetric hydrogen storage properties. Nanotubes, nano scrolls, nano-fibers, fullerenes and graphene sheets are among the different well studied structures. Though the experimental results obtained for hydrogen storage on carbon nanotubes are contradictory because of the presence of metal nano particle impurities and defect structures, but still theoretical and experimental research is going on to see its nature of interaction with hydrogen, curvature effect and the effect of doping on the hydrogen absorption properties.

## 2. Basics of Hydrogen Interaction in Metal Hydride

Here we discuss the hydrogen uptake process of metal. Fig. 1 schematically shows the hydrogen absorption process on the metal surface. The hydrogen absorption process is exothermic and certain amount of heat is released during the hydrogen absorption depending upon the host material.

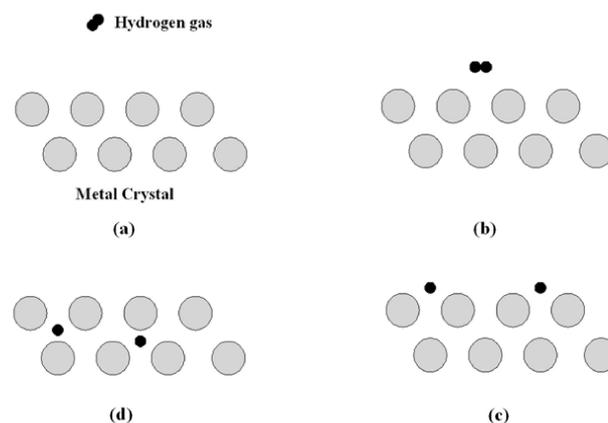


Figure 1. Mechanism of metal hydride formation

Initially the hydrogen molecule approaches to the metal surface [Fig. 1(a)] and interacts with the surface by van der Waals force. Here the hydrogen remains in the physisorbed state [Fig. 1(b)], with typical binding energy of ~10 KJ/mole. In the next step, the hydrogen molecule needs to overcome the activation barrier for dissociation of the H-H bond and after that the hydrogen molecule dissociates into hydrogen atoms [Fig. 1(c)]. The hydrogen atoms get chemisorbed on the surface with the binding energy in the order of 50 KJ/mol-H<sub>2</sub>. After the dissociative chemisorption of the hydrogen atoms, they penetrate into the interior of the metal crystal to form M-H solid solution, which is known as α-phase [Fig. 1(d)]. In most of the cases, the hydrogen atoms occupy interstitial positions (tetrahedral or octahedral) and the cell parameter of the crystal lattice increases. The physical arrangement of the metal atoms may also change during hydride formation. The hydrogen absorption in α-phase is governed by Sievert's law, which states that

$$C_H = kp^{1/2} \quad (1)$$

Where C is the concentration of hydrogen in the α-phase, p is the hydrogen pressure and k is temperature dependent constant. After increase in the concentration of hydrogen in α-phase, the metal-hydrogen phase starts precipitating and the phase is called β-phase.

### 3. Thermodynamics of hydride formation

The thermodynamics of gaseous hydrogen absorption is represented by pressure composition isotherm. The equilibrium or plateau pressure (P<sub>eq</sub>) strongly depends on temperature and is related to the changes of enthalpy (ΔH) and entropy (ΔS), respectively. The enthalpy term characterizes the stability of the metal-hydrogen bond. A plot between equilibrium hydrogen pressure and hydrogen-to-metal ratio at a constant temperature is called pressure-composition isotherm (PCT) [13]. In the PCT curve [Fig. 2], initially the hydrogen pressure increases sharply that means hydrogen diffuse into the interstices of metal or alloy forming solid solution (α-phase).

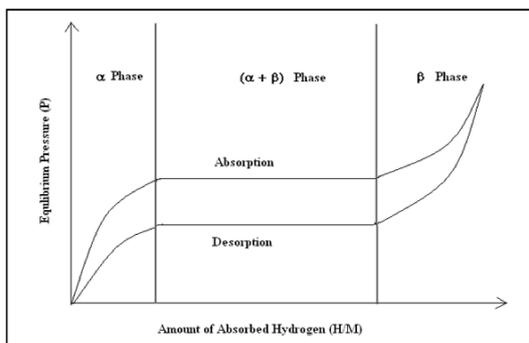


Figure 2. A typical pressure composition isotherm showing the H<sub>2</sub> absorption-desorption profile

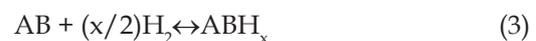
As the hydrogen concentration further increases in the lattice, the hydride phase precipitates. The hydride phase is known as the β-phase. The hydride formation is indicated by the plateau of the plot. In the plateau region, the solid solution and the hydride phase coexist (α & β-phases). The length of the plateau determines how much amount of hydrogen can be stored and recovered by means of a small change in pressure. The last portion represents the hydride phase only, the hydrogen pressure increases steeply with concentration in this region.

Many metal hydrides do not undergo absorption and desorption along the same path, i.e. the absorption curve and desorption curves of metal hydrides are not the same. The path difference between the absorption and desorption isotherms is known as hysteresis. In most of the cases, the desorption plateau is considered as the true plateau, as the equilibrium is reached faster during desorption. The hydride having higher desorption pressure is less stable than the lower desorption pressure hydride.

The reaction of a metal with hydrogen to form metal hydride can be represented by the following equation:



When an intermetallic compound reacts with hydrogen the reaction can be written as follows:



Where, A & B are two elements forming the alloy.

We know from Gibbs free energy relation,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \text{ and } \Delta G^\circ = -(x/2)RT \ln P_{H_2} \quad (4)$$

where ΔG°, ΔH°, and ΔS° are standard free energy, enthalpy and entropy respectively.

The relation between hydrogen pressure and enthalpy of hydride formation can be written as follows.

$$\ln P_{H_2} = (2/x)\Delta H^\circ/RT - (2/x)\Delta S^\circ/R \quad (5)$$

This relation is known as van't Hoff relation. ΔH and ΔS are enthalpy and entropy per mole of H<sub>2</sub> gas respectively. Using van't Hoff relation, the enthalpy and the entropy of the hydride can be found out by studying the pressure composition isotherm at different temperatures. The plateau pressure or equilibrium pressure of the PCT diagram depends on the working temperature. With increase in the temperature, the plateau pressure increases and the plateau region decreases. At a critical temperature (T<sub>c</sub>) no plateau exists. The plot of logarithm of hydrogen pressure verses reciprocal of temperature, i.e. the graph between ln P<sub>H<sub>2</sub></sub> and 1/T is known as van't Hoff plot as

shown in Fig. 3. In the van't Hoff equation, the slope of the line is equal to the enthalpy of formation divided by the gas constant and the intercept is equal to the entropy of formation divided by the gas constant. The value of  $\Delta H$  can be widely different for different metal atoms and alloys as it varies from large negative to large positive value. Some of the typical hydride formation enthalpy values of

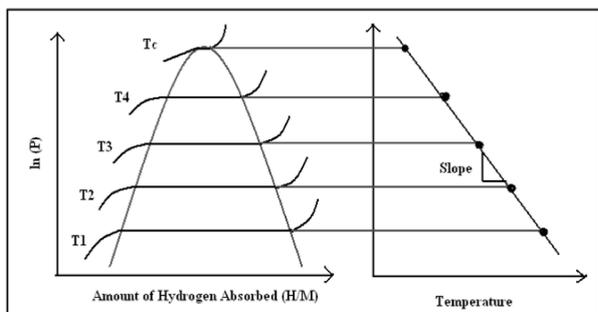


Figure 3. Schematic PCT diagram at different temperatures ( $T_1 < T_2 < T_3 < T_4 < T_c$ ), and the van't Hoff plot

different metals have been listed in Table 1.

The enthalpy and entropy of the hydrides determine the working temperatures and the respective plateau pressures of the storage materials. For most applications, especially for mobile applications, working temperatures below 100 °C or at least below 150 °C are favored. A stable hydride is the one for which the equilibrium pressure lies below 1 atmosphere at 300 K. These hydrides have enthalpy of formation more negative than -40kJ/mole of  $H_2$  [15].

**Table 1: Enthalpy of formation of transition metal hydrides in kJ/mol  $H_2$  [14]**

ScH <sub>2</sub>	TiH <sub>2</sub>	VH <sub>2</sub>	CrH	MnH	FeH	CoH <sub>0.5</sub>	NiH <sub>0.5</sub>
-200	-126	-54	-16	-9	+14	0	-6
YH <sub>2</sub>	ZrH <sub>2</sub>	NbH <sub>2</sub>	MoH	TcH	RuH	RhH <sub>0.5</sub>	PdH <sub>0.5</sub>
-225	-165	-60	-12	+36	+42	+25	-40
LaH <sub>2</sub>	HfH <sub>2</sub>	TaH <sub>0.5</sub>	WH	ReH	OsH	IrH	PtH
-210	-133	-78	+16	+52	+48	+42	+26
ThH <sub>2</sub>	UH <sub>3</sub>	PuH <sub>2</sub>					
-146	-85	-155					

In literature many reports are there, where the enthalpy of formation of the hydride has been found out using both direct and indirect techniques. Some researchers find out the enthalpy value using the combination of a Sievert's type of P-C-T apparatus and a reaction calorimeter [16-18]. This enables direct measurements of Gibbs' free energies and enthalpy simultaneously and it shows the greater accuracy of the enthalpy and entropy values over the entire range.

The use of a heat flow calorimeter with a differential twin cell configuration is another means to study solid-gas reactions [19].

The first report of the intermetallic hydride came in 1958 and several other intermetallic compounds were reported subsequently. Till then many interesting alloys and intermetallic compounds have been identified as hydrogen storage materials, most of which consist of one hydride forming element and one non hydride forming element. Most typical examples are LaNi<sub>5</sub>, FeTi, AB<sub>2</sub> type of Laves phase systems, TiV based solid solutions, and Mg based systems. Due to this thermodynamics criterion, it is very important to know the  $\Delta H$  value of the metal hydride system as it decides whether the metal hydride system is reversible at room temperature or not.

#### 4. Different metal hydride based systems

LaNi<sub>5</sub> based systems are the most well studied hydrogen storage materials. LaNi<sub>5</sub> forms hydride with the formula unit of LaNi<sub>5</sub>H<sub>7</sub> (1.5 wt. %) and can be easily activated. It shows very flat plateau region with low hysteresis. Murray et al [19, 20], used a heat flow calorimeter with the differential twin cell configuration to study metal-hydrogen reactions of LaNi<sub>5</sub> system. Enthalpies for the reaction in the two-phase region of the LaNi<sub>5</sub>-H<sub>2</sub> system are independent of the overall composition but exhibit a small hysteresis and the absorption and desorption enthalpies are found to be -32.30 kJ/mole and -31.83 kJ/mole respectively. The problem with this alloy is that after a few cycles of hydrogen absorption- desorption, the hydrogen storage capacity decreases due to the degradation of the alloy. The thermodynamic properties of the LaNi<sub>5</sub> compounds vary extensively with composition. Several multi-components alloys in this series, La<sub>1-x</sub>RE<sub>x</sub>Ni<sub>5-x</sub>M<sub>x</sub> (RE = mishmetal, Ce, Nd& M = Fe, Co, Ni, Mn, Cu Al, Sn etc.), have been studied comprehensively [21, 22]

The hydrogen storage capacity of the FeTi based intermetallic compound is 1.9 wt. % (it forms FeTiH<sub>2</sub>), and the major advantage of this system is that the constituent elements are inexpensive. But due to the formation of TiO<sub>2</sub> oxide layer the activation of FeTi system is troublesome process. Different substituent elements have been studied to improve its activation and kinetics, and the most effective one is found to be Pd [23, 24].

The investigation of titanium-vanadium alloys generally show formation of two types of hydrides: a mono-hydride with a pseudo-cubic fcc (face centered cubic) structure and a di-hydride with a CaF<sub>2</sub> structure. Usually, the mono-hydride is thermodynamically too stable for practical applications; this makes the usable capacity smaller than the total capacity. If the mono-hydride could

be destabilized without changing its hydrogen storage capacity, then the BCC (Body Centered Cubic) solid solution could be very attractive alloy for commercial applications. Nomura and Akiba [25], in their work on Ti-V-Fe alloy system, have mentioned that ferrovandium may be used as raw materials instead of pure vanadium. Since then, use of ferrovandium or mixture of vanadium and iron has been reported by numerous authors [26-32]. Recently, particular emphasis has been on Ti-V-Cr compositions [33]. Another system that was subject of many studies is Ti-V-Mn [34-36]. Ti was also partially replaced by Fe and the hydrogen absorption properties of  $Ti_{1-x}VFe_x$  ( $x = 0.0, 0.1, 0.15, 0.2$  and  $0.4$ ) alloys were investigated in detail. Fe substituted Ti-V alloys were characterized by XRD and EPMA. It is evident from Fig. 4, that except  $Ti_{0.85}VFe_{0.15}$ , all the other Ti-V-Fe compositions are having mixed phase structure composed of a body centered cubic (bcc) phase and a secondary C14 Laves phase, with former as the major phase. The composition,  $Ti_{0.85}VFe_{0.15}$  is characterized by a single phase bcc structure. The hydrogen storage capacities of  $Ti_{1-x}VFe_x$  alloys as a function of Fe content,  $x$ , are shown in Fig. 5. It is seen that the hydrogen storage capacity of  $Ti_{1-x}VFe_x$  increases with Fe content up to  $x = 0.15$ , but further increase in the Fe content brings down the hydrogen storage capacity drastically. At a high Fe concentration, the bcc phase was found to coexist with the secondary phase. The amount of the hydrogen absorbed in this series of alloys is closely related with the amount of bcc phase present. The bcc phase in Ti-V system is reported to absorb more hydrogen than the secondary phase [17]. The composition  $Ti_{0.85}VFe_{0.15}$  was found to have single phase bcc structure and it shows the maximum storage capacity of 3.7 wt. % among the various Ti-V-Fe compositions studied in this work.

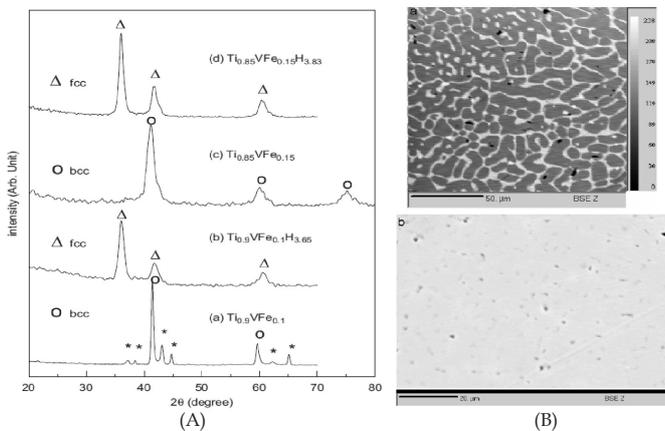


Figure 4: (A) X-ray diffraction patterns for: (a)  $Ti_{0.9}VFe_{0.1}$ , (b)  $Ti_{0.9}VFe_{0.1}H_{3.65}$ , (c)  $Ti_{0.85}VFe_{0.15}$  and (d)  $Ti_{0.85}VFe_{0.15}H_{3.83}$  (the lines corresponding to the secondary phase are marked by '\*') (B) Electron micrographs for: (a)  $Ti_{0.9}VFe_{0.1}$  and (b)  $Ti_{0.85}VFe_{0.15}$  alloys [International Journal of Hydrogen Energy,32, 4973 (2007)]

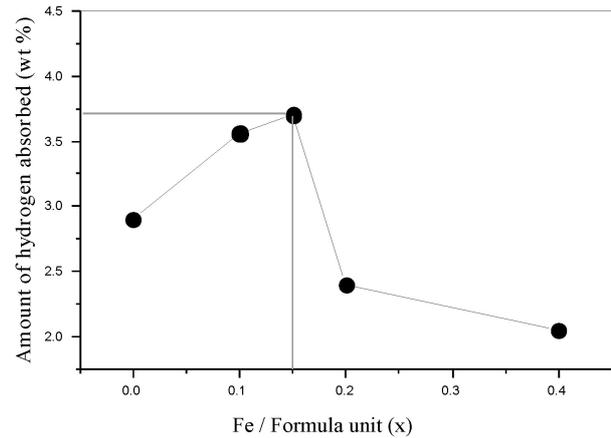


Figure 5. Variation of hydrogen absorption capacity with respect to the Fe content in  $Ti_{1-x}VFe_x$  alloys ( $x = 0.0, 0.1, 0.15, 0.2$  and  $0.4$ ) [International Journal of Hydrogen Energy,32, 4973 (2007)]

The desorption profiles of the saturated hydrides reveal that with increasing Fe concentration the hydrogen desorption temperature decreases. This may be attributed to the fact that with increasing Fe concentration the relative stability of the hydrides decreases and hence the hydrogen desorption takes place at a lower temperature.

The hydrogen absorption properties of  $Ti_{0.85}VFe_{0.15}$  alloy was modified by Zr substitution (5 at. %) at V site to ease the activation as it is known that small amount of Zr substitution eases activation before hydrogen absorption. The alloys and the corresponding hydrides were characterized by X-ray diffraction and Mössbauer spectroscopy. The crystal structure (Fig. 6) shows that 5 at. % of Zr substitution in place of vanadium results in a bi-phasic structure consisting mainly C15 cubic Laves phase along with V based bcc solid solution. The lattice parameter of the C15 cubic Laves phase was found to be 7.36 Å. It may be noted that the C15 cubic Laves phase structure remains unchanged on hydrogenation of  $Ti_{0.85}V_{0.95}Fe_{0.15}Zr_{0.05}$

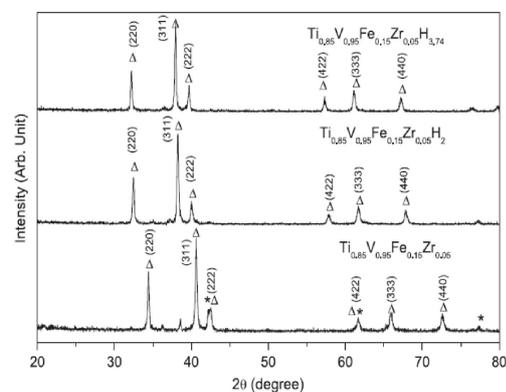
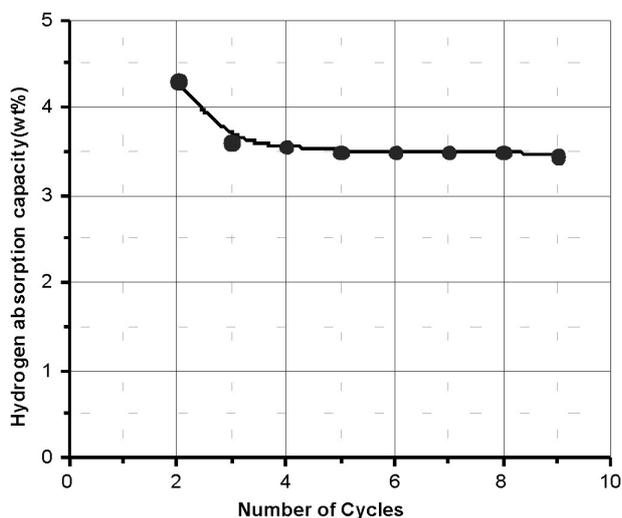


Figure 6. XRD patterns of  $Ti_{0.85}V_{0.95}Fe_{0.15}Zr_{0.05}$ ,  $Ti_{0.85}V_{0.95}Fe_{0.15}Zr_{0.05}H_2$  and  $Ti_{0.85}V_{0.95}Fe_{0.15}Zr_{0.05}H_{3.74}$ . ( $\Delta$  C15 Laves phases, \* V based bcc solid solution) Int. J. of Hydrogen Energy, 33 (2008) 350-55.

alloy though there is an appreciable shift in the XRD peak positions to lower 2-theta values indicating volume expansion due to hydrogenation.

Comparing the hydrogen absorption capacity and the hydrogen desorption properties of  $Ti_{0.85}V_{0.95}Fe_{0.15}Zr_{0.05}$  with those of  $Ti_{0.85}VFe_{0.15}$  it was found that the Zr substitution improves the hydrogen absorption-desorption characteristics of  $Ti_{0.85}VFe_{0.15}$  alloy by decreasing the hysteresis loss without appreciably affecting the maximum hydrogen storage capacity. The effective hydrogen storage capacity was found to improve to 5 at. % of Zr substitution in place of V. The increase in the effective hydrogen storage capacity can be attributed to the fact that Zr substituted alloy has an additional site, which desorbs hydrogen at a lower temperature as compared to Ti-V-Fe system.

Recently, in Ti-Cr-V series [37], we have explored the hydrogen storage properties of  $Ti_2CrV$  alloy. The alloy shows quite high hydrogen storage capacity of 4.37 wt. % at room temperature. The alloy was tested for cyclic stability and Fig. 7 shows the cyclic hydrogen storage capacities of the  $Ti_2CrV$  alloy. The hydrogen storage capacity of the alloy is measured up to 10 cycles and a stable absorption capacity of 3.5 wt.% is found after few cycles. It is found that there is a 20% decrease in the hydrogen absorption capacity after the third cycle, which remains almost constant for the successive cycles [37].



**Figure 7.** Cyclic hydrogen absorption capacity of  $Ti_2CrV$  alloy at room temperature [Int. J. of Hydrogen Energy, 37, 3677 (2012)].

Though the alloy shows promises due to its high hydrogen storage capacity, but the desorption temperature of the alloy is on the higher side for practical application. This type of alloy is relevant for stationary applications and the separation of hydrogen from gaseous mixtures at medium to high temperatures, but not useful for

transport application. For vehicular application, hydrogen storage material should have lower hydrogen desorption temperature and high effective storage capacity. The hydrogen storage properties Ti-Cr-V based system can be tuned with substitution of Ti by other late d-block transition metal elements like Fe, Co and Ni. These late d-block transition metal elements have more numbers of d-electrons, so they generally decrease the hydrogen desorption temperature by decreasing the stability of the hydride [38-40]. We have studied the influence of Fe, Co Ni and Sn substitution for Ti in  $Ti_2CrV$  alloy. We have evaluated the structure, homogeneity, hydrogen storage capacities, pressure composition isotherm, and the desorption profile of  $Ti_{1.9}CrVM_{0.1}$  (M= Fe, Co, Ni and Sn) alloys and  $Ti_{1.8}CrVM_{0.2}$  (M= Co and Ni) alloys [41]. The maximum hydrogen absorption capacities are found to be 4.13, 4.01 4.26, 3.34, 3.84 and 4.00 wt% respectively for the  $Ti_{1.9}CrVFe_{0.1}$ ,  $Ti_{1.9}CrVCo_{0.1}$ ,  $Ti_{1.9}CrVNi_{0.1}$ ,  $Ti_{1.9}CrVSn_{0.1}$ ,  $Ti_{1.8}CrVCo_{0.2}$  and  $Ti_{1.8}CrVNi_{0.2}$  alloys at room temperature. The decomposition temperatures of the hydrides decrease as we go from Fe to Ni substitution with decrease in hydrogen absorption capacity except the Sn substituted alloy and the reduction in desorption temperature increases with increase in concentration of substituent. The study on Sn substituted alloy reveals that the hydrogen absorption capacity decreases with Sn substitution and hydrogen desorption temperature increased significantly. The present study revealed that among the studied alloys, Ni substituted alloy shows a marginal decrease in the storage capacity compared to  $Ti_2CrV$  alloy whereas the decomposition temperature of the hydride decreases drastically, which is very much essential for practical application.

Both vanadium and niobium belong to the same group (Group V), vanadium being a 3d transition metal whereas niobium to 4d series. In addition, enthalpies of formation of hydrides for Nb and V are almost same. It will be interesting to see the effect of replacing vanadium by niobium on the hydrogen storage characteristics in Ti based bcc alloys. The maximum hydrogen absorption capacity of  $Ti_{0.67}Nb_{0.33}$  alloy was found to be 1.76 wt%. From the Ellingham diagram, it is evidenced that the oxygen partial pressure needed to form Ti and Nb oxides are very low; as a result, they have high affinity towards oxygen. Due to the formation of oxide layer on the alloy surface, the hydrogen absorption rate is slow [42, 43] for the Ti-Nb alloy. Nedyakha et al. [44] have shown that, when Fe is added as an additional element to Ti-Nb alloy, its oxidation resistance is greatly improved. Based on the previous studies, iron was incorporated to improve the hydrogenation behavior of  $Ti_{0.67}Nb_{0.33}$  alloy. The Fe substituted alloys show higher hydrogen uptake

compared to parent Ti-Nb alloy. Moreover, the kinetics of hydrogen absorption has also improved which can be explained in terms of trapping energy at subsurface sites. The bonding of the trapped hydrogen at the subsurface sites of Nb is stronger than chemisorption, and hydrogen becomes tightly bound below the first few layers which results in the slow diffusion of hydrogen into the bulk. This is reflected as poor hydrogen absorption kinetics of  $Ti_{0.67}Nb_{0.33}$  alloy. The subsurface acts as a valve and regulates the passage of hydrogen from the surface to the bulk. Due to partial substitution of Nb by smaller atom Fe, strain is generated in the ternary alloys  $Ti_{0.67}Nb_{0.33-x}Fe_x$  ( $x = 0.13, 0.20$ ) which helps to open the "valve" by reducing the subsurface trapping energy. This results in faster rate of hydrogenation reaction in Fe substituted Ti-Nb alloys. Fig. 8 presents the rate of hydrogenation for  $Ti_{0.67}Nb_{0.33-x}Fe_x$  ( $x = 0.00, 0.13, 0.20$ ) alloys as change of reacted fraction ( $\zeta$ ) with time.  $\zeta$  is obtained from the ratio  $\zeta = (P - P(t)) / (P - P_\infty)$  where  $P$  is the initial pressure of the reaction.  $P(t)$  and  $P_\infty$  are the pressures at time  $t$  and final equilibrium, respectively.

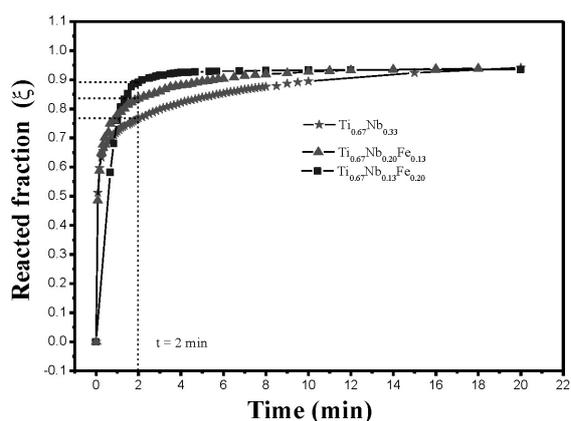


Figure 8. Kinetics of hydrogen absorption for  $Ti_{0.67}Nb_{0.33-x}Fe_x$  ( $x = 0.00, 0.13, 0.20$ ) alloys at RT [Journal of Alloys and Compounds, 585, 120 (2014).]

In  $Ti_{0.67}Nb_{0.33-x}Fe_x$  series,  $Ti_{0.67}Nb_{0.13}Fe_{0.20}$  shows maximum hydrogen absorption capacity and fastest absorption kinetics. Hence, we explored the hydrogenation kinetics of this alloy in detail. Two different types of rate equations were required to fit the kinetic data, indicating two different rate determining steps (rds) during the progress of hydriding reaction. The solid-gas reaction in the ( $\alpha + \beta$ ) mixed phase region and three dimensional diffusion of hydrogen in the  $\beta$ -phase region are the two rate determining steps, and the activation energies for these two processes are 7.34 and 15.1 kJ/mol, respectively [45].

$AB_2$  Laves phases are a class of alloy that is considered to be promising candidates as hydrogen storage materials and

negative electrodes for Ni-MH batteries. It is well known that many of the pseudo binary compounds like  $AB_2$  show excellent hydrogen absorption-desorption properties and can be considered as potential hydrogen storage materials [46, 47]. Many of them can absorb three hydrogen atoms per molecule and exhibit a desorption plateau pressure of around 1 atm. at room temperature. Zr-based  $AB_2$  alloys are of interest, because of their good storage capacity, fast kinetics and easy activation compared to  $LaNi_5$  systems. Their thermodynamics and the electrochemical properties of the Laves phase compounds  $Zr_{1-x}T_xM_{2-y}N_y$  ( $T = Ti, Y, Hf, Sc, Nb$  &  $M/N = V, Cr, Mn, Fe, Co, Ni, Cu, Al, Sn, Ge$ ) can be manipulated easily by substitution [47-51].

$ZrFe_2$  can absorb only a little amount of hydrogen forming solid solution due to the unfavorable thermodynamics. But the thermodynamic properties can be changed drastically by doping V in place of Fe in  $ZrFe_2$  compound. It was found that with the increase in V content the hydrogen absorption capacity increases significantly due to the decrease in the 3d occupation number in the transition elements. The hydrides, i.e.,  $ZrFe_{1.8}V_{0.2}$ ,  $ZrFe_{1.6}V_{0.4}$  and  $ZrFe_{1.4}V_{0.6}$ ,  $ZrFe_{1.2}V_{0.8}$  absorb 2.52, 3.26, 3.61 and 3.78 H/formula unit, respectively. The plateau pressure for hydrogen absorption decreases significantly with increase in the V content, indicating higher thermodynamic stability of the hydrides [52].

The formation enthalpies of the hydrides were found out from the van't Hoff plot and the enthalpies of formation of the hydrides have been found out from the slope. It is seen that with increase in the V content the formation enthalpy becomes more and more negative indicating more stable hydrides [Fig. 9].

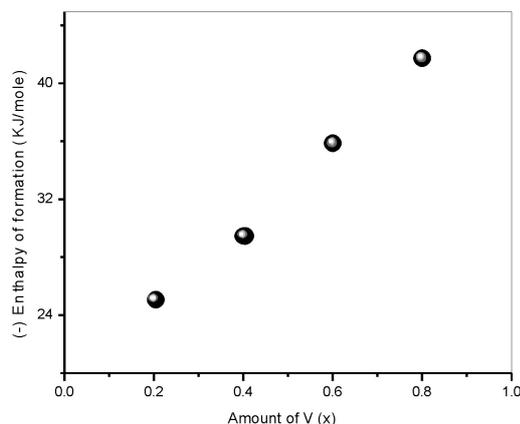


Figure 9. The variation of enthalpy of formation of  $ZrFe_{2-x}V_x$  ( $x = 0.2, 0.4, 0.6, 0.8$ ) [Intermetallics 51 30 (2014)]

The increase in the stability of the hydrides with V substitution was also reflected in the temperature programmed desorption profile, which shows that with

increase in the V content the desorption temperature increases.

Though transition metal hydrides provide high volumetric densities, good kinetic and thermodynamic properties and long term cyclic stability, the gravimetric storage capacities are lower in most of the cases. It is likely that the use of metal hydride in hydrogen storage will be confined to small applications, because of the low energy density and the cost. Due to the high volumetric densities, the metallic hydrides can be used for advanced fuel cell driven submarines, prototype passenger ships, forklifts as well as auxiliary power unit in laptops.

### 5. Mg-based hydrogen storage materials

Light metal hydrides, including Li, Al and Mg, are considered to have potential in the vehicular application due to high gravimetric hydrogen storage capacities. Mg can form  $MgH_2$  with a maximum hydrogen storage capacity of 7.6 wt. %. Furthermore, magnesium is cheap and its ore is abundantly available. It has a medium reactivity towards air and oxygen, which is an advantage over most other light-weight metal hydrides. But the major barrier towards its application as hydrogen storage material is that, it shows a quite sluggish kinetics of hydrogen absorption-desorption, which is mainly diffusion control. The high thermodynamic stability of  $MgH_2$  results in a relatively high desorption enthalpy of 75 kJ.mol  $[H_2]^{-1}$  at standard conditions, which corresponds to an equilibrium temperature of 561 K for  $H_2$ - desorption at 1 bar  $H_2$ . For practical use of  $MgH_2$  as a reversible hydrogen storage material, both the hydrogen sorption rates and the desorption temperatures have to be improved.

In case of bulk Mg, the diffusion of hydrogen atom towards the bulk is very slow. Again after  $MgH_2$  formation, the diffusion of hydrogen becomes much slower. It is documented that the diffusion of hydrogen through  $MgH_2$  is 5000 times slower than pure Mg metal at 350°C [53]. One of the approaches to increase the hydrogen absorption-desorption kinetics is ball milling the Mg powder or the  $MgH_2$  powder. In many reports ball milling has been used successfully as a mean to increase the kinetics [54-57]. By ball milling, the initial powders get heavily deformed and fractured, and slowly with time the particle size decreases. With ball milling, the diffusion path length decreases and the volume fraction inside crystallite becomes less, so the hydrogen diffusion rate increases, as a result, both the hydrogen absorption-desorption rate increases. However, thermodynamics are not affected by such techniques, hence the desorption temperature of  $MgH_2$  is not lowered.

Alloying or doping techniques are able to lower the desorption temperature of  $MgH_2$  by 30-100 K, but this is accompanied by a lower hydrogen storage capacity due to the added weight [58-61]. Addition of catalytic elements like Pd, transition metal elements, Nb, can improve the kinetics of hydrogen absorption by easing the dissociation of hydrogen molecule on the Mg surface. By addition of suitable catalyst, Mg can absorb hydrogen at relatively faster rate at room temperature. Recently, metal oxide catalysts ( $Nb_2O_5$ ,  $V_2O_5$ ,  $Mn_2O_3$ ,  $Cr_2O_3$ ,  $Al_2O_3$ ,  $TiO_2$  etc.) also have drawn much attention, as they also can improve the kinetics of hydrogen absorption in Mg based systems and the catalytic activity found to retain even up to 1000 cycles [62]. Lower desorption temperatures have also been reported for other bulk phases of magnesium hydride, such as, sputtered thin films of Mg [63-69] highly amorphous Mg etc. [59,70]. Moreover, decrease in the particle size has been shown to have a favorable effect on the hydrogen desorption temperature of metal doped magnesium hydrides [71-73]. These results indicate that, after doping, due to the distortions of the  $MgH_2$ -lattice, there is a shift in the desorption temperature and enthalpy value [74-83].

### 6. Summary

In the present paper we have discussed the thermodynamic properties of the metal hydrides and their application as a hydrogen storage material. The van't Hoff plot has been discussed in detail and the methods have been described by which the enthalpy of formation of the metal hydride can be calculated. Several examples have been discussed where doping was shown to change the thermodynamic and hydrogen desorption properties of the metal hydride.

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# Material Challenges in Renewable Hydrogen Production

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## Abstract

Hydrogen, the most abundant element in the universe, does not occur freely on our planet and has to be derived from its combined forms such as water, fossil fuels, hydrocarbons and biomass and the process is energy intensive. Various processes used for hydrogen production can be divided under three categories: thermal, electrolytic, and photolytic. An attempt is made here to present an overview of the renewable hydrogen production technologies and the challenges associated with them that need to be overcome to realize the full potential of this clean energy carrier for sustainable energy supply in the future.

## 1. Introduction

Exploration of alternate energy resources has attained great significance in recent times due to ever-increasing worldwide energy demands, depleting fossil resources and growing concern about global warming due to emission of greenhouse gases (GHG). Viable energy options available today are fossil fuels, hydroelectric, nuclear, solar, wind, geothermal etc. For many applications like in transport sector, usages of a clean and sustainable energy/fuel is in great demand today. Hydrogen is a clean and renewable energy carrier which offers a promising alternative to the fossil fuels, particularly for the transport applications using fuel cell technology. As hydrogen does not occur freely on the earth and is predominantly present as water, fossil fuels and biomass, its production from these sources is energy intensive. Presently, most of the hydrogen required for the consumption by various industries (fertilizer, refinery, electronics, metal, food, etc.), is produced from fossil fuels (~ 96%) using thermal processes like steam methane reforming (SMR), partial oxidation, and gasification of coal or biomass. These processes, however, suffers from a major drawback i.e. generation of CO<sub>2</sub>, a green house gas, as a by-product. The technology for producing hydrogen from a variety of resources, including renewable, is widely investigated [1-3]. Hydrogen production by these processes, however, is costly as compared to SMR. In this context a threshold cost goal for hydrogen production (including its delivery and supply) has been set by the U.S. Department of Energy at \$2.00–\$3.00 kg<sup>-1</sup> so as to make it cost competitive with the petroleum fuels.

## 2. Hydrogen Production Processes

Hydrogen production processes can be broadly classified into three general categories namely thermal, electrolytic, and photolytic [1-4]. These processes along with the raw materials and energy sources used are listed in Table 1.

## 2.1 Thermal Processes

Thermal processes for hydrogen production can be further divided in to two types: one in which energy is used to release hydrogen from various resources, such as natural gas, coal, biomass, liquid fuels, while in other heat (500 - 2000 °C), in combination with closed-chemical cycles also known as thermochemical cycle, produces hydrogen through a series of chemical reactions involving fully recyclable intermediates from renewable resources such as water.

### 2.1.1 Hydrogen from Fossil Fuels

Steam methane reforming, partial oxidation, autothermal reforming and gasification of coal/biomass primarily constitute the first type of thermal processes and these accounts for about 96 % of world's hydrogen production today [3-6]. We will briefly discuss here hydrogen production processes involving natural gas and coal.

#### • Hydrogen from natural gas

Hydrogen is produced from natural gas (major component: methane) by three different chemical processes namely steam methane reforming (SMR), partial oxidation (POX) and autothermal reforming (ATR). SMR involves endothermic conversion of methane and water vapour into hydrogen and carbon monoxide in presence of a nickel catalyst. In addition desulfurization catalysts such as bi-metallic Co-Mo and ZnS are used to remove the sulphur impurity from the methane feed-gas. Among the three processes SMR needs a lower operating temperature (700 - 850 °C), is more efficient (65-80%), does not require oxygen, and yields product with high H<sub>2</sub>/CO ratio (3:1). It does have the highest emissions of the three processes. In POX hydrogen is produced by partially oxidizing (combusting) the hydrocarbon with oxygen. POX being an exothermic process does not require any external heat

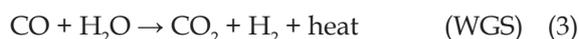
**Table 1: Hydrogen Production Processes**

Process		Raw Materials	Energy Sources
<b>Thermal</b>	Steam Reforming	Natural Gas/hydrocarbons and water	Combustion of natural gas/syngas Concentrated solar thermal power/ Nuclear heat
	Gasification	Coal/carbonaceous materials/ biomass and water	Combustion of coal/ carbonaceous materials/syngas/ biomass Concentrated solar thermal power
	Decomposition	Natural gas/fossil fuel hydro- carbons/biomethane/bio-hy- drocarbons	Natural Gas combustion Concentrated solar thermal power
	Thermolysis	Water	Concentrated solar thermal power
	Thermochemical cycles	Water	Concentrated solar thermal power Nuclear heat
<b>Electrolytic</b>	Electrolysis/High tem- perature steam electroly- sis	Water	Electricity from renewable energy source (wind, geothermal, solar, hydro) Electricity from non-renewables (fossil fuels, nuclear)
<b>Photolytic</b>	Photocatalytic/Photo- electrochemical	Water with/without sacrificial agents	Solar radiation
	Photobiological	Microbial and water	Solar radiation

source and a catalyst for operation and produces a product mix with H<sub>2</sub>/CO ratio (1:1 to 2:1). Besides this POX has minimal methane slip (loss), is more sulfur tolerant than the other processes and can be applied to a wide range of hydrocarbons including natural gas, heavy oils, solid biomass, and coal. Autothermal reforming is a combination of both SMR and POX where partial oxidation provides the heat and steam reforming increases the hydrogen production. ATR is normally carried out at temperatures in range 950 to 1100 °C and pressure as high as 100 bar. Both POX and ATR require an oxygen separation unit in order to feed pure oxygen to the reactor otherwise the product will be diluted with nitrogen (if air is used). Various chemical reactions occurring during reforming include:



Carbon monoxide generated in each of the three processes is reacted with steam to generate hydrogen via water-gas shift reaction (WGS). Normally two types of water-gas-shift reactors one operating at high temperatures (above 350 °C usually with iron catalyst) and the other at low temperatures (210 - 330 °C often with copper catalyst) are employed to improve the hydrogen yield [3].



CO<sub>2</sub> from the product gas (after WGS) is removed by an alkaline-based solution (typically alkanolamines such as methyldiethanolamine) via chemical absorption and the resulting hydrogen-rich gas is further purified via pressure swing adsorption (PSA). Such purification steps, however, add to the production costs and reduce the total efficiency [4].

#### • Hydrogen from coal gasification

Hydrogen can be produced from coal through a variety of gasification processes (e.g. fixed bed, fluidised bed or entrained flow). In this process, pulverised coal reacts with air or oxygen (produced in an air separation unit) and steam at high temperatures in a gasifier, producing raw gas, which is composed of H<sub>2</sub> and CO along with CO<sub>2</sub>, some CH<sub>4</sub> and residual steam (C(s) + O<sub>2</sub> + H<sub>2</sub>O + heat → CO + CO<sub>2</sub> + H<sub>2</sub>). In addition, carbonyl sulphide (COS), hydrogen sulphide (H<sub>2</sub>S) and other impurities are also present in the raw gas. The raw gas is treated with processes similar to those described in natural gas steam reforming to produce a stream of hydrogen, CO and CO<sub>2</sub>. The CO is further reacted with steam to produce H<sub>2</sub> through water-gas shift reaction (Eqn.3).

Compared to steam reforming, coal gasification process is more complex as it requires: (i) more extensive feedstock pre-treatment (such as grinding of coal and drying or preparing a feeding coal-slurry depending on the

gasifier type), (ii) an air separation unit for the production of oxygen for oxygen-blown gasifiers, (iii) multi-stage cleaning of raw syngas (e.g. removal of particulate matter, dust, sulphur) and (iv) further syngas treatment in addition to CO conversion [5].

#### *Material challenges for H<sub>2</sub> production from fossil fuels*

Emission of carbon dioxide still remains a major challenge to make the fossil fuels based hydrogen production processes a zero-emission one. Various CO<sub>2</sub> capture and storage (CCS) technologies including (i) use of deep saline reservoirs, (ii) injection of CO<sub>2</sub> into depleted oil for storage and to enhance oil recovery and (iii) injection into the deep ocean are being explored for this purpose [7]. Also, hydrogen needs to be further purified (to remove the small amount of CO) to make it suitable for the PEM (Proton Exchange Membrane) Fuel Cells applications. This requires development of (a) better catalysts for preferential oxidation of CO [8] and (b) suitable membrane technologies to separate and purify the H<sub>2</sub> from the gas stream [9]. Similarly alternate desulfurization technology needs to be developed for selective alkylation of organo-sulfur molecules present in the fossil fuels. Japan Atomic Energy Research Institute (JAERI) proposes to use a nuclear reactor for supplying heat (800-900 °C) to the steam reforming process which will avoid reactant (methane) loss [10].

#### **2.1.2 Hydrogen from biomass**

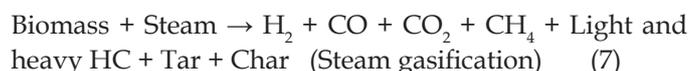
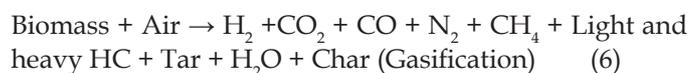
Hydrogen-rich gas can be derived from the biomass via two routes, (a) Thermochemical conversion, and (b) Bio-chemical/biological conversion. The choice of process depends upon the type and quantity of biomass feedstock [4]. We consider here the thermochemical conversion method here while the later procedure is presented under photolysis section. Thermo-chemical conversion is further divided in to (i) pyrolysis followed by reforming, (ii) conventional gasification, and (iii) Super critical water gasification.

Pyrolysis (thermal decomposition in an inert atmosphere) of biomass at 500-600 °C yields char, condensable liquids (tar, oils or bio-oils) and non-condensable gases (Biomass → Bio-oil + Char + Gas). Bio-oil is a mixture of carboxylic acids (mainly acetic and formic), aldehydes and alcohols, and lignin-derived methoxy phenolics (denoted as pyrolytic lignin), present as a low- to medium-molecular weight material. Its composition depends on raw material, the reactor, process conditions (temperature, residence time, and heating rate), and efficiency of the condensation system [11]. Bio-oil can be catalytically steam reformed to hydrogen and CO<sub>2</sub> at 750-850 °C as per the following reactions:



Hydrogen yield from biomass by pyrolysis/reforming process using a nickel based catalyst is reported to be ~ 11.2 wt% (based on weight of biomass; 17.2 g Hydrogen 100 g<sup>-1</sup> bio-oil) which is comparable to that observed with gasification [11].

Gasification of biomass produces combustible gas mixture (CO and H<sub>2</sub> with some CO<sub>2</sub>, water and other hydrocarbons including methane) via partial oxidation at high temperatures (800 to 900 °C). The char produced during fast pyrolysis of biomass is gasified with the help of gasifying agents namely air, oxygen or steam. Various reactions occurring during this process are as follows:



Florin and Harris reported an effective use of calcium oxide as a sorbent for CO<sub>2</sub> capture to increase the hydrogen yield during steam gasification of biomass [12].

As the name suggests super critical water gasification employs water in super critical state (22.1 MPa and 374 °C), where it reacts with the biomass to form CO and which upon reaction with steam produces CO<sub>2</sub> and hydrogen by water gas reaction. This process is highly suitable for biomass with high moisture content (>50%) but it is quite expensive.

#### **2.1.3 Hydrogen from Thermo-chemical splitting of water**

Water an inexhaustible source of hydrogen is quite stable. Thermolysis of water into elemental hydrogen and oxygen requires a temperature in excess of 2500°C (H<sub>2</sub>O → H<sub>2</sub> + ½ O<sub>2</sub>; ΔG<sup>0</sup> = 237 kJ/mol) [13, 14]. Moreover, the problems associated with construction materials for the reactor, effective separation of reaction products (H<sub>2</sub> and O<sub>2</sub>) and prevention of their recombination are quite difficult to overcome to realize water thermolysis. Water, however, can be decomposed at comparatively lower temperatures (~ 1000 °C) employing thermochemical cycles where water is decomposed through a series of chemical reactions involving intermediates that are fully recyclable. The concept of thermochemical production of hydrogen from water was first studied thermodynamically in the 1960s [13]. High temperature processes for hydrogen production are attractive from an efficiency perspective considering the second law of thermodynamics, from which is derived  $\eta = (1 - T_c/T_H)$ , where T<sub>c</sub> and T<sub>H</sub> are the

cold and hot temperatures, respectively. However, some processes may require an input of electrical or mechanical energy. The global process efficiency will then be:

$$\eta = \left( \frac{HHV}{Q + W_{el}/\eta_{el}} \right)$$

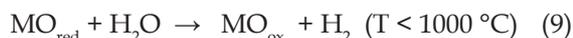
where, HHV is  $W_{el}/\eta_{el}$  r heating value of hydrogen, 286 kJ/mol (energy gained from burning hydrogen in oxygen at ambient conditions, with the initial and final conditions the same at 1 bar and 25 °C), Q - heat required to produce hydrogen,  $W_{el}$  - electrical work,  $\eta_{el}$  - efficiency of electricity production.

More than 200 thermochemical cycles have been reported. Notable among these are Sulfur-Iodine cycle, Hybrid Sulphur cycle, Copper-Chlorine, Calcium-Bromine, ZnO/Zn chemical cycle. Some of the representative thermochemical cycles with reaction steps involved and operating temperature are included in Table 2. Heat required for high-temperature water splitting can be provided by high temperature nuclear reactor (up to about 1000 °C) or solar concentrators (up to about 2000 °C). The major advantage of thermochemical cycles is that they produce hydrogen with near-zero green house gas emissions.

• **Solar-driven thermochemical processes**

Solar hydrogen production from water employing thermochemical cycles shows great promise as one of the long-term alternatives to fossil fuels. Use of concentrated solar radiation as the source of high-temperature process heat has been reported for hydrogen generation in two-step thermochemical cycle based on metal oxide redox pair

[14]. Such cycles proceed with endothermic reduction of a metal oxide at high temperature (above 1300 °C). Then, the reduced oxide or the metal reacts directly with water (exothermic hydrolysis) at lower temperature to generate hydrogen, which reforms the initial metal oxide. The two steps involved are:



Some of the reported metal/metal oxide redox pairs include Mn<sub>3</sub>O<sub>4</sub>/MnO, Co<sub>3</sub>O<sub>4</sub>/CoO, ZnO/Zn, Fe<sub>3</sub>O<sub>4</sub>/FeO, Ce<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>/NbO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>/In, WO<sub>3</sub>/W, CdO/Cd and TiO<sub>2</sub>/TiO<sub>x</sub> [14]. Among these, ZnO/Zn cycle has been investigated extensively and efficiency between 29% and 44% with heat recovery is reported [15].

• **Nuclear-driven thermochemical processes**

The use of high-temperature heat from nuclear plants to drive thermochemical processes for producing hydrogen has been largely governed by the type of nuclear reactors and remained focussed on the three thermochemical cycles namely Sulphur- Iodine (S-I), hybrid sulphur (the Westinghouse cycle) and copper-chlorine [16-18]. Thus, countries like USA, Japan, France, Italy, UK, Korea, China and India are pursuing S-I cycle for large scale production of hydrogen using high grade nuclear heat from very high temperature reactor (VHTR), a Generation IV reactor, expected to produce temperatures (~ 900-1000 °C) of higher efficiencies while Canada has focused its efforts on Cu-Cl cycle (Maximum temperatures requirement < 550 °C) with their Generation IV super-critical water cooled reactor (SCWR). Both sulphur - iodine/ hybrid sulphur and

**Table 2: Some representative thermochemical cycles**

S. No.	Thermochemical Cycle	Reaction steps involved	Temperature (°C)
	Zinc-zinc oxide	a) ZnO → Zn + ½ O <sub>2</sub> (g) b) Zn + H <sub>2</sub> O → ZnO + H <sub>2</sub> (g)	1900 427
	Sulfur-Iodine	a) I <sub>2</sub> (l) + SO <sub>2</sub> (g) + 2H <sub>2</sub> O (l) → 2HI (l) + H <sub>2</sub> SO <sub>4</sub> (l) b) 2HI (g) → I <sub>2</sub> (g) + H <sub>2</sub> (g) c) H <sub>2</sub> SO <sub>4</sub> (l) → H <sub>2</sub> O (g) + SO <sub>2</sub> (g) + ½ O <sub>2</sub> (g)	70 - 120 300 - 450 700 - 900
	Hybrid Sulfur	a) SO <sub>2</sub> (g) + 2 H <sub>2</sub> O + electricity → H <sub>2</sub> SO <sub>4</sub> (l) + H <sub>2</sub> (g) b) H <sub>2</sub> SO <sub>4</sub> (l) → H <sub>2</sub> O (g) + SO <sub>2</sub> (g) + ½ O <sub>2</sub> (g)	80 - 120 (electrolysis) 700 - 900
	Copper - Chlorine	a) 2 Cu (s) + 2 HCl (g) → 2 CuCl (l) + H <sub>2</sub> (g) b) 2 CuCl (s) → 2 CuCl (aq) → CuCl <sub>2</sub> (aq) + Cu (s) c) CuCl <sub>2</sub> (aq) → CuCl <sub>2</sub> (s) d) 2 CuCl <sub>2</sub> (s) + H <sub>2</sub> O (g) → CuO·CuCl <sub>2</sub> (s) + 2 HCl (g) e) CuO·CuCl <sub>2</sub> (s) → 2CuCl (l) + ½ O <sub>2</sub> (g)	430-475 Ambient electrolysis < 100 400 500

copper-chlorine thermochemical process have their relative merits, the former being more efficient (~ 47%) while the later operating at lower temperature has less challenges for equipment material selection and is adaptable to a wider range of heat sources such as geothermal, nuclear, or solar [18]. Some details about the widely investigated sulphur family cycle are presented below. This cycle is actively being pursued at BARC (from 2005 onwards) for large scale hydrogen production and envisages the use the high grade nuclear heat from the proposed compact high temperature reactor (CHTR) to drive the cycle.

### S-I thermochemical cycle

Sulfur-Iodine (S-I) thermochemical cycle is widely considered as a potential choice for large scale production of hydrogen due to its higher efficiency (~ 47%), all fluids process and adaptability with a high temperature nuclear reactor (~ 950°C). This cycle, originally proposed by General Atomics, USA, in mid 1970, comprises of three steps viz, Bunsen reaction, sulphuric acid decomposition and hydriodic acid decomposition, as depicted in Fig. 1. The whole process takes in water and high-temperature heat, particularly, in the acid decomposition steps, and releases hydrogen and oxygen while the reactants SO<sub>2</sub> and iodine are regenerated and recycled in the process. Various factors that influence the efficiency of the S-I cycle are: (a) optimization of Bunsen reaction to achieve phase separation with minimal side reactions, (b) separation of HI from HI-I<sub>2</sub>-H<sub>2</sub>O azeotropic mixture and its decomposition, and (c) kinetics of sulphuric acid decomposition, the most energy-demanding step of this cycle. Development of suitable catalysts which are active and stable for the decomposition of both acids has stimulated and posed challenges to the catalysis researchers.

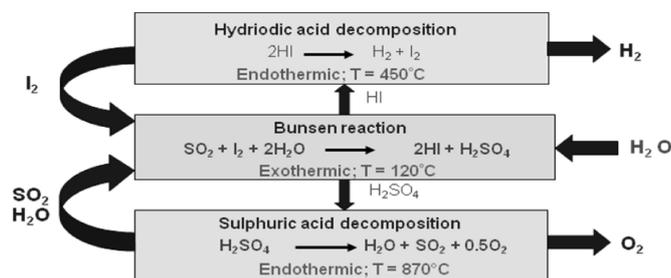


Figure 1: Different steps involved in Sulfur-Iodine thermochemical cycle

In 2004, Japan Atomic Energy Agency (JAEA) reported bench scale test of S-I cycle in a glass setup where continuous production of hydrogen at the rate of 32 NLPH was achieved for 20 h [16]. A successful demonstration of a closed glass loop operation of S-I cycle for 20 h producing 30 NLPH H<sub>2</sub> at BARC, this year has made India the 5<sup>th</sup> nation

in the world to do so [19]. These efforts were supported by the in-house development of an efficient and poison resistant iron oxide based catalysts (Fig. 2) for sulphuric acid decomposition step of the S-I cycle at Chemistry Division, BARC [20]. During this development various oxide/mixed oxides were investigated as a substitute to the noble metal catalyst. Screening results for the different catalysts for sulphuric acid decomposition reaction are presented in Fig. 2 (A). In addition Chemistry Division is developing supported platinum catalysts for liquid phase decomposition of HI [21].

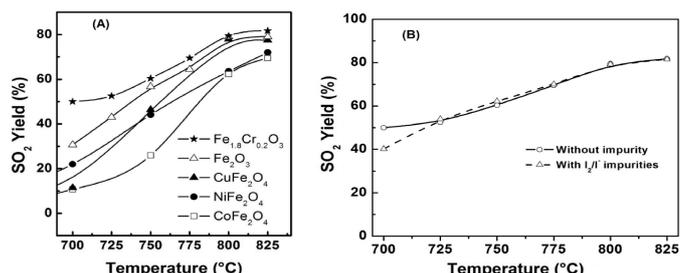


Figure 2: Temperature dependent SO<sub>2</sub> yield during decomposition of sulfuric acid over different catalysts (A) and influence of I/I<sub>2</sub> impurities on SO<sub>2</sub> yield of Fe<sub>1.8</sub>Cr<sub>0.2</sub>O<sub>3</sub> (B); Catalysts amount: 0.2 g; acid (liquid) feed rate: 0.05 ml min<sup>-1</sup> in N<sub>2</sub> carrier gas (flow rate: 40 cc/min); mole fraction of I/I<sub>2</sub> impurities: X<sub>HI</sub> = 3.8 × 10<sup>-3</sup>; X<sub>I<sub>2</sub></sub> = 9 × 10<sup>-4</sup> in 98 wt % H<sub>2</sub>SO<sub>4</sub>.

### Hybrid Sulphur cycle

The Hybrid Sulphur (HyS) cycle (also known as the Westinghouse cycle) does not involve any iodine and therefore problems associated with the iodine section of S-I cycle are avoided here. This cycle consists of two main steps, the electrolysis of aqueous SO<sub>2</sub> gas at around 80 °C to give hydrogen and sulphuric acid, followed by the sulphuric acid decomposition step similar to that of the S-I cycle as shown in Table-2. Whereas water electrolysis requires a potential of 1.23 V, presence of sulphur dioxide (in water) reduces the required electrode potential to a value of 0.17 V, thus resulting in substantial reduction in the energy required for the process. An efficiency of 47% LHV (55% using HHV) is predicted for HyS cycle [17]. There is ample scope for further improvement by reducing the electrode potential and developing better electro-catalysts, structural materials (stable at the high temperatures), H<sub>2</sub>SO<sub>4</sub> decomposition reactor and product separator. Savannah River National Laboratory (SRNL) has recently reported operation of a single cell electrolyser for more than 200 h at a cell temperature, pressure, current density and cell voltage of 80°C, 172 kPa, 500 mAcm<sup>-2</sup> and at 0.76 V, respectively [17].

## Material challenges for the thermochemical processes

The technology of solar- and nuclear-driven high-temperature thermochemical water splitting cycles is in early stage of development and has to overcome several challenges like material of construction, heat transfer medium, development of next generation of nuclear reactor technology, thus needs considerable research efforts.

### 2.2 Electrolytic Processes

Electrolytic processes use electricity to split water into hydrogen and oxygen in an electrolyser without emission of greenhouse gases, provided the source of the electricity used is either a renewable source or a nuclear one. This process is a preferred choice when high purity hydrogen is required. Three different types of electrolysers being used/under development are alkaline, proton exchange membrane (PEM) and solid oxide electrolyte cells (SOEC). The first two are basically low temperature electrolysers which operate at around 80 °C while the operating temperatures in case of SOEC lie in range 500-1000 °C. Salient features of each electrolyser are presented in Table-3. In alkaline electrolyser hydrogen needs to be removed from the water at cathode side through dehumidification while pure hydrogen can be obtained without further separation in PEM electrolyser. On the other hand, hydrogen can be separated from the steam in another stage after leaving the SOEC as shown in Fig. 3.

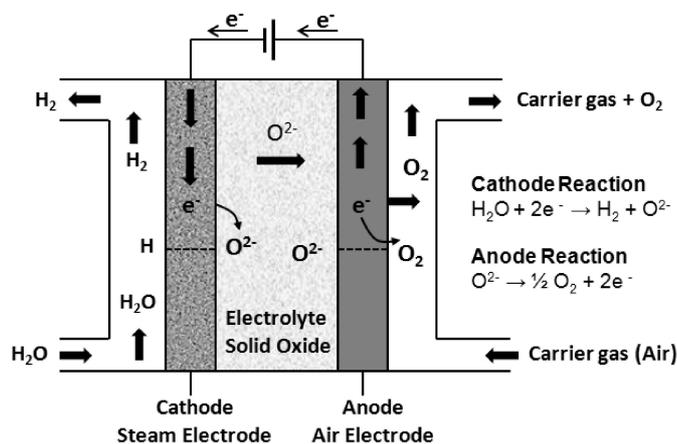


Figure 3: Schematics of a solid oxide electrolyser.

From thermodynamic point of view operation of electrolysis cells at high temperatures is advantageous as substantial part of the required energy ( $\Delta H = W_{\text{elec}} + Q = \Delta G + T\Delta S$ ;  $W_{\text{elec}}$  is electrical work) is supplied as thermal energy (heat brought in by the steam) and accordingly the primary electric energy demand ( $\Delta G$ ), is considerably reduced. Also, at high temperatures the kinetics of the electrolysis is fast, resulting in reduction in electrical losses

in the cell (due to lower ohmic resistance in the electrolyte and lower polarisation losses from the electrode reactions). In recent years, steam electrolysis in solid oxide electrolysis cells (SOECs) has received considerable attention due to its high efficiency and possibility to be coupled with renewable resources. Extensive research is on to identify the best materials for use in SOECs. In the meanwhile, materials used in solid oxide fuel cells (SOFCs) are being utilized as the starting point as the SOECs are essentially SOFCs operating in reverse mode. Similarly efforts are on to integrate electrolyser with power generators such as, nuclear, wind and solar power. Idaho National Laboratory (INL) demonstrated a 15 kW integrated laboratory scale facility with a hydrogen production rate of 0.9 Nm<sup>3</sup>/h [22]. More recently, Li et al [23] reported 500 h operation of a planer SOEC stack comprising of 30 cells (planar cathode-supported Ni-YSZ/YSZ/LSM-YSZ SOEC cells equipped with SUS430 ferritic stainless steel interconnects and glass sealants) at 800 °C and overall hydrogen generation efficiency of ~ 52.7%.

In addition to O<sup>2-</sup> conducting electrolytes, several proton conducting systems like perovskite-structured SrCe<sub>1-x</sub>M<sub>x</sub>O<sub>3</sub> (M: Y, Yb, Mg, or Sc; x = 0.05 - 0.1) and system based on based on BaCeO<sub>3</sub>, CaZrO<sub>3</sub>, SrZrO<sub>3</sub>, and BaZrO<sub>3</sub> have been investigated for the steam electrolysis [24]. While most of these materials are O<sup>2-</sup> conductors in air, they develop proton conductivity in the presence of hydrogen and water. Even though the conductivity of the proton conductors has been improved (with improved processing conditions and through selective doping of material) it remains much lower than the O<sup>2-</sup> conductivity reported for zirconia or ceria-based materials. Due to issues relating to the electrolyte stability, compatibility with other cell components, low ionic conductivity, and difficulties in processing have delayed the device development based on proton conductors.

### Material challenges for the electrolytic processes

As most of the research on SOECs studying performance and durability stays at single cell level, scope for improvement is enormous. Long-term performance degradation (should be less than 1% for 1000 h of operation of the cell) is the biggest challenge for scaling up of high temperature electrolysis technology. This is mainly due to air electrode delamination (most likely caused by the build-up of oxygen partial pressure electrode-electrolyte interface), Cr-vapor poisoning (from Cr-rich alloy interconnects), microstructure degradation (interactions among the cell components causing decrease in conductivity and electrochemical activity), and seal leakage (caused during thermal cycling due to mismatch of coefficient of thermal

**Table 3: Electrolysers for Hydrogen Generation**

Parameters	Alkaline	PEM	SOEC
Operating Temperature (°C)	70 - 90	< 100	500-1000
Electrolyte	KOH <sub>(aq)</sub> , NaOH <sub>(aq)</sub>	Sulfonated polymers like nafion	Ytria stabilized zirconia (YSZ), Scandia stabilized zirconia, doped ceria, LaSrGaMgO <sub>3</sub>
Conducting ion	OH <sup>-</sup>	H <sup>+</sup>	O <sup>2-</sup>
Cathode material	Ni with Pt catalytic coating	Pt black, IrO <sub>2</sub> , RuO <sub>2</sub>	Ni-YSZ cermet, Ni,Cu, Co mixed with/electrolyte materials titanate/ceria, noble metals, LaSr(CrMn)O <sub>3</sub>
Cathodic reaction	2H <sub>2</sub> O + 2 e <sup>-</sup> → H <sub>2</sub> + 2OH <sup>-</sup>	2H <sup>+</sup> + 2 e <sup>-</sup> → H <sub>2</sub>	H <sub>2</sub> O + 2 e <sup>-</sup> → H <sub>2</sub> + O <sup>2-</sup>
Anode material	Ni or Cu-coated with metal oxide	Pt black, IrO <sub>2</sub> , RuO <sub>2</sub>	Perovskite oxides like lanthanum manganate, lanthanum cobalt/iron oxide (LaSrCoO <sub>3</sub> , LaSrFeO <sub>3</sub> , LaSrCoFeO <sub>3</sub> ), BaSrCoFeO <sub>3</sub>
Anodic reaction	2OH <sup>-</sup> → ½ O <sub>2</sub> + H <sub>2</sub> O + 2e <sup>-</sup>	H <sub>2</sub> O → ½ O <sub>2</sub> + 2H <sup>+</sup> + 2 e <sup>-</sup>	O <sup>2-</sup> → ½ O <sub>2</sub> + 2 e <sup>-</sup>
Advantages	Scalable, robust, rapid start-up and shutdown, unlimited thermal cycling capability, can be used with intermittent or widely fluctuating loads, and commercially available (up to 750 Nm <sup>3</sup> H <sub>2</sub> /h).	Scalable, robust, rapid start-up and shutdown, Unlike alkaline electrolyser, no circulation or replenishment of alkaline solution is required.	Can be used with low-grade waste heat from chemical or power plants or solar thermal energy to reduce the electrical power input and increase efficiency.
Disadvantages	High electrical power consumption; high capital cost due to high cost of noble metal electrode.	High electrical power consumption; high capital cost due to high cost of noble metal electrode and membrane materials; degradation and lifetime issues with polymer membranes and cells.	Limitations on construction materials; materials' degradation, and lifetimes; slow start-up and shutdown; limited thermal cycling capability; low level of commercialization.

expansion between the seal and other components). Also issues pertaining to the electrolyte stability, compatibility with other cell components, low ionic conductivity, and difficulties in processing need to be resolved for the development of SOEC devices (both based on oxide ion and proton conductors). Development of suitable cell components material for electrochemical devices (regenerative fuel cells) which can be used for generating hydrogen during off-peak demand hours and a source of power during peak demand is another challenge to be met.

### 2.3 Photolytic Processes

Photolytic processes use light (sunlight) energy to split

water into hydrogen and oxygen. The minimum photon energy thermodynamically required to drive the reaction, H<sub>2</sub>O → H<sub>2</sub> + ½ O<sub>2</sub> is ~ 1.23 eV, which corresponds to a wavelength of ca. 1000 nm, in the near infrared region. Accordingly, it would appear possible to utilize the entire spectral range of visible light (400 < λ < 800 nm) which constitutes ~45% of solar spectrum.

Photolytic processes can be further divided into photoelectrochemical / photocatalytic and photobiological water splitting. Though the photolytic processes are in the very early stages of research, they have long-term potential for sustainable hydrogen production with low environmental impact.

### 2.3.1 Photocatalytic/photoelectrochemical splitting of water

The famous experiments of Fujishima and Honda on photoelectrochemical splitting of water using n-type semiconducting  $\text{TiO}_2$  (rutile) anode photocatalyst in 1972, has opened up the field to the researchers to develop suitable photocatalysts which are efficient and stable and cost-effective in utilizing the solar radiation particularly the visible part of it for hydrogen generation.

Hydrogen production via photocatalytic water splitting can be classified in two types: (i) photochemical-cell reaction (powder catalyst used as suspended particles in solution) form and (ii) photoelectrochemical-cell reaction (catalyst deposited in thin film form on a substrate to form a photo-anode/or photo-electrode). In the second type an external circuit is required to direct the photo-generated electron from photo-anode to a cathode where hydrogen is evolved (similar to electrolysis) while in the first type no external circuit is required and both  $\text{H}_2$  and  $\text{O}_2$  are evolved in the same cell. We shall be confining our discussion here to the photochemical-cell reaction only.

The three basic steps involved during water splitting on a semiconductor photocatalyst, as shown in Fig. 4, are:

- (i) absorption of photons with energies equal or higher than the semiconductor band gap, leading to the generation of electron - hole pairs ( $\text{Semiconductor} + h\nu \rightarrow h_{vb}^+ + e_{cb}^-$ )
- (ii) charge separation followed by two competitive processes namely migration of these photogenerated carriers in the semiconductor particles and charge recombination at both surface and in the bulk,
- (iii) surface chemical reactions (redox reactions) by which adsorbed species (water molecules) are reduced and oxidised by the photogenerated electrons and holes yielding  $\text{H}_2$  and  $\text{O}_2$ , respectively, ( $\text{H}_2\text{O} + 2h^+ \rightarrow \frac{1}{2}\text{O}_2 + 2H^+$  ;  $2H^+ + 2e^- \rightarrow \text{H}_2$ )

The electrons-holes recombination process is greatly influenced by the crystallinity and the particle size of the material (determined by the preparation conditions) and has a strong bearing on the efficiency of a photocatalyst. To prevent the recombination of electron-hole pairs, generally co-catalysts such as Pt, Pd, NiO, and  $\text{RuO}_2$  are incorporated in nanodispersed form on the semiconductor surface.

Separation of the electron-hole pairs and their migration is facilitated by an internal electric field which is created at the hetero-junctions formed between the semiconductor and co-catalyst. Co-catalyst plays another important role in creating active sites and reducing the activation energy or over potential for  $\text{H}_2$ - or  $\text{O}_2$ -evolution reactions on the surface of semiconductors.

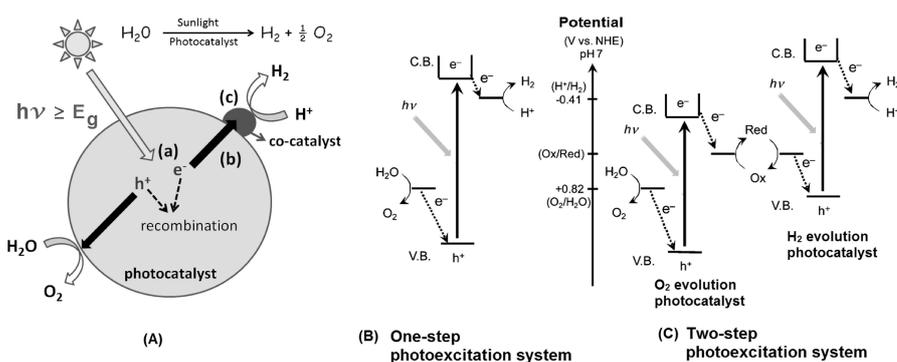


Figure 4. Schematics of water splitting over a typical semiconductor photocatalyst (A), and the energy diagrams for the one-step (B), and two-step photoexcitation systems (C); Processes shown in (A) are: (a): formation of electron-hole pair upon absorption of radiation, b - charge separation followed by migration to surface and (c)- surface chemical reaction by photogenerated electron and holes.

Following properties (semiconducting and electrochemical) are desired in a good photocatalyst for overall splitting of water: (a) band gap:  $< 3$  eV, preferably around 2.0 – 2.2 eV, (b) suitable band-edge potential for overall water splitting [bottom of the conduction band must be more negative than the reduction potential of water to produce  $\text{H}_2$  ( $\text{H}^+/\text{H}_2$ ; 0 V vs NHE), and the top of the valence band must be more positive than the oxidation potential of water ( $\text{O}_2/\text{H}_2\text{O}$ ; 1.23 V vs NHE) to produce  $\text{O}_2$ ] (c) capacity for efficient charge ( $e^-/h^+$ ) separation (d) able to suppress  $e^- - h^+$  pair recombination, (e) stable against corrosion and photocorrosion in aqueous environment, and (f) simple and cost effective synthesis.

Oxide semiconductors are known to be highly stable against photo-corrosion and were extensively investigated as photocatalysts. More than 140 metal oxides, Perovskites and oxynitrides have been reported for photochemical water-splitting reaction, however, majority of them are active under UV irradiation (which comprises of  $\sim 4\%$  of the solar spectrum) due to their large band gaps [25, 26]. Most of these oxides have either transition-metal cations with a  $d^0$  electronic configuration (e.g.,  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Ta}^{5+}$ ,  $\text{Nb}^{5+}$ ,  $\text{W}^{6+}$ , and  $\text{Mo}^{6+}$ ) or typical metal cations with  $d^{10}$  electronic configuration (e.g.,  $\text{In}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Sn}^{4+}$ , and  $\text{Sb}^{5+}$ ) as principal cation components. Nitrides and oxynitrides containing  $d^0$  transition-metal cations like  $\text{Ta}_3\text{N}_5$ ,  $\text{TaON}$ ,

and  $\text{LaTiO}_2\text{N}$  are the other class of compounds that were found to be active [26]. The non-oxides semiconductors such as sulfides are generally unstable and get deactivated due to photocorrosion e.g.,  $\text{CdS} + 2h^+ \rightarrow \text{Cd}^{2+} + \text{S}$  and have to be used in presence of sodium sulfite and sodium sulfide sacrificial agents. Sacrificial agents that are either an electron donor such as methanol,  $\text{S}^{2-}/\text{SO}_3^{2-}$  or an electron acceptor such as  $\text{Ag}^+$  have been widely used to promote formation of either  $\text{H}_2$  or  $\text{O}_2$ , respectively.

There are two main approaches for achieving water splitting using visible light. One approach is to apply a two-step photoexcitation mechanism between two different photocatalysts (a two-step system; Fig. 4C) [27] and the other approach involves one-step photoexcitation system (Fig. 4B) where a conventional photocatalyst is modified to a visible-light responsive photocatalyst using different band engineering methods including introduction of a mid-gap electron donor level (doped materials), hybridization of the O 2p orbital with other orbitals (oxides, oxynitrides and oxysulfides), and the formation of solid solutions. The first approach is inspired by natural photosynthesis in green plants and is also known as the Z-scheme. Here, the water splitting reaction is broken up into two stages: one for  $\text{H}_2$  evolution and the other for  $\text{O}_2$  evolution; these are combined by using a shuttle redox couple (Red/Ox) in the solution. Over a  $\text{H}_2$  evolution photocatalyst, the photoexcited electrons reduce water to  $\text{H}_2$  and holes in the valence band oxidize the reductant (Red) to an oxidant (Ox). The oxidant is reduced back to the reductant by photoexcited electrons generated over an  $\text{O}_2$  evolution photocatalyst where the holes oxidize water to  $\text{O}_2$ . This system thus lowers the energy required for photocatalysis,

allowing visible light to be utilized more efficiently than in conventional one step photoexcitation system. Z-scheme has another advantage of i.e., its ability to separate production of  $\text{H}_2$  and  $\text{O}_2$  by employing a separator, such as a porous glass filter, that permits only redox mediators to be transferred. Such separation of products in a conventional one-step water splitting system is not possible since  $\text{H}_2$  and  $\text{O}_2$  are evolved simultaneously on small semiconductor particles. Z-scheme systems however have a significant disadvantage that the two-step photoexcitation system requires the number of photons two-fold larger than the one-step system to achieve water splitting.

The search for visible-light responsive photocatalysts, especially during the last decade has brought quite a few promising systems, including  $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ -loaded GaN:ZnO (a one-step water splitting system) and a two-step photoexcitation system consisting of Pt/ZrO<sub>2</sub>/TaON and Pt/WO<sub>3</sub> with IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> shuttle redox mediators, where respective apparent quantum yields of about 5.1% has been observed upon illumination at 410 nm and 6.3% upon illumination at 420 nm, respectively [28,29]. Yan et al [30] demonstrated a very high value of apparent quantum yield (~93%) for  $\text{H}_2$  generation using Pt-PdS/CdS photocatalyst under visible light irradiation ( $\lambda > 400$  nm). Some of these results are included in Table 4. Recent results from Chemistry Division, BARC, on water splitting reaction using copper-doped titania (AQY = 5.8%) and ZrO<sub>2</sub>-TiO<sub>2</sub>-CdS nano-composite photocatalysts are presented in Figs. 5 and 6, respectively.

For more details on photocatalytic splitting of water some excellent reviews can be referred [30,31].

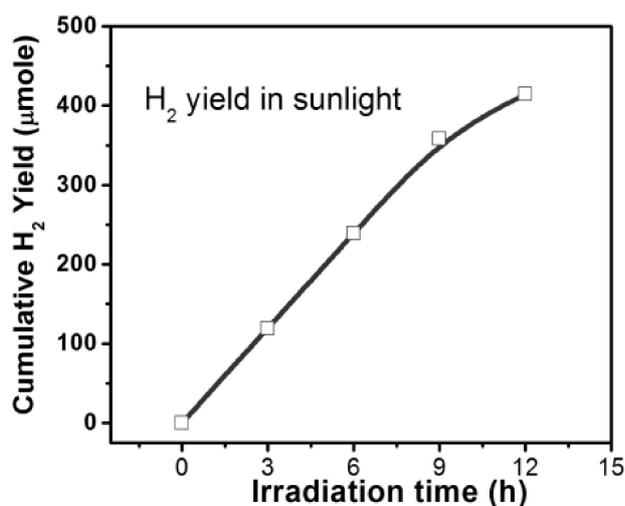


Figure 5. Time dependent photocatalytic activity of  $\text{Pt}/\text{Cu}_{0.02}\text{Ti}_{0.98}\text{O}_2$  for hydrogen generation under sun-light irradiation. Reaction conditions: 50 mg catalyst suspended in 15 ml of aqueous solution containing methanol (water : methanol :: 2:1)

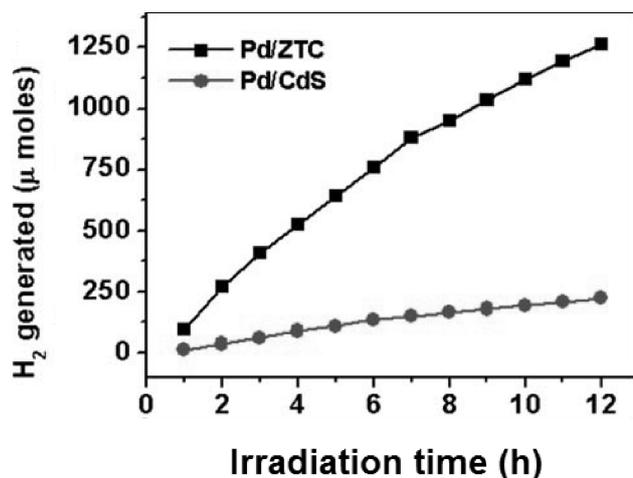


Figure 6. Time dependent photocatalytic activity of Pd/CdS, and Pd/ZrO<sub>2</sub>-TiO<sub>2</sub>-CdS (Pd/ZTC) for hydrogen generation under fluorescent lamp (total  $36 \times 8 = 288$  W), Reaction conditions: 50 mg catalyst suspended in 25 ml of aqueous solution containing Na<sub>2</sub>SO<sub>3</sub> (0.8 M) and Na<sub>2</sub>S (0.6 M) in 1:1 ratio by volume

**Table 4: Some of the recent results reported on photocatalytic generation of hydrogen from water using visible radiation**

Conditions					Activity		Reference
Photocatalyst	Co-catalyst	Sacrificial agent	lamp	Wave length (nm)	H <sub>2</sub> (μ mol h <sup>-1</sup> g <sup>-1</sup> )	App. Quantum yield* (%)	
CdS	Pt-PdS	S <sup>2-</sup> /SO <sub>3</sub> <sup>2-</sup>	300 W Xe	420	29,233	93	Yan et al, <i>J.Catal.</i> 266 (2009) 165.
NiS/CdS				420		51.3	Zhang et al, <i>Chem. Com.</i> 46 (2010) 7631.
CdS-Ti-MCM-41	RuO <sub>2</sub>	Ethanol	-	Visible	2730	36.3	Peng et al, <i>Chem. Com.</i> 49 (2013) 3221.
CdS-CdSe	Pt	Methanol	300 W Xe	450	40,000	20	Amirav et al, <i>J. Phys. Chem. Lett.</i> 1(2010) 1051
CuGa <sub>2</sub> In <sub>3</sub> S <sub>8</sub>	Rh	S <sup>2-</sup> /SO <sub>3</sub> <sup>2-</sup>	300 W Xe	560	-	15	Kaga et al, <i>Chem. Com.</i> 46 (2010) 3779.
LaTiO <sub>2</sub> N	CoOx	-	-	440		27.1	Matoba et al, <i>Chem.-Eur. J.</i> 17(2011) 14731.
Black TiO <sub>2</sub>	Pt	Methanol	Solar simulator with filter	>400 >660	100 10,000		Chen et al, <i>Science</i> , 331 (2011) 746.
ZrO <sub>2</sub> -TaON and WO <sub>3</sub>	Pt	None	300 W Xe	420	150	6.3	Maeda et al, <i>J. Am. Chem. Soc.</i> , 132 (2010) 5858.
ZrO <sub>2</sub> -TiO <sub>2</sub> -CdS	Pd	S <sup>2-</sup> /SO <sub>3</sub> <sup>2-</sup>	288 W, Ordinary fluorescent lamp	Visible region with ~3% UV	2100	11.5	Sasikala et al, <i>J. Colloid Interface Sci.</i> 409 (2013) 135

\*- AQY(%) = (A x R/I) 100 where A, R, and I represent coefficients based on the reactions (H<sub>2</sub> evolution -2; O<sub>2</sub> evolution -4), the H<sub>2</sub> or O<sub>2</sub> evolution rate, and the rate of incident photons, respectively

### Material challenges for photocatalytic/ photoelectrochemical splitting of water

Achieving photocatalytic splitting of water under visible light (400nm < λ < 800 nm) with good efficiency, without using any sacrificial agents, still remains a challenge to use this process for large scale generation of hydrogen. Also the mechanism of water reduction and oxidation on the semiconductor surface including issues related to the charge transfer between semiconductors and co-catalysts, its dependence on the structural and electronic features of the interface, influence of surface impurities and preparation conditions needs more detailed investigations so as to improve the water splitting photocatalyst.

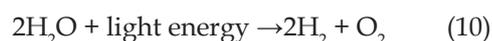
#### 1.3.2 Hydrogen via photobiological splitting of water

Photobiological splitting of water is also known as direct photolysis where hydrogen is produced from water using sunlight and specialized micro-organisms, such as green algae and cyanobacteria. Just as plants produce oxygen during photosynthesis, these micro-organisms consume water and produce hydrogen as a by-product of their natural metabolic processes. Currently, the microbes split

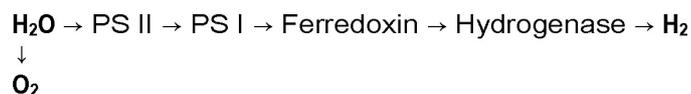
water much too slowly to be used for efficient, commercial hydrogen production. However, efforts are on to modify the micro-organisms and to identify other naturally occurring microbes that can produce hydrogen at higher rates. Other bio-processes being developed for hydrogen generation include anaerobic digestion, dark-fermentation of organic material and hybrid biohydrogen production using electrochemical processes [32-34]. Hydrogen can be produced from renewable biomass materials including organic-based starch industry waste, industrial waste biodiesel, lignocellulosic materials such as wood and its products, food, household waste and others. Some of these processes are discussed below:

- Biophotolysis of water using green algae and blue-green algae (cyanobacteria)

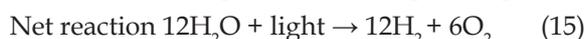
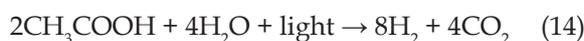
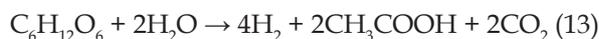
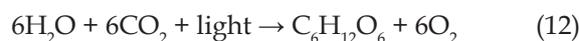
Green algae and blue-green algae split water molecules into hydrogen ion and oxygen via direct and indirect biophotolysis, respectively. In direct photolysis green algae produces hydrogen from water by following general reaction:



The well-known  $H_2$ -producing green algae, *Chlamydomonas reinhardtii*, under anaerobic conditions, can either generate  $H_2$  or use  $H_2$  as an electron donor. The generated hydrogen ions are converted into hydrogen gas in the medium with electrons (donated by reduced ferredoxin) by hydrogenase enzyme present in the cells. Light energy absorbed by photosystem II (PS II) generates electrons which are transferred to ferredoxin using light energy absorbed by photosystem I (PS I). A reversible hydrogenase accepts electrons directly from the reduced ferredoxin to generate  $H_2$  in presence of hydrogenase, as follows:



Hydrogen generation from water by indirect biophotolysis route involves several steps: (i) biomass production by photosynthesis, (ii) biomass concentration, (iii) dark aerobic fermentation produces 4 mol hydrogen/glucose mol in the algal cells, together with 2 mol of acetate, and (iv) conversion of 2 mol of acetate in to hydrogen. This process can be classified in to two distinct groups, one of which is depending on the light and the other is light independent process.



The advantage of biophotolysis is that, there is no need of adding substrate as nutrients. Water is the primary electron donor required for the production of hydrogen gas. Sunlight and  $CO_2$  are the basic inputs needed to grow the cyanobacteria or microalga on biophotolysis process through the hydrogenase enzyme. Production of hydrogen gas by green algae and cyanobacteria is one of the methods that produce renewable energy without emission of GHG.

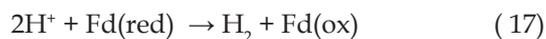
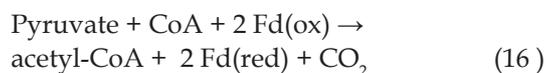
### 1.3.3 Bio hydrogen from Biomass

Biological hydrogen production from carbohydrate-rich biomass can be achieved through an anaerobic process known as dark fermentation and a photosynthesis process known as photo-fermentation.

#### • Dark fermentation

In dark fermentation process, glucose (representative of biomass) is initially converted to pyruvate by the glycolytic pathways. This is oxidized to acetyl-CoA, converted to acetyl phosphate and ultimately resulting in the generation of ATP and the excretion of acetate. Pyruvate oxidation to

acetyl-CoA requires ferredoxin (Fd) reduction. Reduced Fd is oxidized by hydrogenase which generates Fd(ox) and releases electrons to produce molecular hydrogen. The overall process can be described as follows:

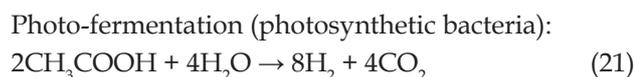
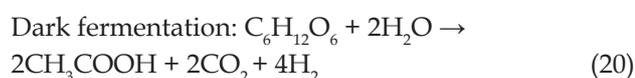


Anaerobic fermentation enables the mass production of hydrogen via relatively simple processes from a wide spectrum of potentially utilizable substrates, including refuse and waste products. Carbohydrates, mainly glucose, are the preferred carbon sources for fermentation processes, which largely produce hydrogen along with acetic/butyric acids, as follows:



#### • Use of fermentative and photosynthetic bacteria

In such system the anaerobic fermentation of carbohydrate/or organic wastes produces low molecular weight organic acids intermediates in the first step, which are converted into hydrogen by the photosynthetic bacteria in the second step in a photo-bioreactor. The two steps involved are as follows:

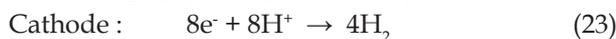


Hydrogen production through dark-fermentation has advantages and more profitable than photo-fermentation processes because of its ability to continuously produce hydrogen and does not depend on energy provided by sunlight. However, by combining dark and photo-fermentation processes both generation of  $H_2$  and treatment of organic waste can be achieved together. Das et al [34] reported successful operation of a hydrogen-biogas producing reactor (capacity 1.48  $m^3$ ) for 200 days and achieved maximum hydrogen production rate of 5.57  $m^3 H_2/m^3d$  using molasses as the substrate.  $H_2$  in the product stream (mostly  $CO_2$  and  $H_2$ ) ranged from 40% to 52%.

#### • Use of bioelectrochemical assisted bio-reactor

Microbial fuel cell (MFC) produces protons and electrons due to the oxidation of organic matter by the bacteria. By electrochemically augmenting the cathode potential of MFC, hydrogen can be directly produced from the organic matter at a much lower voltage than that

required for H<sub>2</sub> generation from water via electrolysis. In a typical MFC, the open circuit potential of the anode is ~300mV. The half reactions occurring at the anode and cathode, with acetate oxidized at the anode, are as follows:



Generation of hydrogen at the cathode will require a potential of at least  $E^0 = -410\text{mV}$  at pH 7.0. Thus, hydrogen can theoretically be produced at the cathode by applying a circuit voltage greater than 110mV (i.e., 410–300mV). This voltage is substantially lower than that required for hydrogen derived from the electrolysis of water, which is theoretically 1230mV at neutral pH. Such bio-electrochemically assisted microbial systems, in combination with hydrogen fermentation process (producing 2 to 3 mol of H<sub>2</sub>/mol glucose) have the potential to produce 8 to 9 mol H<sub>2</sub>/mol glucose at an energy cost equivalent to 1.2mol H<sub>2</sub>/mol glucose [33].

Each of the biohydrogen production processes stated above has its own advantages and disadvantages. The best approach to maximize the production of hydrogen gas is to combine them.

#### Material challenges to Biophotolytic H<sub>2</sub> production

Green algal H<sub>2</sub> has the potential to be a sustainable fuel of the future, but has to overcome several challenges such as low photochemical efficiency of biophotolysis, scalability and affordability of the process. There is also a need to identify microbes that can utilize hemicellulose and cellulose directly. Efficient and scalable designs will be required for the successful applications of the microbial electrolysis process.

#### Conclusion

Most of the hydrogen production techniques from non-fossil fuels such as biomass gasification or pyrolysis, biological, photo catalytic, thermo-chemical methods using nuclear and solar energy etc. are in early stage of development. These technologies need to be developed further and demonstrated so that they become technically viable, reliable, and cost competitive with conventional fuels.

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## Materials of Construction for Iodine – Sulfur Thermochemical Process

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### Abstract

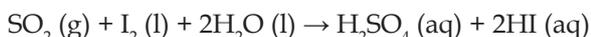
The Iodine – Sulfur thermochemical process consists of three chemical reactions that together split of water into hydrogen and oxygen. This process involves corrosive chemicals such as hydrogen iodide, iodine and sulfuric acid. The environments of hydrogen iodide and iodine are extremely corrosive and the temperature ranges upto around 500 °C. Concentrated sulfuric acid (98 wt%) also requires to be handled upto 900 °C. This paper gives comprehensive summary of the materials of construction used in the plant operation of iodine – sulfur process. Tantalum, glass lined, PFA lined and quartz materials were used in the plant operation in the field and are found to be suitable for the demonstration of Iodine – Sulfur process at laboratory and pilot plant scale. The shortlisted materials from literature and their corrosion rate at the test conditions are also reported in this paper.

### Introduction

The Iodine sulfur thermo-chemical process splits water to produce hydrogen using chemical energy and heat. This process involves three main reactions, ie. Bunsen reaction, hydrogen iodide decomposition reaction and sulfuric acid decomposition reaction.

#### i) Bunsen Reaction

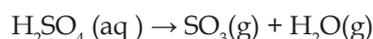
In this reaction, sulfur dioxide, iodine and water are reacted to form the products sulfuric acid and hydriodic acid



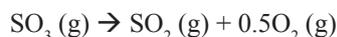
This is an exothermic reaction that is carried out at around 60 °C to 120 °C temperature. In the presence of excess iodine, the product acids form two distinct phases, i.e. sulfuric acid phase (lighter phase) containing sulfuric acid and water and HIx phase (heavier phase) containing hydriodic acid, iodine and water. These two acids formed as the product phases are purified and decomposed.

#### ii) Sulfuric acid decomposition

The sulfuric acid decomposition involves two endothermic reactions; in the first reaction sulfuric acid is decomposed to form Sulfur trioxide and water. This occurs at around 400 °C.

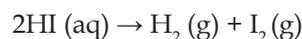


In the second reaction, SO<sub>3</sub> is decomposed to form SO<sub>2</sub> and oxygen at 900°C

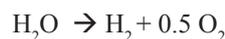


#### iii) Hydrogen iodide decomposition

In this endothermic reaction, hydrogen iodide is decomposed at around 450 °C to form hydrogen and iodine.



These three reactions together constitute splitting of water into hydrogen and oxygen as products.



The block diagram of Iodine – Sulfur thermo-chemical process is as shown in Fig. 1. The complete closed loop process can be divided into three sections.

- I) Bunsen Section
- II) Sulfuric acid section
- III) HIx section

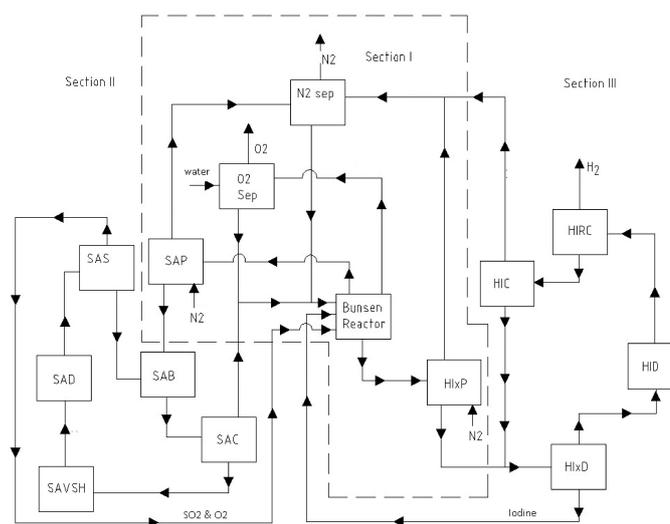


Figure 1: Block Diagram of IS process

- I) Bunsen Section: This section includes Bunsen reactor with liquid – liquid phase separator, sulfuric acid purifier and HIx purifier. In the Bunsen reactor, sulfur dioxide, water and iodine are reacted to form sulfuric acid and hydroiodic acid as products.

II) Sulfuric acid section: This section includes sulfuric acid concentrator (distillation column with condenser and reboiler), sulfuric acid decomposer,  $\text{SO}_3$  decomposer and sulfuric acid product separator (gas - liquid condenser). In this section, sulfuric acid is concentrated, that is excess water is removed then it is decomposed to form  $\text{SO}_3$  and water. The  $\text{SO}_3$  formed is further decomposed to form  $\text{SO}_2$  and oxygen.

III) Hydriodic acid section: This section includes  $\text{HI}_x$  distillation column with reboiler and condenser, HI vaporizer (reboiler), HI decomposer, HI reflux condenser and HI concentrator column with reboiler. In this section, iodine is removed as bottom product from  $\text{HI}_x$  distillation column. The top product containing hydrogen iodide and water is sent to HI decomposer to form hydrogen and iodine.

Thus as an overall process, water is split into hydrogen and oxygen. All the other compounds formed are recycled back in the process. This process has advantages over other thermochemical water splitting processes; this involves relatively small number of chemical reactions, has good thermal efficiency and is a completely fluid process (gaseous and liquid phases). But, Iodine - Sulfur thermochemical process involves corrosive chemicals such as sulfuric acid, hydriodic acid, iodine, sulfur dioxide and sulfur trioxide. These chemicals may be present together such as hydrogen iodide, sulfuric acid and sulfur dioxide in Bunsen reactor, sulfuric acid purifiers, hydriodic acid purifiers or individual chemicals such as sulfuric acid, sulfur dioxide and sulfur trioxide may be present in various equipments such as sulfuric acid concentrator, sulfuric acid and  $\text{SO}_3$  decomposers or in sulfuric acid reboilers and condensers. Similarly hydrogen iodide and iodine is present in hydrogen iodide distillation column with condenser and reboiler, hydrogen iodide decomposer and hydrogen iodide reflux column. The temperature in Iodine-Sulfur thermochemical process ranges from room temperature to as high as  $900^\circ\text{C}$ . The reaction environment created by HI and iodine is extremely corrosive and the temperature is upto  $500^\circ\text{C}$ . The appropriate materials of construction are required to handle concentrated sulfuric acid as well as sulfuric acid vapors to a maximum temperature of  $900^\circ\text{C}$ . Candidate materials have to be screened from the viewpoint of corrosion resistance for continuous and long term usage.

### Glass closed loop process for Hydrogen production

At BARC, Mumbai, the glass closed loop IS process for hydrogen production has been successfully demonstrated for continuous hydrogen production for about 20 hrs

at the rate of 30 Nlph. The figures 2, 3 and 4 represent Bunsen reactor and liquid-liquid separator, sulfuric acid decomposer and  $\text{SO}_3$  decomposer,  $\text{HI}_x$  distillation column and HI decomposer respectively. The materials of construction used were borosilicate glass for equipments operating below  $250^\circ\text{C}$  and Quartz (fused silica glass) was used for equipments operating above  $250^\circ\text{C}$ . The valves



Figure 2: Bunsen Reactor of glass system and liquid liquid separator



Figure 3: Sulfuric acid decomposer (left) and  $\text{SO}_3$  decomposer (right) during operation.

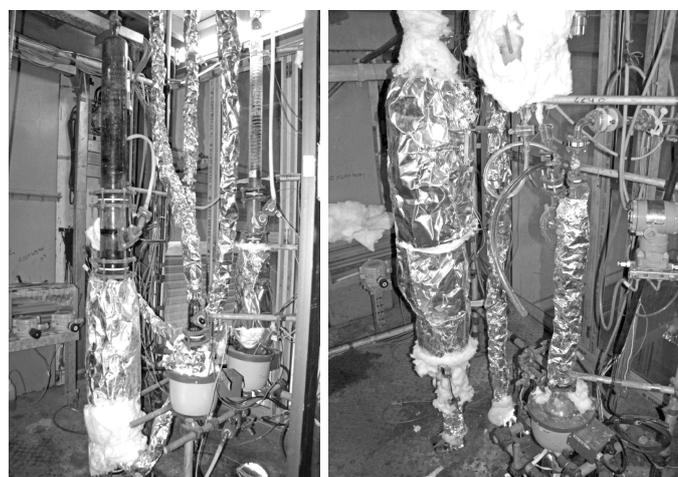


Figure 4:  $\text{HI}_x$  distillation (left) and Hydrogen Iodide decomposer (right) during operation.

were made of glass and used in zones of temperature below 250 °C. All connecting lines were made of flexible PTFE tubes.

### Bunsen Metallic Plant of Iodine – Sulfur process

Metallic Bunsen plant, involves Bunsen section of Iodine – Sulfur process that can be operated at pressures upto 8 bar and temperatures ranging from room temperature upto 150 °C. The Bunsen reaction is carried in this plant. The feed chemicals such as process water, iodine, sulfuric acid and hydriodic acid are sent from the feed tanks.

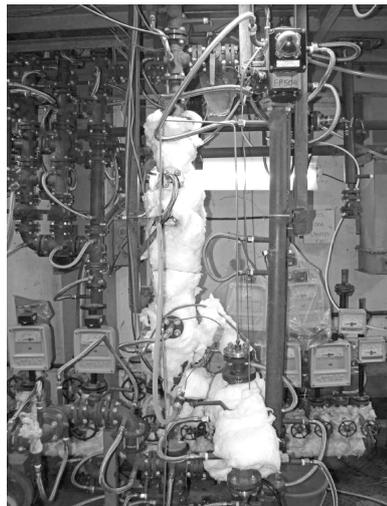


Figure 5: Bunsen reactor and liquid liquid separator (metallic system)

Sulfur dioxide gas is sent from gas cylinder. These chemicals are sent in Bunsen reactor, where Bunsen reaction is carried out and then the products are sent to liquid – liquid separator. In the liquid – liquid separator the two product acid phases are separated and collected in product tanks. The Bunsen and liquid – liquid separator for the metallic plant are as shown in Fig. 5.

### Materials of Construction for Bunsen Section:-

Bunsen section of Iodine – sulfur process involves chemicals that are hydriodic acid, iodine, sulfuric acid, sulfur dioxide and water.

The materials of construction used in the metallic Bunsen section are as follows. All the pipelines were PTFE lined (internally) on mild steel. All the feed and product tanks were glass lined from inside on mild steel. The reactor was made of Tantalum tube inside Stainless steel pipe. Pressure is measured with remote seal assembly of tantalum diaphragm. Level is measured using guided wave (PTFE tube) Radar level transmitters and differential pressure transmitters.

The Materials of constructions for flow transmitters are as following:

- i. DM water – Coriolis Mass flowmeter of SS 316
- ii. Iodine – Electromagnetic mass flowmeter – Tantalum Electrode and PFA lined
- iii. Sulfur dioxide - Coriolis mass flowmeter of SS 316
- iv. Sulfuric acid – Coriolis mass flowmeter - Hastelloy C 376
- v. Hydriodic acid – Electromagnetic mass flowmeter –

- Tantalum electrode and PFA lined
- vi. Oxygen – Coriolis mass flowmeter - SS 316

### Materials of Construction for Sulfuric acid Section

Sulfuric acid section includes sulfuric acid concentrator, sulfuric acid vaporizer, sulfuric acid decomposer, SO<sub>3</sub> decomposer that forms SO<sub>2</sub> and oxygen. The products from the SO<sub>3</sub> decomposer are sent into the condenser to separate SO<sub>2</sub> and O<sub>2</sub> from unreacted sulfuric acid and water. The temperature in this section range from 150 °C to as high as 900 °C. The choice of gaskets is also crucial while finalizing the materials of construction.

In the glass closed loop process for hydrogen production, the equipments such as SO<sub>3</sub> decomposer, sulfuric acid decomposer, and sulfuric concentrator (reboiler and column) were made of quartz to sustain the high temperatures. Other equipments, such as condensers are made of borosilicate glass for low temperature operation.

Chemical Technology Division is involved in designing and fabrication of integrated sulfuric acid concentrator and decomposer operating at around 20 bar (g) and temperatures upto 900 °C. The equipment consists of a stainless steel vessel where hot helium gas is used for heating. The dilute sulfuric acid enters from top of the vessel in the tubes. Then sulfuric acid is concentrated with hot outflow of gases and decomposition occurs inside bayonet tubes made of Silicon Carbide. The shell containing sulfuric acid feed and product is of Incoloy 800 H. The gaskets used are corrosion resistant Incoloy 800 H spring energized metal gaskets.

The suggested materials of construction for sulfuric acid section as per Japan Atomic Energy Research Institute[1] are Tantalum and Zirconia for high temperature and concentrated sulfuric acid environments from equipments ranging from sulfuric acid concentrator to decomposer and temperatures ranging from 150 °C to 900 °C.

R. H. Jones and G. J. Thomas [2] suggested materials of construction for concentrated sulfuric acid at high temperatures, Silicon carbide showed excellent corrosion resistance with corrosion rate of around 0.002 g/m<sup>2</sup>-h, Si<sub>3</sub>N<sub>4</sub> showed corrosion rate of around 0.007 g/m<sup>2</sup>-h, Fe-20 Si showed corrosion rate of around 0.13 g/m<sup>2</sup>-h in 95 % wt concentrated sulfuric acid solution at 460 °C. Tantalum showed excellent corrosion resistance with corrosion rate in the range of 0.04 mm/yr in 98 % wt sulfuric acid solution upto 200 °C. Incoloy 800 H has shown best performance with a corrosion rate of less than 0.1 mm/yr at 900 °C.

S. Kubo et. al. [3,4] suggested that, Incoloy 825, Incoloy 800 and Hastelloy C 276 showed minimum corrosion rate in gaseous sulfuric acid environments upto temperature of 900 °C. The corrosion rate of Incoloy 825 was around 3.5

mm/yr, Incoloy 800 was around 6.1 mm/yr and Hastelloy C 276 was around 6.1 mm/yr at 900 °C. JIS SUS329J1 and Inconel 625 also showed good corrosion resistance in this environment. The corrosion rate of JIS SUS329J1 was 8.8 mm/yr and Inconel 625 was 7.0 mm/yr at 900 °C. The corrosion rates of JIS SUS304 and JIS SUS310S were 8.8 mm/yr and 7.9 mm/yr respectively.

For bubbling sulfuric acid upto 98 wt %, high Si cast iron (15 wt % Si) showed minimum corrosion with corrosion rate of 0.1 mm/yr, followed by Tantalum with a corrosion rate of 27 mm/yr and Hastelloy B2 with a corrosion rate of 63 mm/yr. For pressurized sulfuric acid near bubbling temperatures at 2 MPa (g) Silicon Carbide (SiC) showed corrosion rate of 0.05 g/m<sup>2</sup>-day, Si-SiC (SiC 80 wt % and Si 20 wt %) showed corrosion rate of 0.1 g/m<sup>2</sup>-day, Si<sub>3</sub>N<sub>4</sub> showed corrosion rate of 0.2 g/m<sup>2</sup>-day.

### Materials of Construction for Hydrogen Iodide Section

Hydriodic acid section includes HIx distillation, hydriodic acid vaporizer, hydriodic acid decomposer, to form hydrogen and Iodine. The products from the hydriodic acid decomposer are sent into the condenser to separate hydrogen and Iodine from unreacted hydriodic acid, water and iodine. The temperature in this section ranges from 150 °C to as high as 500 °C. The choice of gaskets is also crucial while finalizing the materials of construction.

In the glass closed loop process for hydrogen production, the equipments such as hydriodic acid decomposer, and hydriodic acid distillation (reboiler and column) were made of quartz to sustain the high temperatures. Other equipments, such as condensers were made of borosilicate glass for low temperature operation.

Chemical Technology Division is also involved in designing and fabrication of equipments of HI section for the metallic plant, such as HIx distillation column with condenser and reboiler, HI vaporizer, HI decomposer and condenser after the decomposer to separate hydrogen gas from iodine and unreacted reactants such as hydrogen iodide (with water). The HIx distillation column would be tantalum lined with spring energized metal gaskets, HI decomposer will also be tantalum lined on stainless steel. The reboilers would be tantalum lined from inside and the heating coils would be made of tantalum. Similarly in the condensers, those are shell and tube condensers with process fluid in tube side and utility (process water) in shell side. The tubes would be made of tantalum and shell would be tantalum lined. All the process piping above 150°C would be tantalum lined and piping below 150°C would be glass lined.

Japan Atomic Energy Research Institute [1] reported that, Tantalum and Silicon Carbide showed excellent corrosion resistance in boiling HI environment upto a

temperature of 300 °C and pressure of 2.0 MPa. Whereas corrosion rate for Zirconium is around 3.5 mm/yr at 300 °C and pressure of 2.0 MPa and for Niobium, the corrosion rate was around 1.1 mm/yr at 240 °C and pressure of 2.0 MPa. For gaseous HI decomposer environments upto 400 °C, tantalum, titanium, zirconium and Si<sub>3</sub>N<sub>4</sub> showed excellent corrosion resistance. Silicon Carbide (SiC) showed corrosion rate of around 1 mm/yr in gaseous HI environment.

R. H. Jones and G. J. Thomas [2] suggested, materials of construction for HI (30 % wt) in temperature range of atmospheric to 500 °C that molybdenum and tantalum showed excellent corrosion resistance. Silicon Carbide (SiC) based materials both sintered and chemical vapor deposition (CVD) SiC have shown very low corrosion rates when tested in HIx upto 300 °C. Tantalum -2.5 tungsten alloy also showed good corrosion resistance upto temperature of around 300 °C.

S. Kubo and H. Sato [3] suggested that, tantalum, niobium, zirconium and silicon carbide showed excellent corrosion resistance in boiling HIx atmospheres upto pressures of 20 bar and temperatures upto 300 °C. For gaseous hydriodic acid atmospheres upto 400 °C, ceramics Si<sub>3</sub>N<sub>4</sub> and SiC showed excellent corrosion resistance. Among metals tantalum, zirconium and titanium showed excellent corrosion resistance.

### Conclusions:

A detailed review of materials of construction of components for iodine-sulfur thermochemical process has been given in this paper. From the review, it can be concluded that the materials of construction for metallic Iodine - Sulfur process system for hydrogen production are; glass lined and tantalum etc for Bunsen section, SiC, SiC lined, incoloy 800 etc for sulfuric acid section and tantalum lined for HIx section. However, the finalized materials of construction need to be evaluated based on cost, fabricability, availability of gaskets and actual plant operating conditions including thermal cycling and high pressures. This will help in commercialization of iodine - sulfur process.

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	<p>Mr. Sujeesh S has completed B. Tech in Chemical Engineering from Kerala University in year 2010. After successful completion of OCES -2010 training program, he has joined as scientific officer in Chemical Technology Division of BARC. He is involved in process equipment design, project engineering and experimental work of sulfuric acid section &amp; integrated sulfuric acid decomposer.</p>
	<p>Mr. Nafees Ahmed is M. Tech in Chemical Engineering from Homi Bhabha National Institute in year 2010. After successful completion of OCES -2006 training program, he has joined as Scientific Officer Chemical Technology Division of BARC. He is involved in process equipment design, process simulation, project engineering and experimental work of Bunsen section.</p>
	<p>Mr. Shrinivas Rao as Head, Materials Development Section, Chemical Technology Division is overall in-charge of the demonstration of I-S thermochemical process for hydrogen production. He has successfully led the team and demonstrated closed loop IS process in glass system</p>
	<p>Mr. Ashis Sanyal as Head, Chemical Technology Division is guiding hydrogen program on storage and production by I-S thermochemical process.</p>

# Application of Membrane Technology in IS Thermochemical Cycle

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## Abstract

One of the most promising routes currently under development for sustainable hydrogen production is the Iodine Sulphur (IS) thermochemical water splitting cycle. The most important stage in determining overall process efficiency and feasibility of the cycle is the separation of  $HI_x$ , a mixture of HI,  $H_2O$  and  $I_2$  and decomposition of HI. A major improvement in overall efficiency of the IS cycle can be achieved by optimizing the HI decomposition step. This paper highlights the drawbacks persisting in the  $HI_x$  processing stage of the IS cycle and investigates the scope for applying membrane separations to HI decomposition section, with the aim of improving the overall efficiency of the process. Work carried out in this research centre towards development and application of EED (Electro-electro dialysis) and membrane reactor for HI decomposition studies has also been discussed.

*Key words: Hydrogen, thermochemical cycle, Membrane reactor, Electrodialysis*

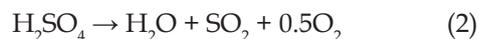
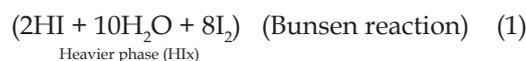
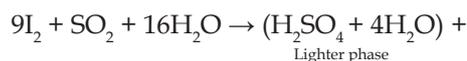
## 1. Introduction

### 1.1 IS thermochemical cycle

Research and development is constantly underway to create the next generation energy technology, since energy needs will continue to increase. Future energy sources must also be environment friendly and economical. With these factors in mind, many believe that hydrogen is poised to be the next big revolution in the energy market. Hydrogen is one of the clean energy media without carbon dioxide emission. Among the methods of hydrogen production, steam reforming and water electrolysis are proven and used extensively for the production of hydrogen today. On the other hand, thermochemical cycles are of particular interest because unlike contemporary methods, it produces hydrogen efficiently with no carbon dioxide as by-product and it does not depend on depleting fossil fuels, while having a potential advantage in terms of sustainable hydrogen production.

Among the large scale, cost effective and environment friendly thermochemical processes, iodine-sulphur (IS) thermochemical cycle is a quite promising one. The IS thermochemical process is one of the promising processes of hydrogen production amongst all the alternatives available keeping in view the predicted thermo-chemical efficiency and its ability to couple it to a high temperature nuclear reactor [1-6]. An upper bound and a best estimate of the efficiency of a thermochemical IS water splitting cycle coupled with a high temperature nuclear reactor operating between 760 K and 1144 K has been proposed by Goldstein et al [4], where an upper bound of 51% was found assuming ideal reversible chemical reactions and constraints related

to the heat exchange between helium and chemical process. The IS process consists of the following reactions:



In IS cycle, sulfuric acid cannot be separated from hydrogen iodide, by thermal means, without reversing the equilibria. This separation is readily accomplished in the presence of a large excess of iodine, with the formation of two immiscible liquid phases, a light  $H_2SO_4/H_2O$  phase and a heavy  $HI_x$  ( $HI/I_2/H_2O$ ) phase, which essentially poses tremendous difficulty in the successive processing of  $HI_x$  stream.

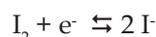
In Section 3 of the cycle, the HI phase can be first concentrated by distillation and the  $HI_x$  distillate at azeotropic composition (13% molar in HI) is decomposed in the vapor phase according to the third reaction. HI decomposition can be accomplished by either reactive or extractive distillation. Reactive distillation is a simple one step process.  $HI_x$  solution boils at temperatures approaching 300°C. Operating pressure is under these conditions are in the range of 20-50 bars. On the other hand, in the process of extractive distillation, iodine separation from  $HI_x$  is made effective at 120°C using  $H_3PO_4$  followed by distillation of  $HI_x$  and subsequent concentration of  $H_3PO_4$ .  $HI_x$  solution is extremely corrosive. Glass can be chosen as a suitable material for handling the corrosive properties of the solution, but this requires intricate and special measures

to operate at these high pressures. On the other hand, extractive distillation suffers from a serious drawback of addition another chemical species and making the IS cycle more complex to process further. Another challenge involved is that the equilibrium conversion of HI is only around 23% at 450 °C. Low decomposition ratio leads to the increase of the amount of recycle materials (HI, I<sub>2</sub>, H<sub>2</sub>O) and therefore decreases the thermal efficiency. Against a single-step reactive distillation, a combination of membrane based technologies, i.e., electro-electro dialysis (EED) employing proton exchange membrane and membrane reactors (employing inorganic/ metallic membranes) together have got immense potential to overcome criticalities (w.r.t. high temperature, high pressure, highly corrosive environment) associated with HI decomposition steps as mentioned above, and help in realizing the overall predicted efficiency of the IS cycle. The present paper intends to highlight the importance of membrane based technologies in the IS cycle as well as the associated challenges. The work carried out in this research centre is also summarized.

## 2. Role of membranes in HI concentration

The product from first step of IS thermochemical cycle (that is the Bunsen Section) consists of HI<sub>x</sub> solution which contains excess amount of iodine, water and only 13 molar % of HI. This causes a thermal burden on the subsequent stages of HI decomposition. A significant amount of energy is consumed in the concentration of HI<sub>x</sub> solution coming out of Bunsen reactor. The HI<sub>x</sub> from the Bunsen reaction stage is a pseudo-azeotropic mixture thereby increasing the heat requirement substantially to affect the concentration process [7, 8]. In order to improve the concentration of the HI<sub>x</sub> phase after the Bunsen reaction, the General Atomic proposed the use of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) for the concentration of the HI solution [9]. A vapour with a 99.7% molar in HI was obtained. But, the remaining H<sub>3</sub>PO<sub>4</sub> solution was concentrated by using large amounts of heat and electricity. In contrary to that, an EED concentration method was proposed by Arifal et al. and Onuki et al. [10, 11]. The EED process for concentration of HI<sub>x</sub> suggested by Onuki et al. [11] was found effective in concentrating the HI<sub>x</sub> for the HI decomposition step. The energy consumption has been found to be lower than the other alternatives like extractive and reactive distillation. EED was also carried out for the HI concentration from HI<sub>x</sub> solution to improve the HI decomposition reaction in the IS process [12]. The EED experimental setup consisted of reservoirs with glass tubes formed by double jacket to control the temperature in the anolyte and catholyte. A peristaltic pump was used to control the flow rate of the HI<sub>x</sub> solution. To avoid a pressure increase in the glass reservoirs and also to

minimize the dissipation of HI vapor, the condensers were equipped in reservoirs. Thermocouples were fitted in the cell, reservoirs, and glass tube lines that were located in the cell inlet to maintain the temperature. Fig.1 illustrates the EED setup. The half-cell was composed of a carbon plate, gasket, electrode, and cation exchange membrane. An activated carbon cloth was used as the electrode, and a commercial cation exchange membrane (Nafion 117) was employed in a cell. In the EED, the electrode reaction was the following redox reaction of iodine to iodide ions at the cathode:



The iodide ions react with H<sup>+</sup> ions in the catholyte and hence, the HI mole fraction of the catholyte increases while that of the anolyte decreases.

Work carried out in Desalination Division, BARC, for HI concentration studies using EED has been discussed in subsequent sections.

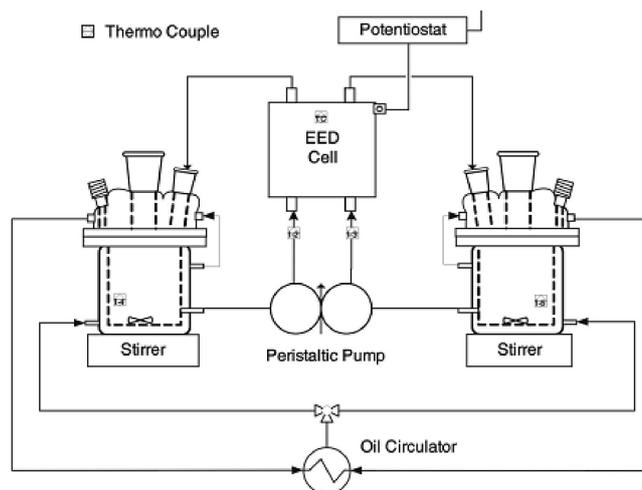


Figure 1: Schematic EED setup (Adapted from Ref. 12)

## 3. Role of membranes in HI decomposition

HI decomposition and *in situ* hydrogen separation can be made effective by employing a membrane reactor (MR), which is a unit that combines reaction and separation, i.e., it is a reactor which separates one or more components from the reaction mixture *in situ* as the reaction proceeds. Membranes and membrane reactors for pure hydrogen production are widely investigated not only because of the important application areas of hydrogen, but especially because mechanically and chemically stable membranes with high perm-selectivity towards hydrogen are available. The most important area is hence, the development of suitable gas-permeable membranes and membrane reactors compatible with the process environment for enhancement of the equilibrium decomposition conversion

of HI, which is the most intricate step as far as the overall process efficiency is concerned. There are two main advantages in particular offered by MRs: if the membrane is very selective with regard to a specific product, then it is possible to obtain a very pure compound in the same equipment that is used to produce it; furthermore, in the case of reversible reactions, removing one or more reaction products, as they are generated, allows conversions higher than equilibrium values. Another important advantage is it establishes a synergy between separation and reaction. The continuous separation of one or more of the products (e.g., hydrogen in this case) is reflected by an increase in yield and/or selectivity.

Studies have been carried out regarding the application of MRs in several processes involving hydrogen production, particularly the ones using fossil fuels (steam methane reforming and water gas shift reactions). However, the application of MRs in the area of HI decomposition is far from being matured and detailed experimental and modeling studies need to be carried out in this direction. Equilibrium conversion of HI is around 23% at 450 °C without hydrogen removal. Kar et al. [13] cited that the low decomposition ratio leads to the increase of the amount of recycle materials (HI, I<sub>2</sub>, H<sub>2</sub>O) and therefore decreases the thermal efficiency. In order to overcome the low efficiency due to the poor equilibrium decomposition of HI, ongoing research is dedicated toward development of a hydrogen-permselective membrane reactor. Silica membranes prepared by chemical vapor deposition were applied to the decomposition reaction of HI by Nomura et al [14] in order to improve one-pass conversion of HI. Norman et al. [15] estimated the thermal efficiency of the IS process to produce H<sub>2</sub> from water to be 47%. Membrane techniques aimed for the application in HI decomposition procedure were investigated and a continuous and stable operation of the bench-scale apparatus was successfully carried out by Kasahara et al [16] for all sections of the IS process. Flow sheet study was carried out on the application of membranes for HI processing by the research group and an upper bound thermal efficiency was estimated to be 57%. However, thermal efficiency based on more realistic parameters from experimental results was found out to be only 34%. A preliminary flowsheet of an electro dialysis cell and MR embedded IS cycle was developed by Shin et al [17]. Catalytic decomposition of hydrogen iodide in a membrane reactor was investigated theoretically [18] for the application to the hydrogen production step in the thermochemical IS process. It was found from the study that more than 90% conversion can be attained using the membrane reactor with the homemade silica membrane in a single pass.

#### 4. Work carried out in BARC

Desalination Division, BARC is engaged in the development of membranes and membrane based devices for HI concentration as well as HI decomposition. HI is concentrated from a pseudo-azeotropic HI<sub>x</sub> solution using EED followed by the decomposition of HI using a MR. It is believed that EED coupled with membrane reactor can be a suitable alternative against the reactive distillation column, keeping in view several issues cited above. The work carried out is summarized in subsequent sections.

##### 4.1 Studies on HI concentration using EED

To design and fabricate a leak-proof and corrosion resistant EED cell is a challenge. The EED cell was fabricated which comprises of glass-filled PTFE support plate, expanded PTFE gasket, Pt electrode and proton exchange membrane as shown in Fig. 2. Experiments were conducted with HI<sub>x</sub> (HI, iodine and water mixture) solution at temperatures upto 100 °C. The catholyte and anolyte flow rate was maintained at 150 mL/minute for a membrane area of 100 sq. cm. At a voltage of 0.3 V, the HI solution (40 wt % HI, 3 % iodine and rest water) was concentrated at catholyte by about 7 % w.r.t. HI and depleted by about 8 % w.r.t. iodine. The detailed parametric studies with variation of HI<sub>x</sub> composition, catholyte/anolyte flow rate, electrode material, temperature of HI solution etc. are underway. Fig. 3 shows the actual experimental EED setup as installed in Desalination Division.

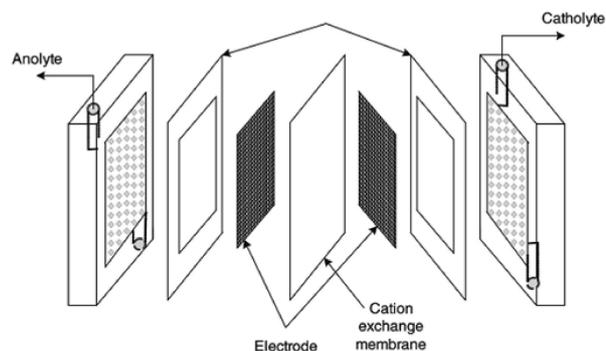


Figure 2: Components of EED cell (Adapted from Ref. 12)

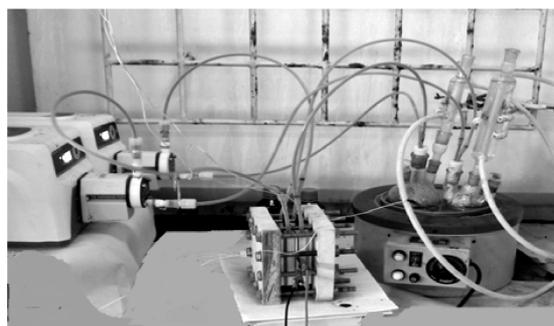


Figure 3: Experimental setup for EED for HI concentration studies

## 4.2 Membrane reactor development and HI decomposition studies

MR development includes two important challenges: first, the development of hydrogen permselective defect free membrane; second, the design and fabrication of a MR which should accommodate the membrane in a leak proof arrangement with provisions for feed, product, reject lines as well as catalyst port. An attempt has been made to develop silica membrane [19] on alumina support with graded porosity using sol-gel processing. The process was carried out using dip-coating technique on a highly porous alumina fiberboard support. A detailed study on the surface morphology and cross-sections of monoliths and membranes were studied by scanning electron microscope (Fig 4).

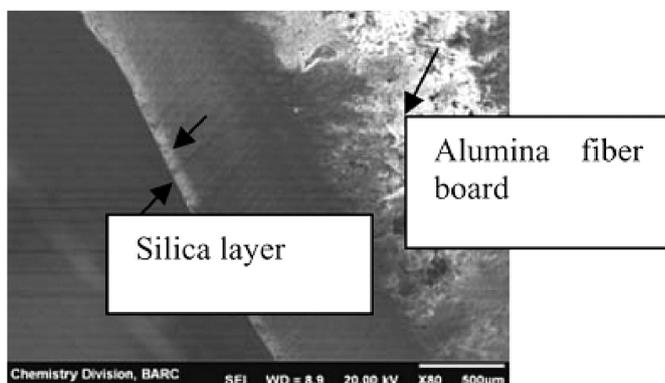


Figure 4: Cross-section of alumina-supported silica membrane

The efforts subsequently were oriented towards development of bench scale tubular membrane of 25 cm length and 1 cm OD (Fig 5) with permselectivity of 6 against argon. The as-prepared silica membrane was encapsulated in a custom-made stainless steel membrane holder and sealed completely (Fig 6) to study the permeation properties of tubular support and silica membranes over the temperature range of 30-500°C and pressure difference range of 0.2-2 bar.

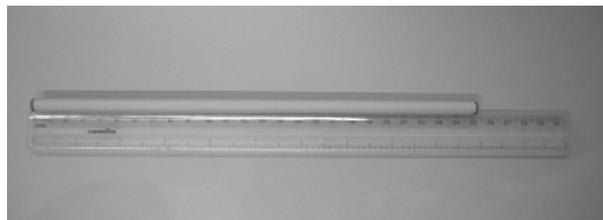


Figure 5: Tubular membrane developed in-house

On the other hand, to ensure superior thermal, mechanical, and chemical resistance ability, an all silica DDR (deca dodecahedral rhombohedral) zeolite membrane with dense, interlocked structure was developed in

collaboration with Central Glass & Ceramics Research Institute (CGCRI), Kolkata for separation of H<sub>2</sub> from HI/I<sub>2</sub> mixture of HI decomposition reaction [20].

A prototype membrane reactor was developed in-house (Fig.6) to study the permeation properties of tubular support at ambient temperature and pressure difference range of 1-2 kg/cm<sup>2</sup> using the experimental setup depicted in the schematic comprising of gas purification panel, mass flow controllers, high temperature furnace, gas chromatograph (GC) etc. as shown in Fig. 7.

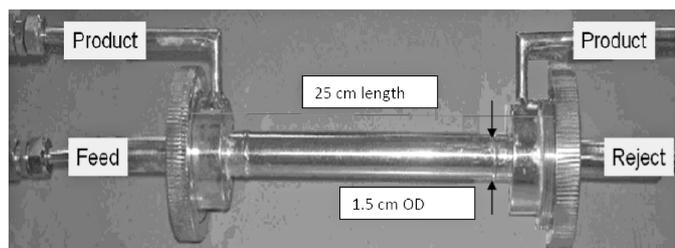
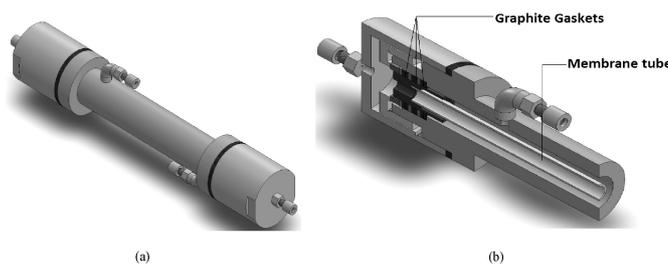


Figure 6. Prototype membrane reactor developed in-house: (a) 3D schematic of membrane reactor; (b) 3D schematic of cross sectional membrane reactor showing the membrane sealed with the end connections; (c) Actual view of membrane reactor with dimensions

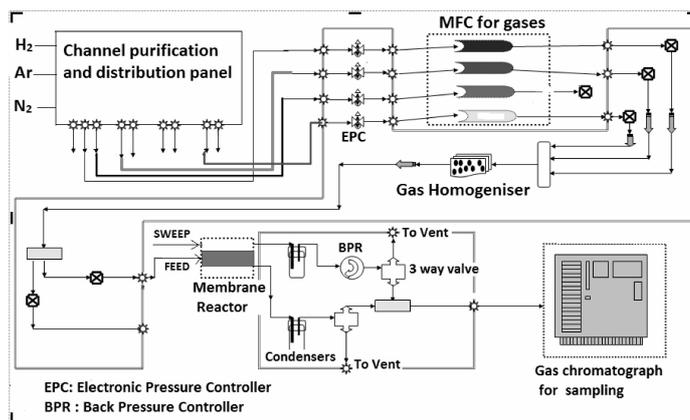


Figure 7: Schematic of gas permeation set up

The HI decomposition set up comprising of HI vapouriser, vertical furnace, band heaters and cold trap has been designed, fabricated and installed (Fig. 8). For trial run of the setup, decomposition of azeotropic HI (57 wt % HI in water) was carried out at 450 ° C in a tubular

reactor packed with Pt-alumina catalyst. Nitrogen was used as a sweep gas to carry the HI vapour to the reactor from HI vapouriser. The produced hydrogen, iodine and unreacted HI were passed through cold trap to condense HI and iodine. Hydrogen gas was produced which was detected by portable hydrogen detector. Studies are in progress to measure the extent of HI decomposition and optimize various associated parameters.



Figure 8: HI decomposition setup

### 4.3 Corrosion stability studies

The immersion coupon tests were conducted with both alumina support tube as well as zeolite coated alumina tubes to ensure their corrosion resistance behavior under HI environment. Alumina support tube was cut into pieces and immersed in HI-water azeotrope (55 wt % HI) at a temperature of 120-130°C under reflux environment as shown in Fig 9. Full form SEM and XRD analysis was also done for the tube samples (non-coated, single coated and double coated) which were exposed to heated HI for about 120 hours.

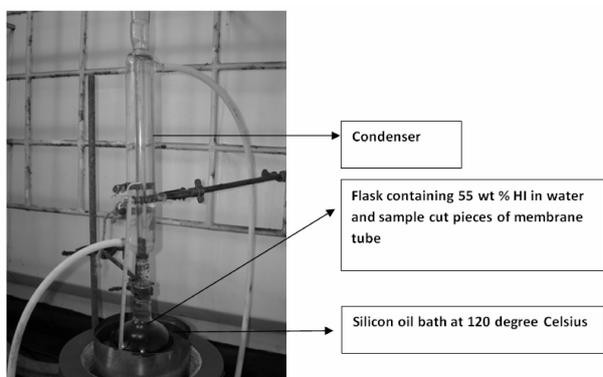


Figure 9: Set up for corrosion studies of HI decomposition reaction

The corrosion studies confirmed that no discernible changes took place in the clay alumina tube samples (with and without zeolite coating) when immersed in HI-water

azeotrope (55 wt % HI) at a temperature of 120-130°C under reflux environment, for about 120 hours [20]. The scanning electron microscopy (SEM) images of the support tube samples exposed to HI solution for about 60 h in heated condition (130 °C) and about 455 h at room temperature were taken. XRD analysis was carried out for the tube samples (non-coated, single coated and double coated) which were exposed to heated HI for about 120 h. Fig. 10 (a and b) indicate the change in microstructure features of outer surface of support tube before and after exposure. Fig. 10 (c and d) show the morphological features of inner side of tube before and after HI exposure. SEM images showed that deposition of iodine had taken place in the samples, which is not significant enough to affect the ultimate performance (flux and selectivity) of membrane. Fig. 11 shows the XRD images of the tube samples [non-coated

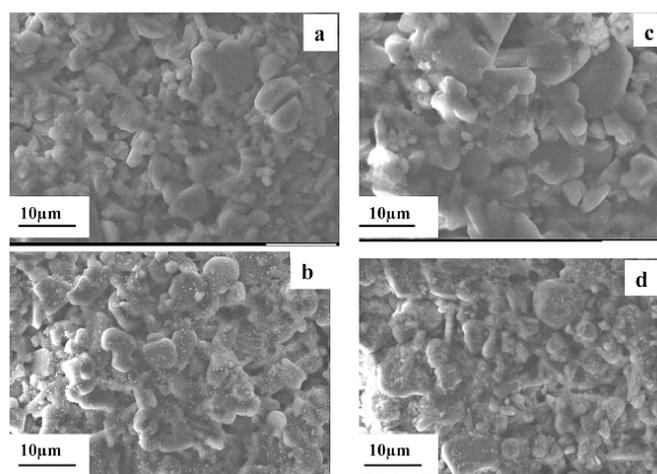


Figure 10: FESEM micrograph of support tube (a) outer surface before HI treatment; (b) outer surface after HI treatment; (c) inner surface before HI treatment; (d) inner surface after HI treatment.

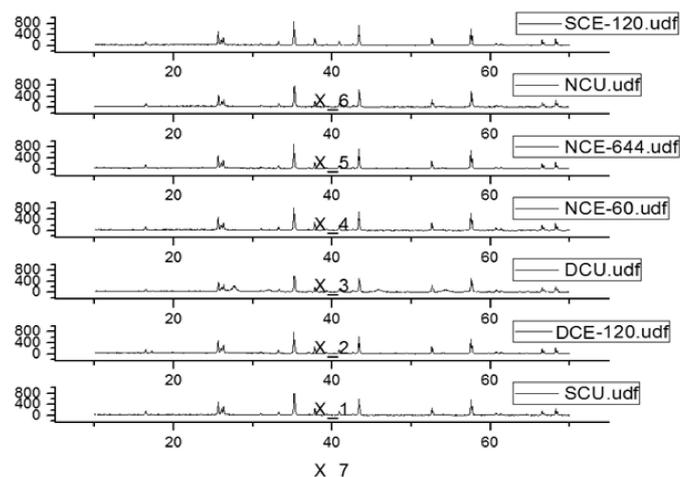


Figure 11: XRD images of the tube samples (non-coated, single coated and double coated) which were exposed to heated HI solution for period of 120 hours.

(NC), single coated (SC) and double coated (DC)] which were exposed to heated HI solution upto a period of 120 hours. The figure also shows the XRD image of unexposed tube sample. "U" stands for unexposed samples and "E" stands for exposed samples. The XRD results confirm that no observable chemical changes have occurred in the samples (both bare tubes and zeolite coated tubes) after they are exposed to HI-H<sub>2</sub>O environment at a temperature of about 130 °C. The membranes are stable with respect to operation under HI environment.

#### 1.4 Modeling studies

The CFD (computational fluid dynamics) modeling was carried out using COMSOL to develop an understanding of membrane reactor and its performance and effectiveness in increasing the conversion of HI decomposition reaction of IS thermochemical cycle [20]. The results showed that using a PBMR (packed bed membrane reactor) instead of a PBR (packed bed reactor) leads to significant process intensification. Relative influence of different variables on conversion in a membrane reactor was also studied. It is observed that wall temperature of reactor has got a dominant influence on conversion. Among other parameters, reactor diameter, packed bed porosity and feed temperature also affect conversion significantly.

Studies on catalyst activity and non-isothermality in packed bed and coated wall configurations were also carried out [21]. Simulations to assess the impact of deviations from isothermality in packed bed reactors on the rates of HI decomposition were carried out. The activity of activated carbon catalyst for the decomposition of HI was measured in packed bed and coated wall membrane reactors of various sizes. The smaller diameter reactor showed higher apparent catalyst activity. The diameter required for a packed bed reactor to achieve near isothermal operation was estimated to be less than 1 mm. The reactivity results showed that the reactors suffered from significant temperature gradients. For a packed bed reactor, it was found that for the catalyst weight to feed flow rate ratio should be more than 40 to achieve conversion greater than 90% for the values of reactor diameter considered in the study (1, 2, 4 and 10 mm). For a coated wall reactor, it was found that less than 0.5 mm diameter is required to achieve near isothermal operation. In the coated wall configuration, the coating thickness affects the conversion for small diameter (0.5 - 1 mm) reactors, but the effect gets diminished for higher reactor diameters.

Evaluation of different approaches of scale-up of packed bed membrane reactor (PBMR) was also made by numerical simulations. A small-scale PBMR reactor (length = 1 m and diameter = 0.1 m) gives 83.4% conversion. The

conversion obtained in a longer PBMR handling twice the feed velocity of the small-scale PBMR (keeping residence time constant) is 82%. The PBMR having twice the diameter of the small-scale PBMR gave only 61% conversion. Residence time of reactant species was constant in all the cases. The conversion obtained in the longer PBMR is almost same as that obtained in the small-scale PBMR but pressure drop is observed to be much higher. Hence, to scale up the membrane reactor, an effective way would be to put small diameter reactors in parallel than having a reactor with larger diameter.

#### 4. Conclusion

It is believed that inclusion of membrane based technologies in the processing of HI<sub>x</sub> section of IS thermochemical process would be a sincere augmentation to the existing and proven technologies. The identification and development of a defect-free, high flux, hydrogen-permselective membrane, chemically compatible catalyst, suitable MR configuration configuration (packed bed or coated wall), corrosion-resistant reactor material, and high temperature sealants are the key milestones, and the work on each of the associated fields is in progress in Desalination Division to achieve the desired objectives. On the other hand, efforts are underway to gather the data pertaining to the corrosion stability analysis of all the systems/components in real HI decomposition stream as shown in Fig. 12.

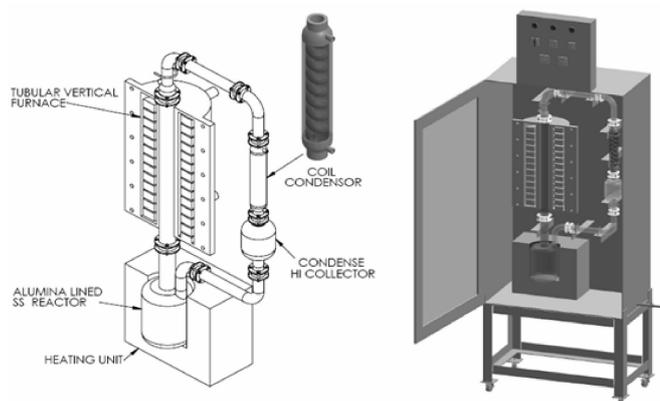


Figure 12: Setup for corrosion resistance studies in simulated experimental conditions

Modelling studies are underway on EED process to assess the influence of important operating conditions on its performance. Presently, work carried out has been limited to batch studies on HI concentration and HI decomposition in isolation from each other. Further to this, both the systems (EED and MR) will be integrated and experimental studies will be made in a continuous mode to assess the performance of the system in entirety. Refractory

membrane materials like tantalum and niobium, which have got inherent infinite selectivity towards hydrogen, and reasonable corrosion stability against HI environment, are under development.

### Acknowledgement

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# An Overview of Material Requirements for Copper-Chlorine Thermochemical Cycle: ONGC Energy Centre Perspective

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## Abstract:

Thermochemical Hydrogen generation by water splitting processes is gaining popularity in view of their potential for meeting massive scale energy requirements in near future although their temperature requirement is very high. Thermochemical Copper-Chlorine cyclic process that works at 550 °C is one of the many cyclic processes reported and being pursued. Although the temperature requirement of this cycle is relatively less and the reported process scheme appears simple despite solid handling problems, several technical issues need to be addressed including the material challenges to make the process commercially viable for hydrogen generation in an affordable way. The paper discuss the details of process along with reported variations in terms of improving the simplicity in operations and increasing the operational efficiency besides the focus on material challenges and way forward in ONGC Energy Centre perspective.

## 1. Introduction

Growing concern on environmental pollution as a result of excessive use of hydrocarbons that are fast depleting from the planet earth has prompted fast track research on several alternative sources of energy. However, in view of limitations of popular primary energy sources like Solar, wind, Geo-thermal, Nuclear etc., that cannot substitute the existing fossil based economy, hydrogen, an energy carrier is considered to be the future fuel [1]. At present it is mostly produced from fossil fuels for captive use at refineries, fertilizer industries etc., and thus the need of hour is to focus on development of non-polluting technologies. Hydrogen generation by closed-loop thermochemical water splitting processes that work at high temperatures (500-2000 °C) are thus gaining momentum as they have the potential for massive scale applications using Nuclear/Solar sources.

Among several cycles reported in the literature [2-4], Copper-Chlorine (Cu-Cl) cycle requires relatively less temperature of 550 °C. Argonne National Laboratories (ANL), US has first introduced the conceptual hybrid Cu-Cl cycle [5] that involves a series of coupled electrochemical and thermochemical reactions to form a closed-loop. The very reason that this cycle does not involve catalytic processes as compared to Iodine-Sulfur cycle which works at very high temperature ~900 °C makes it less complicated. But still, for reasons not clearly understood, except ANL, USA and Atomic Energy of Canada Ltd (AECL), Canada the cycle is not pursued by many cross-continental researchers who otherwise are active in I-S cycle studies. Thus the

available information in the literature is confined to a couple of sources only. The situation needs to be improved in the coming years for finding techno-economically feasible solutions in the long run. Thus it makes business sense for development of a suitable technology for this cycle as it appears lucrative primarily due to expected benefits like achievable efficiencies of the order of 50%, availability of a wide choice of materials and a flexible heat source. Nevertheless, current studies are still at R&D stage more precisely at lab engineering scale of development and thus certain material issues viz., extensive solid handling, material challenges involved in handling known corrosive chemicals like aqueous / gaseous HCl, oxygen, Chlorine etc., up to 550 °C and operation of electrochemical cells in conjunction with chemical reactors for continuous operations need to be addressed before reaching commercial scales. Recently, several variations of the cycle are reported in the literature that focus on reduction in number of steps, ease of operation with a minimum solid handling etc., leading to increase the operational efficiency. Current R&D activities around the world indicate that this cycle is extensively pursued by ANL and Atomic Energy Commission Ltd (AECL), Canada and their partner universities mainly University of Ontario Institute of Technology (UOIT). In India, ONGC Energy Centre (OEC) in collaboration with various technical universities is in the process of development of this cycle. The proof of concept of this cycle has been reported with several variations but still the closed-loop establishment is yet to be reported and thus materials suitable for technology development are still indicative in nature. The present paper attempts to present

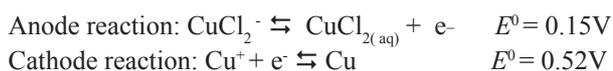
an over view of development of Cu-Cl cycle with a focus on material requirements as perceived by OEC to enable further research on finding techno-economically viable solutions in the overall development of this cycle.

## 2. Cu-Cl Process:

As per the initial ANL scheme, in this cycle water is split into hydrogen and oxygen using a combination of chemical and electrochemical reactions involving copper and its compounds without involving any catalysts. It involves extensive handling of solid copper compounds and gaseous/aqueous HCl at high temperatures that are produced and regenerated within the cycle. The sequence of cyclic processes as reported by Rosen et al [6] form a conceptual loop consists of following five steps:

1.  $2\text{Cu(s)} + 2\text{HCl(g)} \rightarrow 2\text{CuCl(l)} + \text{H}_2\text{(g)}$  450°C
2.  $4\text{CuCl(s)} + 4\text{Cl}^-\text{(aq)} \rightarrow 4\text{CuCl}_2^-\text{(aq)}$   
 $4\text{CuCl}_2^-\text{(aq)} \rightarrow 2\text{CuCl}_2\text{(aq)} + 2\text{Cu(s)} + 4\text{Cl}^-\text{(aq)}$  30°C  
*(Electrolytic reaction)\**
3.  $2\text{CuCl}_2\text{(aq)} \rightarrow 2\text{CuCl}_2\text{(s)}$  100°C
4.  $2\text{CuCl}_2\text{(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CuO.CuCl}_2\text{(s)} + 2\text{HCl(g)}$  400°C
5.  $\text{CuO.CuCl}_2\text{(s)} \rightarrow 2\text{CuCl(l)} + 1/2\text{O}_2\text{(g)}$  500°C

In the first step, solid copper is fed into reactor along with a stream of HCl gas to form hydrogen gas and molten CuCl at 450°C; the latter being cooled and by solubilized in a sufficiently concentrated HCl (5 - 6 N) to feed to a membrane electrochemical reactor where it is disproportionated to fine solid copper powder and acidic aqueous  $\text{CuCl}_2$  as per the following details:



$\text{CuCl}_2$  solution is dried to separate from aqueous HCl to get  $\text{CuCl}_2$  powder and then hydrolyzed at elevated temperatures to obtain copper oxychloride ( $\text{Cu}_2\text{OCl}_2$ ) which is finally decomposed to get oxygen and CuCl.

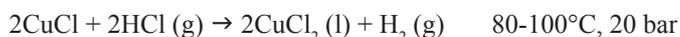
## 3. Some challenges

Although these reactions appear simple, there are several practical difficulties associated with some of the reactions. For instance, electrochemical generation of copper particles at required 3 - 5  $\mu\text{m}$  in an efficient way is a tough task. Another difficulty associated with the electrochemical reaction is the selection of membrane suitable for long-term applications as at present, the choice for commercial applications is limited. In hydrolysis reaction, excess amount of steam is required to produce desired results and thus making it a difficult task in latter stages to remove the excess water. In addition, although

ANL has reported the formation of copper oxychloride detailed laboratory studies by OEC and collaborators [7] that it is difficult to get the reported products under normal operating conditions leaving aside the difficulties associated with its characterization. Simulations and Modeling of entire cycle is another challenge in view of difficulties associated with solid handling and problems encountered in electrochemical simulations. Recent developments in Aspen simulations give a ray of hope but still there is a dearth of information for successful application. Detailed calculations of thermal energy requirements of the cycle involving exothermic ( $-330\text{ kJmol}^{-1}$ ) and endothermic ( $680\text{ kJmol}^{-1}$ ) components of heat including electrochemical work suggest that there is a lot of scope for improving the overall heat to hydrogen efficiency of the cycle >40% with proper heat management. However, as observed by Rosen [4], exergy analyses are needed to understand and reduce losses.

## 4. An over view of recent developments in Cu-Cl cycle:

The recent modification of the five-step cycle as reported by Lewis et al [8] outlined that the first two reactions can be replaced with a single electrochemical step:



where, the cathodic reaction of original electrochemical reaction is replaced with a hydrogen generation reaction. This approach involves minimal solid handling to the extent of eliminating solid copper handling and is further pursued by ANL and AECL. However, as observed by OEC and collaborators [9] the method has its own difficulties of handling high pressure electrochemical systems besides finding highly stable, selective and cost-effective membranes that are industrially acceptable in the long-run.

Lewis et al [10] have indicated the possibility of replacing  $\text{CuCl}_2$  hydrolysis and Copper oxy-chloride decomposition steps with a single oxygen generation step directly from hydrolysis step at about 700°C.

It leads to understanding from the above developments that it is possible that entire five step-cycle can be reduced to a simple 2-step cycle. Although this latest development is beneficial to the extent of reducing no. of steps to facilitate operational simplicity, it will invite more challenges of choice of heat source, material for equipment at high temperatures and product separations making it not very popular.

In a series of communications, Lewis et al [11-13] described the evaluation methodology; selection criteria of alternative cycles and the efficiency calculation, updating thermodynamic data base, development of a robust flow sheet using Aspen Plus simulator by optimizing the energy usage within the cycle, design of a conceptual process incorporating the Aspen Plus mass and energy flows, efficiency(40%) calculation and estimation of energy costs (\$3.30/kg) based on hydrogen production plant capacity of 125M.T/day. Orhan et al [14] have done cost analysis and sensitivity analysis of a Cu-Cl pilot plant with an associated parametric study taking several scenarios into consideration. The scale-up of the Cu-Cl cycle from proof-of-principle tests to a larger engineering scale of 3 kg/day is currently under development at the University of Ontario Institute of Technology in collaboration with its partners that include Atomic Energy of Canada Limited (AECL). Feasibility study of a solar based Cu-Cl cycle was reported by Ghandeharium et al [15] in which details of solar energy source, different capacities at three different locations in Canada, efficiencies etc. Naterer et al [16-17] have given details of individual process and reactor developments within the Cu-Cl cycle (5-step and 4-step processes), thermochemical properties, advanced materials, controls, safety, reliability, life cycle assessment, simulations/ modeling, economic analysis of electrolysis at off-peak hours, and integrating hydrogen plants in conjunction with Canada's nuclear power plants, especially with Super Critical Water Reactor [SCWR]. Wang et al [18] discussed thermodynamic and experimental studies leading to process integration of hydrolysis electrochemical and oxygen generation reactions mainly focusing on various technical challenges associated with the closed-loop operation of the cycle.

In a series of recent communications, Naterer et al [19] reported simulations, thermochemical data, advanced materials, safety, reliability and economics of the Cu-Cl cycle. Aspen Plus simulations of various system configurations were performed to improve the cycle efficiency, modeling of the linkage between nuclear and hydrogen plants demonstrates how the Cu-Cl cycle could be integrated with a Super Critical Water Reactor; Canada's Generation IV reactor (SCWR). Useful fundamental data viz., Chemical potentials, solubility, formation of Cu(I) and Cu(II) complexes and properties of  $\text{Cu}_2\text{OCl}_2$ , Cu(I) and Cu(II) chloride species were also reported by these researchers. Development of new advanced materials with improved corrosion resistance in relation to performance of new anode electrode structures and thermal spray coatings was also presented [20]. In a detailed communication, unit operation experiments viz., in hydrolysis, electrolyzer,

studies on corrosion resistant coating materials and system integration were reported by Naterer and co-researchers [21] recently. Some of the studies include long-term electrolyzer performance over 1600 h of operation at constant voltage of 0.7V, membrane performance studies, scaling up of electrolyzer to 300 cm<sup>2</sup> that showed a current density of 550mA/cm<sup>2</sup> at 0.7V was also reported. Design of a molten salt reactor, parametric study of multi-generation energy systems incorporating the Cu-Cl cycle leading to estimation of overall energy efficiency of 57% and exergy efficiency of hydrogen production up to 90%

OEC and collaborators [22] have successfully established the proof of concept of this cycle using a combination of electrochemical and thermochemical reactions and are in the process of developing the closed loop using metallic (Hastelloy) reactor system for generation of hydrogen @ 25 LPH. The electrochemical reaction involves copper and  $\text{CuCl}_2$  generation process which is carried out at room temperature. While the cell is fabricated with an acrylic material, copper and Platinum / Graphite electrodes separated by a commercially available anion-exchange membrane are employed.

### 5. Materials for use in Cu-Cl cycle:

Although it is interpreted that since the maximum operating temperature of this cycle involves about 550°C, there is a wide choice of materials lining up for its development. Thus the eventual commercial success of the cycle depends on material research. As suggested by Wong and Tessler [23] while taking decisions on the materials of construction(MoC), several aspects like resistance to corrosive media, thermal conductivity mechanical and creep properties, allowance for non- destructive testing during fabrication and also in service hot and cold formability, weldability, and availability need to be considered to make building of a hydrogen production plant practical.

As seen in the cycle, maximum solid handling is involved in almost every reaction step which is the main inconvenience in plant level operations, keeping aside their exact contribution to corrosivity of the metals employed. The cycle contains a mixed (oxidizing and reducing) environment and thus right choice of materials need to be specific to the given conditions. Several alloy materials containing high Ni/Cr content like Hastelloy C-22, 24, 276 etc., are reported [24-26] in the literature for HCl,  $\text{Cl}_2$ ,  $\text{CuCl}_2$  environments under the operating temperatures of the cycle but one needs to confirm their practical utility by conducting suitable tests for prolonged periods of time. To start with, the prevailing industrial practice of corrosion

allowance of < 0.1 mmy is the right guideline for selection of materials.

Rosen et al [6] observed that high performance metal alloys cannot withstand corrosive fluids over a long duration. High temperature alloys with coatings of silicone based ceramics appear promising in this regard, but their thermal behaviour and surface interactions in high-temperature multiphase conditions must be studied. Further data is needed to better understand the functionality of these materials with the working fluids in the Cu-Cl cycle. This includes thermal behaviour, mechanical stresses, and fracture toughness, strength and corrosion resistance over time. Nokleby et al [27] suggest spray coatings, nickel-based alloys, glass-lined steel, refractory and other advanced materials are the subjects of research to meet these material challenges. While examining various metals for suitable application in this cycle, these authors expressed that since the predominant Ni and Cr species are solids it suggests that a corrosion resistant protective layer could be formed on the metal. Based on this logic, they continued work [19-20] on several other combinations of Ni-based alloys to assess their suitability and have discussed various options. It was opined that Ni and Cr species can be used as coatings on metal since they form corrosion resistant protective layer on the metal. Among corrosion resistant coatings viz., nickel alloy, Zirconia, alumina etc., Zirconia seems to have performed better than alumina. Stainless steel showed poorer corrosion resistance in this cycle. Glass lined metal as a material of construction materials of construction for the CuCl/HCl electrolyzer may be suitable however it was found that glass may dissolve up to 0.7 mm/ annum in aqueous conditions ceramic carbon electrodes (CCE) for the anode of the CuCl/HCl electrolysis cell. While the recent development of CCE for use in this cycle for use as anodic materials in place of costly Platinum is currently pursued by ANL-AECL and their collaborators, simultaneous thrust [19-21] on reduction in the total amount of Platinum to ~0.3mg appeared meeting the requirements in electrolytic hydrogen generation step.

Besides selecting the material of construction for reactors, electrodes etc., one has to look out for equally important area, membranes used in this process. A detailed review [28] on membranes gives the recent developments along with relative merits and demerits of wide range of membranes including zeolite membranes, silica membranes in addition to metallic membranes and may be taken as a good guideline in this aspect. From this review it appears that almost all the available membranes do not have much tolerance for moisture. It can be visualized

that the cycle requires membranes in several reactions for use in prevailing wet mineral acid media viz., HCl-H<sub>2</sub>O and also for gaseous separations like H<sub>2</sub>-N<sub>2</sub>, O<sub>2</sub>-N<sub>2</sub>, Cl<sub>2</sub>-N<sub>2</sub> etc. These are required in hydrogen / oxygen generation reactions where the products are to be separated from carrier gas and water vapour etc., electrochemical reactors that need both anion / cation exchange membranes as may be the case with the modified cycle, separation of HCl from water etc. While anion-exchange membranes are required for the reactions involving copper recovery, the cation-exchange membranes are needed in electrochemical hydrogen generation reactions.

Besides material of construction and other issues, it is well reported that commercial success of these cycles is dependent on easily available and affordable viable heat source which is expected to be either Nuclear and / or Solar. But issues related to coupling of these sources to thermochemical cycle still need to be addressed. AECL has initiated some work on this aspect in context with the envisaged application using SCWR [28] or solar driven molten salt reactor [29].

## 6. Need of the hour:

As there are no proven off the shelf solutions available for immediate applications to take these processes to commercial scale and the current status of the work is now at a lab engineering scale in order to go beyond this stage, transforming the available knowledge and expertise to develop technologies on a fast track mode is the need of hour. Needless to emphasize the fact that before taking these studies to next higher levels, several technical issues related to processes, materials, sources for their fabrication / supply etc., need to be addressed by pooling scattered domestic solutions and/or cross-continental cooperation so that the technologies can be developed at the earliest in a techno-economically feasible way. Some of the challenges that need to be addressed include:

### 6.1 Modification in Process

The existing processes are based on lab scale experiments and available process gadgets. Thus it is required to develop:

- Energy efficient process schemes to modify the conventional schemes to facilitate ease of operation, safety of resources etc.
- Better separation strategies including membrane separations in place of distillations wherever applicable
- Handling solids flow to and fro reactors

- Handling corrosive acids especially the azeotropes HCl-H<sub>2</sub>O
- Improvement in Simulation / Modeling studies for quick solutions that accommodate wider options for solid handling
- Electrochemical generation of fine particles (< 2 μm sized)
- Minimization of aerial oxidation of reactants/products in Cu-Cl cycle

## 6.2. Identification of Alternate Materials

As already mentioned, the current development of this cycle is based on the experience and knowledge of some groups/ individual researchers working in specified areas and to a certain extent is confined to certain pockets. However, with the advent of Science & Technology, scattered solutions that exist might be getting unnoticed. Thus it is felt that a broader outlook with a commercial angle is thus required to explore the possibility of using alternate materials in various reactions involved in these cyclic processes.

- Non-Platinum electrode materials for use in HCl media for use up to 100°C and 24 bar including electro-catalysts
- Electrochemical cells for HT-HP operation for prolonged period applications
- Membranes for use in prevailing wet mineral acid media viz., HCl-H<sub>2</sub>O and also for gaseous separations like H<sub>2</sub>-N<sub>2</sub>, O<sub>2</sub>-N<sub>2</sub>, Cl<sub>2</sub>-N<sub>2</sub> etc.
- Reactor materials for use in Cu-Cl cycle for various reactions up to 530 °C.
- At present, there is a limited choice of materials for use in this cycle. Although high Ni-Cr based alloys appear to work, supporting information is very limited.

## 6.3 Testing Facilities

The existing corrosion testing facilities for screening materials do not provide ample scope to work at very H.T-H.P conditions in acid media prevailing in both the cycles. Thus it is needed to:

- Develop testing facilities for screening available materials for their corrosion resistance / behaviour up to 600 °C and pressures up to 20 bars.
- Create facilities for assessing mechanical properties of materials under operating conditions
- To develop standards /codes for materials testing etc.

## 6.4. Development of Materials

As understood several materials reported in the literature need to be developed at large scale to cater to growing needs in near future. A preliminary market survey does not indicate their availability in the open market ingeniously. It is thus required to:

- Out of box solutions to phase out use of noble /exotic metals with easily available and affordable metals/ materials.
- Develop alloys containing some typical combinations of selected metals to avoid costly materials like Platinum.
- Develop indigenous sources of fabricators for specified materials
- Develop alternate materials viz., membranes, electro-catalysts etc., that are stable/durable for longer times under the operating conditions
- Use of composites wherever applicable

## 7. Conclusion

- Hydrogen is set to take a lead role in energy business in future; large scale technology development to generate it in an easily available and affordable way is required.
- Development of closed-loop thermochemical hydrogen generation technologies using Nuclear and/or Solar heat source through Copper-Chlorine cyclic processes appears lucrative but technical challenges need to be addressed.
- There is a gap between current research efforts on development of materials to contain the prevailing harsh acidic environment in this process before commercial realizations.
- Although good no. of materials are available for applications in acid media in the specified temperature range of the cycle, their suitability needs to be ascertained
- Hastelloy, Inconel appear useful for MoC in Cu-Cl cycle but their ultimate utility at commercial level needs to be examined by conducting long-term tests under prevailing harsh conditions preferably at different laboratories for taking plant level decisions.
- Besides reactor materials, equal emphasis needs to be laid on development of catalysts, membranes etc.
- The much talked about coupling of heat source viz., Nuclear and /or Solar Thermal to Thermochemical

cycle is a challenge in view of material issues and thus need to be addressed in parallel

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# Design of Photoelectrochemical Materials Via Non-Native Nanostructures and their “Click” Assembly into Photoreactor

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## Abstract

The goal of economical photoelectrochemical (PEC) water splitting has gained more importance in view of the dwindling non-renewable energy resources. In this context, the search for a good photomaterial is restricted within earth abundant elements and its compounds having good photon absorption in solar spectrum, effective charge-carrier separation and surface electrochemistry. We propose that modulation of desirable material properties can be achieved by stabilization of ‘non-native’ structures which are nanostructures having discrete translational symmetry in the sub-surface regions different from that present in the sub-surface regions of large crystals. These non-native structures have different physico-chemical properties (e.g. band-gap, band-edge) and catalytic activity in comparison to bulk ‘native’ structure due to different chemical coordination. One of the effective ways to circumvent charge-carrier separation and transport is through design of heterostructures via native phase and non-native phase. The proposed design is found to give higher photon absorption compared to individual phases. Finally, “click chemistry” is utilized as a tool to assemble stable photo-electrodes into solar chemical reactors. Further, a small scale modular PEC device has been fabricated (which can be scaled up) to test the fabricated photo electrodes.

## Introduction

A large portion of world energy consumption is derived from non-renewable energy resources such as natural gas, oil, and coal. Replacing this source of energy by environmentally friendly solar energy has been drawing more attention than ever before [1,2]. The available solar energy can be harvested in a photovoltaic device (PV), where it may be either directly converted to electrical energy or captured in a photo-electrochemical cell (PEC) device through performing an endothermic reaction such as water splitting [3-5], oxidation reactions [6], CO<sub>2</sub> conversion [7] and in the process generating solar-produced chemicals or fuels. A sustainable approach to large-scale solar-energy devices relies on two qualitatively different approaches, namely, high-cost and high-efficiency devices or relatively lower-cost and lower efficiency devices. Central to the latter approach is the utilization of liquid-phase processing of earth-abundant compounds that do not rely on expensive single-crystal substrates, thin films, or vacuum fabrication techniques. Semiconductors play a central role in such devices, and there have been many efforts to improve its photocatalytic efficiency. The choice of semiconductor material is constrained by limiting factors such as (1) band-gap in visible region, (2) low light penetration depth, (3) chemical stability, (4) high conductivity of majority and minority carriers with high lifetime and (5) desirable flat band positions for surface redox reactions.

The development of highly efficient corrosion-resistant photoelectrode materials and their processing technologies are most important in the context of efficient hydrogen production from solar energy through water photolysis. The most challenging aspects or important parameters in meeting this are band-gap tuning, band-edge alignments, surface activity, stability in solution, and most importantly abundant availability or low cost. To date, no suitable material (nanostructure/film) has been demonstrated to meet all the requirements. Therefore, a fundamental materials research is needed for tailoring band-gap and band edge alignments for proper solar absorption and charge carrier transport and movements. Further, we require rational strategy to modify the surface chemistry and associated effects on surface as well as bulk semiconducting properties (e.g. light absorption, interfacial charge transfers including Schottky and Helmholtz barrier, flatband potential, etc.) which profoundly influence the efficiency of photo materials. In addition, corrosion and photo-corrosion problems limit the efficiency of PEC water splitting.

**Native/Non-native structures:** While modulation of properties via variations in chemical composition has been explored extensively in the context of hydrogen generation using photo-electrochemical (PEC) systems, comprehensive modulation of properties via variation of nanostructure has not been pursued. Engineering of material properties can be

done by modulating the subsurface and surface structure of nanomaterials in a controlled manner. In this context, we introduce the concept of “non-native” structures, which are nanostructures in which the discrete translational symmetry in the sub-surface regions is different from that of the discrete translation symmetry present in the sub-surface regions of large crystals [8]. The sub-surface structure of the large crystals is identified as the native structure of the material. These non-native structures are stable in nano-regime due to having less surface energy than their bulk structure counterpart. Studies suggest that the non-native structures are stabilized stable up to a critical size after which it undergoes phase transformation to its native structure. To analyze the energy landscape below and above this critical size, the total energy of the a thin film is partitioned in following way,

$$E_t = (1 - 2)E_{ss} + 2E_s = 1E_{ss} + \gamma \quad (1)$$

$$\text{and } [\gamma = 2(E_s - E_{ss})] \quad (2)$$

Where  $E_t$  is the total energy of a thin film having ‘ $l$ ’ number of stoichiometric layer,  $E_s$  is the energy associated with the surface layer,  $E_{ss}$  is the energy associated with the sub-surface layers and  $\gamma$  is the surface energy. Below the critical thickness ( $n_c$ ), the non-native structure is thermodynamically stable and satisfy the following inequality,

$$n_c(E_s^N - E_s^{NN}) > (\gamma^{NN} - \gamma^N) \quad (3)$$

As the chemical coordination is different in the native and non-native structures, properties like band-gap, band-edges and surface electrocatalytic properties is also different.

Since non-native structures are typically more stable as nanostructures, they will provide higher surface area with larger number of active sites. To illustrate these concepts, we give example of  $TiO_2$  and  $Fe_2O_3$  which are most widely used PEC materials. Among the polymorphs of  $TiO_2$ , we are considering anatase and rutile which are photocatalytically active. Rutile structure is identified as a thermodynamically stable polymorph (native structure) while anatase structure is identified as its metastable counterpart (non-native structure). Both computational and experimental data suggests that anatase structure is stable at lower length scale (<14nm) while its polymorphic counterpart is stable in higher length scale (>14nm)[9]. Anatase and rutile has a band gap 3.2eV and 3.0eV respectively and their band-edges are suitable for water-splitting. Anatase is generally found to be more photocatalytically active than rutile. Similarly in  $Fe_2O_3$ , it is found that they have four polymorphs.  $\alpha$ -  $Fe_2O_3$  is found to be thermodynamically stable bulk ‘native’ phase ( $p > 50nm$ ) while  $\beta$ - and  $\epsilon$ - are

non-native structures which are stable in  $30 < p < 50nm$  and  $8 < p < 30nm$  regime where  $p$  is the particle size[10]. The non-native phases are reported to be more photocatalytically active than its native counterpart[11].

Though there is considerable literature on specific non-native structures, there is distinct lack of literature that gives generalized heuristics and strategies for the synthesis of non-native structures. One synthetic method is the application of high pressure if the lattice volume of the non-native structure is less than that of native structure (e.g.  $LaVO_4$ ,  $CdSe$ )[12,13]. The application of pressure need not be always through external pressure. Pseudomorphic growth upon sacrificial shell template results in stabilization of core materials even in atmospheric pressure due to stress exerted by shell [14]. In this regard, we specifically investigated  $ZnS@CdSe@ZnS$  system and found  $CdSe$  transforms to non-native (RS) structure even at atmospheric pressures [14]. Similar observations have been made in non-native  $Fe_2O_3$  polymorphs where  $SiO_2$  template is used [10]. Among other methods, synthesis of structure is performed in high concentration of strongly bound ligands. The non-native structures are often formed in early stages of growth. If the ligands can arrest the growth of structures by binding to them, they lower the surface energy of crystals and in the process lower the total energy of the system as well as providing steric hindrance to the growth of native structure. The non-native structures of  $MnSe$  [15],  $CoO$ [16-18],  $MnS$ [19] are stabilized by these methods. To arrest the growth of non-native structures, low reaction temperature is being maintained in solution based synthesis.

Through synthesis of non-native structures of earth abundant elements, we can expand the material space of suitable materials for PEC application. The synthesis of these non-native nanostructures have several advantages like 1) surface/volume ratio 2) quantum confinement effect, and 3) enhanced electrodynamic interactions from the point of PC/PEC applications. From the view of PEC water splitting, a main prerequisite of any semiconductor material (nanoparticle and/or bulk) is to have efficient charge separation upon light excitation [20]. Upon light absorption, the formed excitons (electron-hole pair) have to be “split” and reach to the surface to facilitate respective redox reactions.

**Heterojunctions:** It is to be noted that the typical diffusion length of electrons/holes is less than 10 nm before they recombine with holes/electrons and migrate or diffuse. Hence, there is a need for developing new strategies for attaining effective charge carrier separation. In this context, the concept of heterojunctions has been

introduced, in which junction formed between electron donating and accepting materials [21] with proper band alignments and will facilitate effective charge separation at the interface due to band bending.

An interface formed between regions of dissimilar materials (metals, semiconductors or insulators) is abbreviated as heterojunction and the combination of multiple heterojunctions together in a system or a device is called a heterostructure. Properly designed heterostructures typically involve modification of the electronic structure at the interface that facilitates optical absorption, charge separation, and enhances the kinetics of surface reaction [22] as schematically shown in **Figure-1A**.

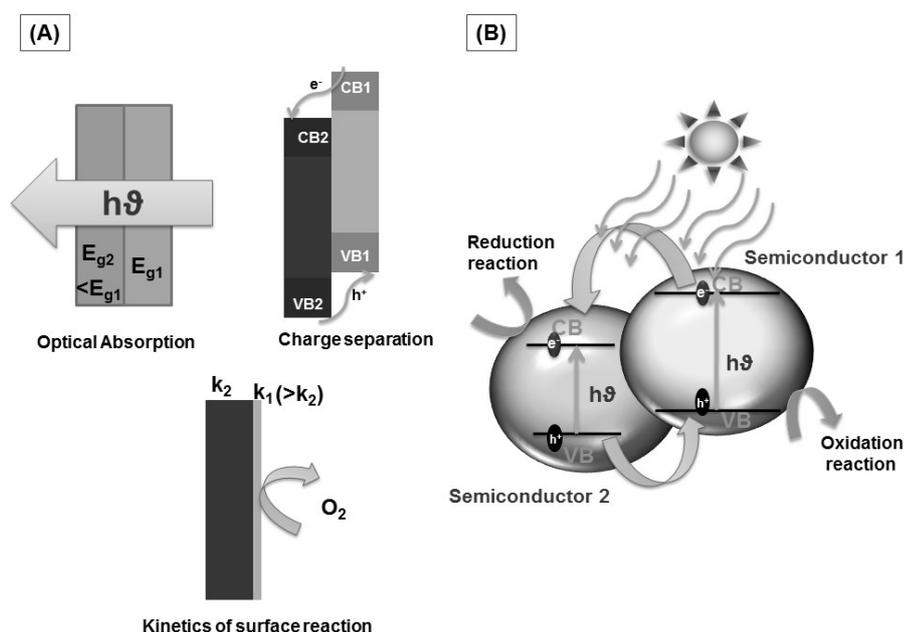


Figure 1. A Schematic illustration of primary processes responsible for performance enhancement in heterostructure systems, Adapted from ref [22]; (B) charge transfer in a coupled semiconductor-semiconductor system with proper band alignments in transferring charge carriers.

When two materials/phases/particles are coupled, the effective driving force for electrons and holes transport depends on their proper band alignments and band edge positions (Fig. 1B). Further, three important aspects are essential in forming heterostructures, which are, 1) uniform size of the individual components, 2) Smooth and defect free interfaces and

3) Good stability [23]. Furthermore, the interface and interfacial strain between two phases plays a major role in heterostructure formation. Different degrees of interfacial strain will lead to the formation of different type of heterostructures e.g. 1) a well matched lattice parameters of crystalline phases lead to core/shell heterostructures formation [14] or 2) if there is overall lattice mismatch along certain miller indices with existence of coincident site lattices (i.e. systems with reduced symmetry compared to symmetric core-shell structures) leads to anisotropic heterostructures (usually called as Dimers or oligomers) [24].

Heterostructures are classified into type-I, type-II and type-III configurations (schematically elaborated in Fig. 2) based on the band alignment at the core-shell interface. The band gap of the core is narrower than band gap of shell e.g. CdSe core/ ZnS shell nanocrystals fall under type-I core-shell category and the shell material is utilized to improve the optical properties by passivation of the core [25]. In the inverse type-I system, the band gap of core is broader than the band gap of shell which permits both the charge carriers to reside in the shell e.g. ZnSe core/CdSe shell fall under this classification [26]. In type-II system, the valence and conduction band of core lies below the valence and conduction band of shell respectively or vice-versa e.g. Anatase/Rutile  $TiO_2$ , CdTe/ ZnTe and CdS/ ZnSe [27]. Figure 2 illustrates these configurations based on these band alignment positions that are feasible for fast charge carrier movements.

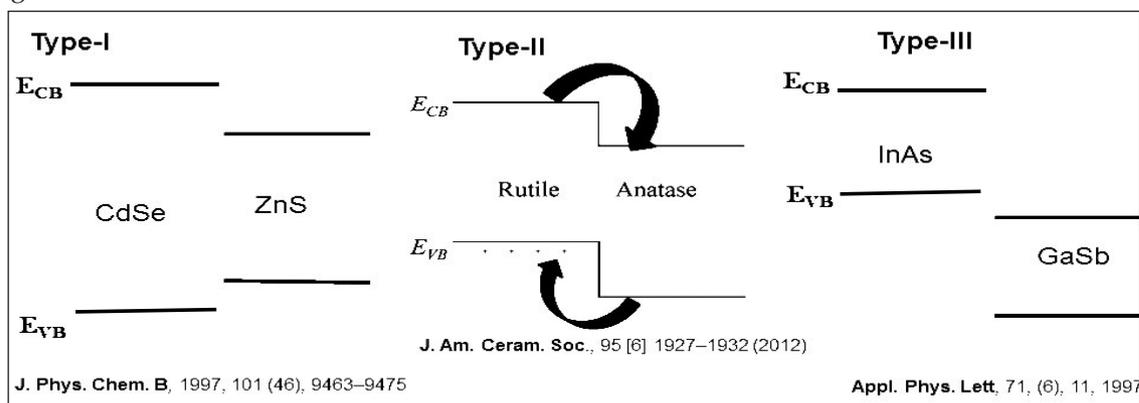


Figure 2: Classification of heterostructures and catalyst design based on different band alignment positions.

### Iso-material heterostructure

Iso-material heterostructures are formed by material of similar chemical composition e.g. anatase-rutile  $\text{TiO}_2$ , rutile-brookite  $\text{TiO}_2$ , brookite-anatase  $\text{TiO}_2$ , monoclinic-orthorhombic  $\text{WO}_3$  and  $\alpha$ - $\beta$   $\text{Ga}_2\text{O}_3$ . The advantage of iso-material heterostructures is in it having lesser interfacial defects due to better lattice match at the interface between phases, which helps to facilitate charge carrier movements apart from synergistic effect associated in some materials like  $\text{TiO}_2$  (P25 Degussa). Due to the "intimate" co-existence of anatase and rutile phases it is observed that P25 Degussa is more effective than a system consisting of pure rutile or anatase [28]. It can be noted that the interfacial charge carrier transport in  $\text{TiO}_2$  polymorphic heterojunctions can be explained in two main pathways: 1) due to lower CB minimum, rutile phase acts as a passive electron sink and captures electrons from anatase phase [29] and 2) transport of electrons from the rutile to anatase occurs *via* lower energy electron trapping sites of anatase phase [30]. It is worth noting that the charge carrier transport from one phase to other depends on the particle size, surface energy, localized electronic states and structural interface in the bandgap of anatase/rutile phases.

### Processing of PEC electrodes and their present status

Generally photoelectrodes (metal and/or metal-semiconductor heterostructures) are fabricated through physical mixing [31], electrochemical deposition [32], non-covalent interactions [33], spin coating [34], Langmuir Blodgett [35], Doctor Blade [36] and sputtering. However, all these fabricated heterostructures are stable only under certain chemical conditions such as operating pH, temperature/potential or concentration/scan rate/current because of the relatively weak interactions between the constituent entities with the surface; Hence, it is expected that covalently bound interfaces would enhance the stability of such heterostructures and thereby enhance the performance of the PEC water splitting. Click chemistry is a versatile tool to fabricate such metal-semiconductor heterostructures [37] and have provided stable heterostructures in the context of solar hydrogen production.

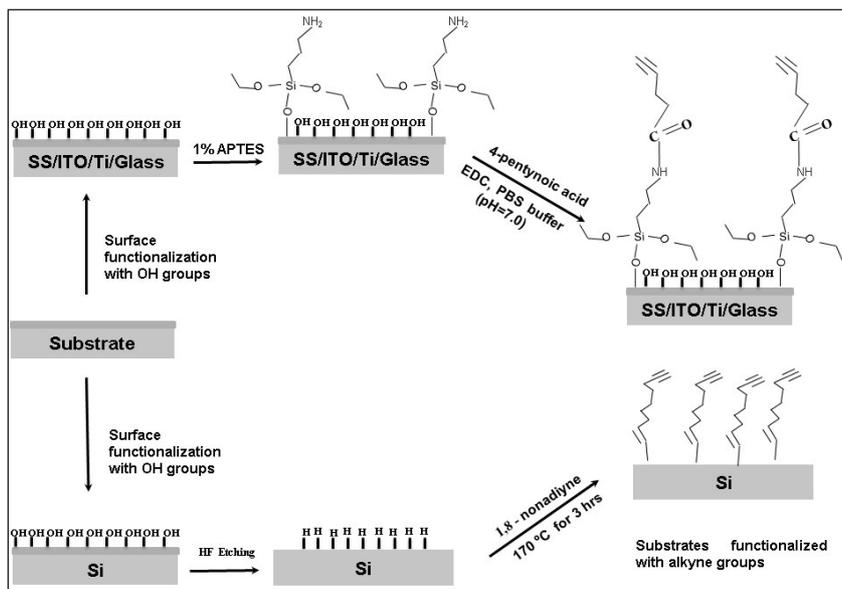
### "Click" chemistry for fabrication of photoelectrodes

"Click" chemistry (usually called as copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction) is a widely used tool to attach particle to particle and/or particle to substrate surface via strong covalent linkages of triazole moieties and proceeds with high yields

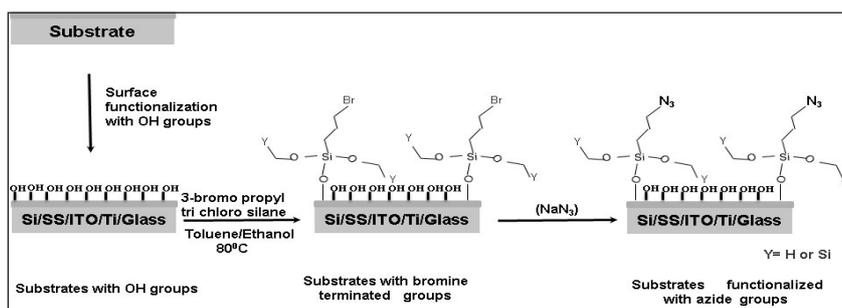
with no by-products. It can be inferred from literature that this approach is applicable to variety of material synthesis applications such as functionalization of polymers and dendrimers [38], polysaccharides [39], DNA [40], and a variety of bulk surfaces including gold [37] and silica [41] as well as different conducting (e.g. ITO, SS, Ti) [37,42] and non-conducting (e.g. glass or polymer surfaces) [43,44].

The utilization of this approach offers a number of advantages: (1) the triazole linkage between the click moieties offers high stability, even under highly oxidizing conditions, and supports electron transfer [45]; (2) it circumvents the problem of aggregation associated with the thermal processing of nanoparticles and offers the ability to modify electrodes even at room temperature (RT); (3) scalable to large areas, and (4) flexibility and control in the formation of multilayers of differing metallic-semiconductor nanoparticles and enabling versatile heterostructure fabrication approach compared to other chemical approaches. Further, this method is applicable to any type of nanoparticle (metal, semiconductor or insulator) and any type of surface (conducting surfaces like ITO, SS, Si wafer, or non-conducting surfaces like glass and polymer matrices). We have optimized protocols for alkyne (Figure 3a) and azide (Figure 3b) functionalization of different substrates. Further, Figure 3c explains the broad applicability of click conjugation to different alkyne/azide moiety containing particle with alternative azide/alkyne group functionalized substrate. This approach of click reaction makes it modular and applicable to any surface or particle and has emerged as a facile and versatile approach to achieve chemical assembly of materials via covalent bonds [46]. It is to be noted that the heterostructures fabricated from this approach is active for surface electrochemistry and stable under external potentials or potentials generated because of the absorption of solar radiation. Our recent article demonstrates the wide applicability of click chemistry approach in fabrication of metal-semiconductor heterostructures. The tailor made nanostructures on different substrates (ITO, SS, Si-wafer and Ti) showed excellent stability as well as activity in enhancing the photocatalytic water splitting as well as methanol oxidation reaction schemes.

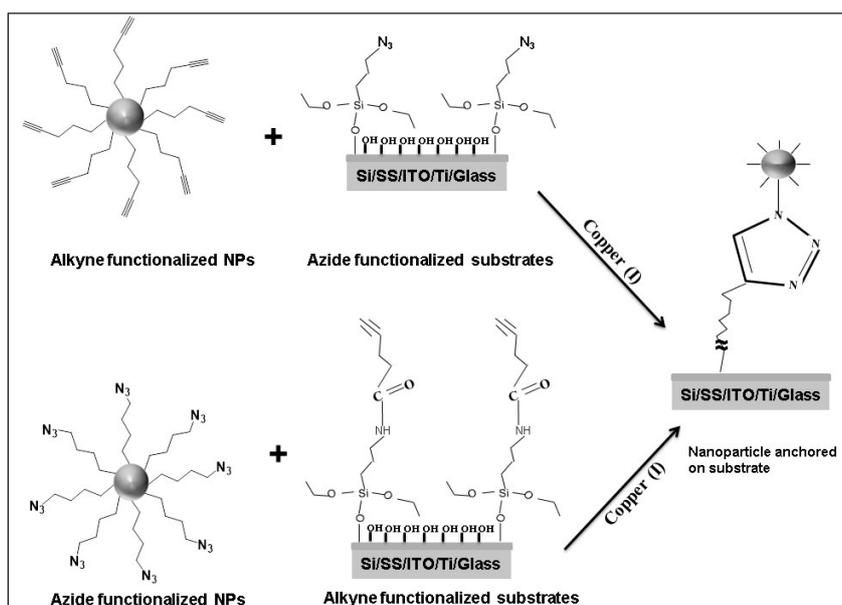
We know that the performance of any heterojunctions (oxide/oxide or metal/oxide or metal/metal) is critically dependent on their ability to achieve intimate mixing and electrical contact between different materials [37]. In general, heterojunctions can be formed via a range of physical methods such as physical mixing [47], and sequential deposition methods [48]. However, when material is in the form of nanoparticles, chemical assembly



**Figure 3a:** Alkyne functionalization of different conducting substrates (Si, SS, ITO, and Ti) and non-conducting substrate (glass)



**Figure 3b:** Azide functionalization of different conducting substrates (Si, SS, ITO, and Ti) and non-conducting substrate (glass)



**Figure 3c:** Click reaction of nanoparticle containing alkyne moiety with azide functionalized substrate and vice versa

methods are always better than physical methods and offer a highly scalable approach towards the formation of heterojunctions [49]. The heterojunctions formed between material interfaces are electronically conducting and allow facile transfer of charge carriers which will improve the performance of the operation as shown in our recent article. The covalent linkages formed between metal (Au)–semiconductor (TiO<sub>2</sub>) heterostructures are stable enough to degrade the Rhodamine (RhB) dye effectively by utilizing the photon flux (in terms of SPR effect of gold) and heterojunctions.

### “Click” chemistry of metal oxides

The usage or the potential effectiveness of CuAAC for the modification of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles with a diverse array of functional species including small molecules and polymers has been demonstrated recently [50]. Further, it is versatile and modular approach applicable to other metal oxides such as TiO<sub>2</sub> as demonstrated by our group [51], WO<sub>3</sub> [52], ZnO [53] and SiO<sub>2</sub> [41]; Further other semiconductors such as CdSe [54] and Si-111[55]. Recently several articles are focusing more on click chemistry of nano surfaces [56] and nanoparticle modification strategies[57].

### Reactor design and fabrication

**Essential rationale:** PEC water splitting is multipronged research in which development of efficient photo electrode material is critical. Nevertheless the PEC device development has to go hand in hand which in turn will reduce barriers in commercializing this technology. Till now, there is no standard device and testing procedure for studying the performance of new photo electrode materials. Although, several articles [58] and reviews [59] are available on photo reactor design, focused rational reactor design which can be utilized across the full range of applications of photo catalysis/PEC in both small and large scale is scanty.

Very few groups have developed small scale PEC reactor to test their photo electrode materials and such reactors have not been optimized too. By considering the

forementioned factors a small scale PEC device has been designed and fabricated. Hence, our development and scale-up efforts have focus mainly on design that are most suitable in applications and have potential in commercial development of solar energy conversion schemes. The ensuing discussion will focus on the factors one need to consider while designing PEC water splitting device/small scale reactor.

### Primary functions of the reactor

- It should hold the electrodes in an orientation that allows for photons impingement on to the electrode surface in an uniform manner.
- It should allow for pumping and distribution of the electrolyte across the electrode surface i.e. high mass transfer rate.
- It should have a separation/removal/safety mechanism for the products  $H_2$  and  $O_2$  as this is an explosive mixture.
- Transferring of charge carriers to counter electrodes with minimal overpotential.

### Need for Design of a Photoreactor

Design of an electro/photoelectrochemical reactor with separate gas evolving chambers is a challenging task due to the complexity involved in heterogeneous catalytic splitting of water. Multiphase flow in any reactor is stochastic in nature. The physics and effects of bubble nucleation, growth and detachment will play an important role in reaction rate. It is very important to consider the bubble size and bubble hydrodynamics in photoreactor design, wherein bubble photon reflectivity and light path distance increases the overall over potential of the system. Generally, photoreactors differ significantly from normal chemical reactors based on one major aspect of physical geometry which ensures proper collection of photons effectively on to the photocatalyst, apart from operational parameters such as temperature, pressure which come under secondary importance. Several other parameters affect resistances such as ohmic drops, contact resistance and mass transfer limitations. Overall, design of a PEC reactor comprises of two parts: reactor design and photo electrode design. Most of the previous works are primarily focused on photo-electrode design rather than mechanical device design, even though both play a significant role in achieving the reasonable efficiency of solar to hydrogen conversion from water photo-oxidation.

For large scale applications, the reactor configuration should be a continuous type reactor, have the option of stacking a number of cells to intensify the process, have minimum pressure drop, high mass transfer rate and

uniform distribution of light. Furthermore, the reactor should be modular enough to test different kind of photo electrode materials, configurations and biasing. Last but not least, fabrication and design should include minimum over potential losses, maximum photon absorption and high mass transfer rates. From literature reports, planar type is more efficient than other configurations and it is easier to scale up. Further, a small scale reactor should be modular enough to adopt different PE configurations in order to get the true or overall efficiency. At the end by considering all the pros and the cons, a modular photo electrochemical reactor design has been developed keeping in view of listed design principles.

### Design Constraints

- Light collection/absorption by the semiconductor photoanode: maximizing photon absorption per unit volume of reactor.
- Reactor design also should be suitable to be use with focused/concentrated sunlight to intensify operation of the PEC reactor.
- High mass transfer rates, to develop the optimum electrochemical efficiency i.e. Increasing the value of limiting current density
- Separation of products to prevent back reactions in order to increase overall process efficiency. Avoid explosive mixtures of  $H_2$  and  $O_2$ .
- Optimization of potential distribution in the cell to minimizes ohmic losses in the solution.
- Reactor materials need to be compatible with electrolyte solution and impervious to hydrogen penetration.
- Cost effective

### Prototype model of a PEC reactor

Reactor design mainly depends upon the Photo electrode (PE) configuration. PE configuration should have minimum overpotential loss, low recombination rate, efficient transport of charge carriers. In order to test the photo electrode materials developed by different investigators the small scale reactor should be modular enough to adopt different PE configurations in order to get the true solar to energy efficiency and the parameters affecting the overall efficiency. The developed reactor is small scale, planar type, continuous mode, having different reaction chambers separated by a membrane. This planar model is very simple to operate, flexibility to change the electrodes and easy to scale up. The front panel of the reactor is flat which ensures maximum photons to pass through the chamber. The figures below depict the exploded view of the reactor assembly.

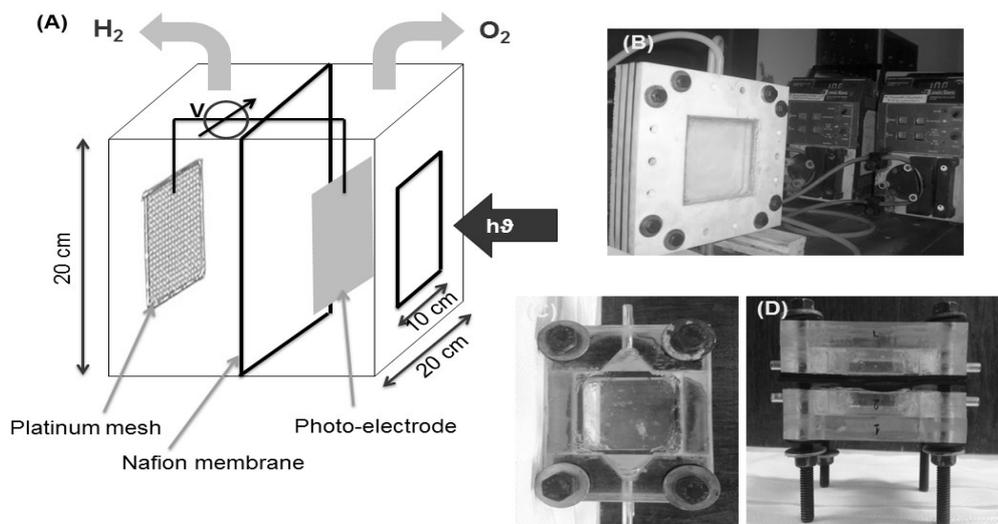


Figure 4: (A) Prototype reactor model (20cm\*20cm) (B) Fabricated photoreactor assembly (20cm\*20cm); and fabricated photoreactor assembly (10cm\*10cm) (C) front view and (D) side view

## Mechanical Design

The body structure can be made with PTFE or PVDF materials which are highly stable in both alkaline and acidic electrolyte mediums. The fabrication of square type modular construction involves 3 major parts: 1) front plate made up of quartz glass, which has optimum light transmitting properties (fixed using sealant material), 2) Nafion membrane, a high conducting proton transport barrier (placed in between two reaction chambers), 3) reaction chamber having inlet and outlet for electrolyte entry and exit. Further, the fabricated reactor can be used for both front and back ends light illumination (in case of both working and counter electrodes are photon absorbing materials).

## Future outlook and conclusion

The present target of any PEC material is to achieve a current density of 10 mA/cm<sup>2</sup> upon solar light illumination. However, with present available material design, this target is yet to be achieved. To expand the choice of the materials, we have focused on exploring native/non-native structures of materials as they provide a systematic manner for modulating the chemical coordination in the bulk, interface between two crystal phases and at the surface, which in turn will facilitate modulation of band-gap, electron-hole separation and surface electrochemistry. From practical utility of these materials, it is not enough to synthesize a material, but it is also important to attach the material to a substrate for long sustainable usage. In this context, we have suggested using 'click chemistry' to fabricate stable photoelectrodes which are found to be stable and active even under harsh conditions. Finally a prototype reactor has been designed and fabricated for scale up studies.

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# Recent Trends in Material Development for Photoelectrochemical route of Solar Hydrogen Production

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## 1. Introduction

Renewable and clean natural resources includes solar, wind, geothermal, hydro and biomass. Our energy demand mainly relies on the energy input from fossil fuels, but the fact is, this source of energy is finite and also contributing towards the climate change because of associated release of various harmful emissions into the atmosphere which in turn results in adverse and significant health, climate and environmental impacts. Solar energy is a perpetual energy source as it is vast and inexhaustible source and does not contribute to environmental issues. There is an urgent need to understand that world needs to retrofit its current energy generation source with the new alternative energy source which is inexhaustible and therefore provides long-term energy security with zero emissions.

Hydrogen is emerging as an *emission free-alternative energy carrier*. It has immense potential to fulfill our increasing energy demands. The High amount of energy is stored within the H-H bond and 1 kg of hydrogen produces energy equivalent to 2.7 kg of gasoline. On combustion, it produces H<sub>2</sub>O with release of high energy[1][36]. Solar energy induced hydrogen generation by splitting of water is an important area of research and world over researchers are trying to attain breakthrough in this technology.

The work in the area of H<sub>2</sub> generation by water splitting was pioneered by *Fujishima* and *Honda* in 1972. But the research in this area to develop an efficient semiconductor device to split water for H<sub>2</sub> generation is still progressive. Various modification techniques have been adopted to enhance the response of semiconductors in terms of stability and efficiency.

This communication attempts to discuss the research being pursued at Dayalbagh Educational Institute with special reference to the modifications being attempted to improve the efficiency of reaction.

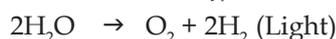
## 2. Photoelectrochemical Water Splitting Method for Hydrogen Generation

PEC technology for splitting of water into hydrogen and oxygen by the direct use of sunlight is an ideal and promising method for hydrogen production because it uses solar energy and water both of which are renewable and on combustion of H<sub>2</sub>, water is obtained as the byproduct.

This process involves solar energy collection and electrolysis of water in a single photocell. When in an aqueous electrolyte, semiconductor with the right set of properties is immersed and irradiated with sunlight, the photon energy is converted to electrical energy, which then gets further converted into chemical energy (water is broken into hydrogen and oxygen). Thus intermittent solar energy gets converted into an inherently more storable form of energy, that of chemical bonds of H<sub>2</sub>.

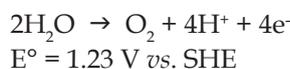
The photoelectrochemical cell has two electrodes mainly, a semiconductor (possessing either p-or n-type conductivity) as working electrode and platinum(Pt) as counter electrode. However in most measurements reference electrode is also employed to investigate half reactions in the PEC cell. When semiconductor is n-type it behaves as photoanode and oxygen is evolved, on the contrary when semiconductor is p-type it behaves as photocathode and H<sub>2</sub> is evolved on it [2].

The process is also known as *artificial photosynthesis* as the light-driven splitting of water takes place into H<sub>2</sub> and O<sub>2</sub>. This process is thermodynamically an uphill reaction with positive  $\Delta G \approx 237.2$  kJ/mol and negative  $\Delta E^\circ = -1.23$  V

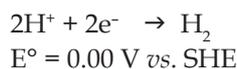


In photoelectrochemical (PEC) cell oxidation and reduction half-cell reactions takes place at two different electrodes separately, and for the reaction to proceed 1.23 V must be provided externally.

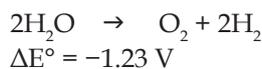
Oxidation:



Reduction:



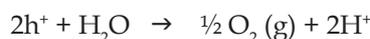
Overall:



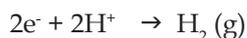
But energy losses (- 0.8 eV) associated with the recombination losses of the photogenerated charge carriers, resistance of the electrodes and electrical connections and voltage losses at the contacts etc., voltage of 1.6-2.0 eV is needed for spontaneous water splitting.

The illuminating light should have band gap equal or larger than band gap ( $E_g$ ) of the semiconductor which results in generation of electron-hole pairs. In n-type semiconductor electrode, at semiconductor surface holes react with water molecules resulting into  $O_2$  formation whereas electrons travel through substrate and then to external circuit and are transported to the counter electrode where they reduce  $H^+$  into  $H_2$ . On the contrary, p-type semiconductor electrode produces  $H_2$  and  $O_2$  at semiconductor electrode and at counter electrode respectively. The mechanism of PEC water splitting can be summarized as:

First the absorption of light near the surface of the semiconductor creates electron-hole pairs. Then holes (minority carriers) drift to the surface of the semiconductor (the photo anode) where they react with water to produce oxygen.



Electrons (majority carriers) are conducted to a metal electrode (typically Pt) where they combine with  $H^+$  ions in the electrolyte solution to make  $H_2$



Transport of  $H^+$  from the anode to the cathode through the electrolyte completes the electrochemical circuit. The overall reaction:



### 3. Semiconductor Electrode: Heart of PEC System

Photoelectrochemical hydrogen production cell performance depends upon the properties of the semiconductor. Semiconductor being photoactive absorbs light near its surface and generates electron-hole pairs. It is the governing factor for controlling efficiency of the system based on the following issues:

1. *Optimum optical function required for maximal absorption of solar energy*

Band gap of material should lie between 1.6 -2.0 eV (including thermodynamic and overpotential losses). The material should show absorption in visible light as UV portion is just the 4% of the total solar spectrum [3].

2. *Corrosion resistance and long-term stability in aqueous electrolyte*

The stability limits the usefulness of many photo-active materials as non-oxide semiconductors, such as Si, GaAs, GaP, CdS, etc., prevents electron transfer across the semiconductor/electrolyte interface either by their dissolution or forming a thin oxide film. Apart from this

all metal oxide photo-anodes are thermodynamically unstable, as the photo-generated holes oxidises the semiconductor [4].

3. *Band edges of semiconductor must straddle  $H_2O$  redox potentials*

For p- type photocathode- conduction band minimum (CBM) should be higher (more negative in potential) than the water reduction potential ( $H^+/H_2$ ) likewise for n-type photoanode valence band maximum (VBM), lower (more positive in potential) than the water oxidation potential ( $O_2/H_2O$ ) [5].

4. *Life time of charge carriers should be large*

The light absorption in space charge region and distance travelled by electron and holes (called as diffusion length) before recombination in semiconductor contribute to photoresponse. This diffusion length should be comparable or larger than thickness of the film which increases the lifetime of charge carriers. The photogenerated charge carriers should be separated before the recombination [2].

### 4. Requirements to Make PEC Technology Commercially Viable

Efficiency of 12.4% with p-/n-GaAs photoanode and aGaInP<sub>2</sub> photocathode and over 18% for a multijunction cell have been achieved but these systems don't perform well as they undergo photocorrosion [6].

To generate  $H_2$  at commercial level using photoelectrochemical water splitting technology, the system should achieve the following goals [7].

- ✓ Durability > 2000h
- ✓ Low cost of manufacturing and ease of maintenance
- ✓ Conversion efficiency, solar to hydrogen (STH) > 10%
- ✓ Current Density ( $J_{ph}$ ) = 10-15 mA/cm<sup>2</sup>

The scientific communities world over is searching to develop a semiconductor with all above desired characteristics but this is still an elusive goal to get an efficient and stable material.

High band gap materials show poor harvesting and absorb in UV but show high stability in aqueous electrolyte, e.g.:  $TiO_2$ ,  $WO_3$ ,  $SrTiO_3$ ,  $BaTiO_3$ ,  $SnO_2$ ,  $ZnO$  while low band gap materials are good harvesters but show poor stability in aqueous electrolyte, e.g.: Si, GaAs, InP, CdTe, CdSe, CuO. Optimal band gap semiconductor is  $Cu_2O$  which absorb in visible light but show photocorrosion.  $Fe_2O_3$  is an intermediate band gap semiconductor material which absorbs the visible light but offers redox level mismatch,

low mobility of holes and trapping of electrons by oxygen-deficient iron sites [2].

## 5. Modification Strategies Adopted for Improving Material Performance

The group at DEI, Agra is focusing on various emerging areas in field of PEC water splitting for H<sub>2</sub> generation to develop an efficient and stable semiconductor by various technologies. The extensive studies have been performed to get understanding on the effect of various modifications. All the reported work have been justified and supported by various characterization techniques such as XRD (x-ray diffractometer), UV-Visible spectroscopy, SEM (Scanning Electron Microscopy), AFM (Atomic Force Microscopy), TEM (Tunneling Electron Microscopy), EDX (Energy Dispersive X-ray Spectroscopy), Raman, XPS (X-ray Photoelectron Spectroscopy), Mott-Schottky analysis, I-V (Current-Voltage) characterization, efficiency measurement with ABPE (Applied Bias to Current Conversion Efficiency) and IPCE (Incident Photon To Current Conversion Efficiency).

Various modification strategies have been adopted to improve the material performance by various researchers. Brief description of the modifications being attempted by the group at DEI, Dayalbagh, Agra are summarized below.

### Doping

Doping is the process of introducing impurities into the material to modify its electrical and optical properties. This method is useful in shifting the absorption of wide band gap material towards visible region. Doping results in reduced/minimal electron-hole recombination.

Upadhyay et al (2011 & 2014) studied Ag doped Cu<sub>2</sub>O and Fe doped BaTiO<sub>3</sub> and computational results obtained through first-principles Density Functional Theory were

validated by experimental results.

The results obtained in various study for maximum photoresponse giving material are given below:

### Bilayered System

Bilayered system is one of the best strategy to achieve good performing material in terms of PEC response. The system combines properties of two semiconductors (one with a wide band gap and other with a small/mid bandgap). For small band gap semiconductor to sensitize the large band gap semiconductor through efficient electron or hole injection by visible light absorption both should have proper positioning of conduction and valence bands. Transfer of electrons enhance charge separation and reduces recombination by forming a potential gradient at the interface. The bilayered system covers broad visible spectrum and thereby facilitates enhanced photocurrent and improved photoconversion efficiency.

The heterojunction of SrTiO<sub>3</sub>/Cu<sub>2</sub>O heterojunction systems was studied by Sharma et al (2014). The variation adopted was varying thickness of Cu<sub>2</sub>O over SrTiO<sub>3</sub> and the photoresponse was 34 times higher than pristine SrTiO<sub>3</sub>. Likewise Surbhi et al (2013) investigated the CuO/SrTiO<sub>3</sub> system and photoresponse was eight times higher than that for CuO and 30 times higher than that for pristine SrTiO<sub>3</sub>. Improved photoresponse was attributed to improved conductivity and separation of the photogenerated charge carriers at the interface and higher value of flatband potential.

The summary of the various systems investigated is given below:

### Swift Heavy Ion Irradiation

Swift heavy ions (SHI) create variety of defect states in the material. The energetic ions interact with the material

Systems Investigated	Method of preparation	Current Obtained (mA/cm <sup>2</sup> )	Applied Bias (V/SCE)
1 at. % Ag doped Cu <sub>2</sub> O [8]	Spray Pyrolysis	2.34	0.80
1.0 at% Cd doped TiO <sub>2</sub> [9]	Sol-Gel	0.8	0.8
1 at% Cu doped ZnO [10]	Sol-Gel	0.7	0
0.2 at% Fe doped TiO <sub>2</sub> [11]	Sol-Gel	0.92	0
2 at% Fe doped BaTiO <sub>3</sub> [12]	Polymeric Precursor Route	2.55	0.5
0.02 M Ti doped Fe <sub>2</sub> O <sub>3</sub> [13]	Spray Pyrolysis	1.98	0.5
5 at. % Zn doped Fe <sub>2</sub> O <sub>3</sub> [14]	Spray Pyrolysis	0.64	0.7
2 at. % Zr doped Fe <sub>2</sub> O <sub>3</sub> [15]	Electrodeposition	2.1	0.6
1 at. % Ag doped ZnO [16]	Electrodeposition	0.81	0
5 at % Ni doped Cr-ZnO [17]	Sol-gel method	1.18	0.5

Systems Investigated	Method of preparation	Current Obtained (mA/cm <sup>2</sup> )	Applied Bias (V/SCE)
SrTiO <sub>3</sub> /Cu <sub>2</sub> O [18]	Sol-gel & Spray Pyrolysis	2.44	0.95
CuO/SrTiO <sub>3</sub> [19]	Sol-gel	1.85	0.90
Fe-TiO <sub>2</sub> /Zn-Fe <sub>2</sub> O <sub>3</sub> [20]	Sol-gel & Spray Pyrolysis	1.65	0.90
α-Fe <sub>2</sub> O <sub>3</sub> /Cu <sub>2</sub> O [21]	Spray Pyrolysis	0.32	0.8

by losing energy and therefore modify the material properties. Depending upon ion energy, fluence and ion species these energetic beams can induce structural and morphological changes in the form of grain fragmentation or defects. Such modification alters the properties such as band gap, resistance and structural defects, which are expected to modify the photoelectrochemical response of the material. Our group has investigated various materials by irradiating ions at various fluences by different ions at the Inter University Accelerator Centre (IUAC, New Delhi). The results of reported work are summarized here as:

The increased response of two to ten folds in the entire study was attributed to the lower resistivity, maximum flatband potential, improved optical absorption capability, increased roughness, and decrease in the average grain diameter for the material giving highest photoelectrochemical response.

### Surface Modification

The group has worked to modify the surface by decorating it with Zn dots on Fe<sub>2</sub>O<sub>3</sub> surface. Zn dots were deposited using thermal evaporation technique. The optimum size of Zn dots of around 23 nm showed best photoresponse with photocurrent density of 1.28 mA/cm<sup>2</sup> at 0.7V/SCE [32]. The surface sensitization by CdSe quantum dot on alpha-Fe<sub>2</sub>O<sub>3</sub> deposited by electrodeposition showed photocurrent of 1.14 mA/cm<sup>2</sup> at 0.8V/SCE [33] and 0.55 mA/cm<sup>2</sup> for nanoporous Fe<sub>2</sub>O<sub>3</sub> deposited by spray pyrolysis [34].

The work is also under study by decorating the surface with plasmons with noble metal nanoparticles. The surface etching studies using various acids has also been performed to understand the altered photoresponse of the material.

Systems Investigated	Method of preparation	Ion/ Energy/ Fluence	Current Obtained (mA/cm <sup>2</sup> )	Applied Bias (V/SCE)
2% Cr- Fe <sub>2</sub> O <sub>3</sub> [22]	Spray Pyrolysis	170MeVAu <sup>13+</sup> 10 <sup>12</sup> ions/cm <sup>2</sup>	2.5	0.95
Fe <sub>2</sub> O <sub>3</sub> [23]	Spray Pyrolysis	120MeVAg <sup>9+</sup> 10 <sup>13</sup> ions/cm <sup>2</sup>	0.32	0.95
Fe <sub>2</sub> O <sub>3</sub> [24]	Spray Pyrolysis	100MeVSi <sup>7+</sup> 2 x 10 <sup>13</sup> ions/cm <sup>2</sup>	0.36	0.95
Fe <sub>2</sub> O <sub>3</sub> [25]	Electrodeposition	100 MeV Si <sup>8+</sup> 5x10 <sup>12</sup> ions/cm <sup>2</sup>	3.0	0.75
CuO [26]	Spray Pyrolysis	170 MeVAu <sup>13+</sup> 10 <sup>13</sup> ions/cm <sup>2</sup>	1.04	0.3
BaTiO <sub>3</sub> [27]	Sol-Gel	100 MeVSi <sup>8+</sup> 5 x 10 <sup>11</sup> ions/cm <sup>2</sup>	0.7	0.4
BaTiO <sub>3</sub> [28]	Sol-Gel	120 MeVAg <sup>9+</sup> 10 <sup>11</sup> ions/cm <sup>2</sup>	1.78	0.4
SrTiO <sub>3</sub> [29]	Sol-Gel	120 MeVAg <sup>9+</sup> 3x10 <sup>12</sup> ions/cm <sup>2</sup>	0.16	0
TiO <sub>2</sub> [30]	Sol-Gel	120 MeVAg <sup>9+</sup> 5x10 <sup>11</sup> ions/cm <sup>2</sup>	0.76	0
ZnO [31]	Sol-Gel	120 MeVAg <sup>9+</sup> 3x10 <sup>12</sup> ions/cm <sup>2</sup>	0.0011	0

## Composite System

Iron oxide photoanodes were modified by graphene nanoplates ( $\text{Fe}_2\text{O}_3$ -GNP) which acted as conducting scaffolds in photoelectrochemical (PEC) cell for hydrogen generation. The enhanced photoresponse was obtained which may be due to the increased charge transfer at junction of semiconductor/electrolyte and red - shift in the UV-vis spectra of the composite. Photocurrent density of  $2.5 \text{ mA/cm}^2$  at  $0.75 \text{ V/SCE}$  was observed for the  $0.2 \text{ wt\%}$  GNP modified  $\alpha\text{-Fe}_2\text{O}_3$  [35].

## Bioinspired Materials

Taking inspiration from natural photosynthesis, PEC can be called as “*Artificial Photosynthesis*” where the photons absorbed from solar spectrum by a semiconductor material is used to split water molecule to produce hydrogen and oxygen as a by product. Semiconductor material behaves like an *artificial leaf* where the whole reaction process takes place.

The group at DEI is also developing biologically inspired methods and materials that can be presented as new tools for the design of novel photoelectrochemically active materials. Bioinspired materials are the novel materials which mimic the functional trick (minimal structure required for a catalyst to achieve the biological function) of an active site which are responsible for carrying out oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Such molecules under study include Phycocyanins, Hydrogenase mimic etc.

## 6. Conclusions

Various group of researchers both at national and international level are working in this exciting area of PEC splitting of water for hydrogen generation with the objective to modify and develop the material system which can split water efficiently and economically. While a lot has been learnt and done in the past more than 3 decades success appears to be at some distance which all of us hope to achieve shortly with hard sustained work.

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