Absorption and Desorption Of Hydrogen in Metal Hydrides

By

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AMIN ABDELKHALIQ EL AMIN MOHAMED

ABSTRACT

Hydrogen storage is a significant challenge for the development and viability of hydrogen mobile and stationary applications. Current hydrogen storage approaches involve compressed hydrogen gas tanks, liquid hydrogen tanks, cryogenic compressed hydrogen, metal hydrides, high-surface-area adsorbents, and chemical hydrogen storage materials.

Storage as a gas or liquid or storage in metal hydrides or high-surface-area adsorbents constitutes "reversible" on-board hydrogen storage systems because hydrogen regeneration or refill can take place on-board the vehicle. For chemical hydrogen storage approaches (such as a chemical reaction on-board the vehicle to produce hydrogen), hydrogen regeneration is not possible on-board the vehicle; and thus, these spent materials must be removed from the vehicle and regenerated off-board.

Storage of hydrogen in metal hydrides has a drawback of a heavy absorbent material, but the advantage of a smaller pressure and less safety precautions.

Thus, the objective of the project is to study the thermodynamics and kinetics of hydrogen storage in metal hydrides with minimum loss of energy and at low cost, for affordability for mobile applications.

ACKNOWLEDGMENT

In the name of God the most merciful, the compassionate. I would like to take this opportunity to thank all the people who have given help, support and encouragement to me during my Final Year Project.

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INTRODUCTION

1.1 Background of study

It is widely believed that hydrogen will within a few tens of years become the fuel that powers most vehicles and portable devices, i.e. hydrogen will become the means of storing and transporting energy. The reason is the depletion of oil and the relatively facile production of hydrogen from the various renewable sources of energy - hydroelectric, wind, solar, geothermal - with water being the only raw material needed. To release the energy, hydrogen can be burned in an efficient and clean way in a fuel cell to form water again, or made to drive an electrochemical cell as in the commonly used nickel-hydride battery. As concerns over air pollution and global warming increase, the incentive to switch to clean and efficient hydrogen economy becomes greater and the transition may occur well before oil reserves are depleted (after all, Stone Age did not end because mankind ran out of stones!). This development is of particular interest to people living in Iceland, a country rich in renewable energy resources but poor in raw materials. It seems imperative that Icelanders follow closely the advances in hydrogen technology and, preferably, move to a front-line position and contribute to the development.

Metal hydride technology uses metals and metal alloys to adsorb hydrogen under moderate pressure and temperature, creating hydrides. A metal hydride tank contains a granular metal, which adsorbs hydrogen and releases it with the application of heat. The heat may be supplied as excess heat from a fuel cell. Conventional high capacity metal hydrides require high temperatures (300°-350°C) to liberate hydrogen, but sufficient heat is not generally available in fuel cell transportation applications.

The project title is "Absorption and desorption of hydrogen in metal hydrides". Metal hydrides have the potential for reversible on-board hydrogen storage and release at low temperatures and pressures. This is based on using the waste heat to release the hydrogen from the storage medium.

- **Absorption.** In absorptive hydrogen storage, hydrogen is absorbed directly into the bulk of the material. In simple crystalline metal hydrides, this absorption occurs by the incorporation of atomic hydrogen into interstitial sites in the crystallographic lattice structure.
- **Desorption.** When the hydrogen is released from or through the surface of the hydrides.

One of the major issues with complex metal hydride materials, due to the reaction enthalpies involved, is thermal management during refueling. Depending on the amount of hydrogen stored and refueling time required, megawatts to half a GIGAWATT must be handled during recharging on-board vehicular systems with metal hydrides. Reversibility of these and new materials also needs to be demonstrated for over a thousand cycles.

Metal hydrides, like $NaAlH_4$, $LaNi_5H_6$ and $TiFeH_2$, with varying degrees of efficiency, can be used as a storage medium for hydrogen. Some are easy-to-fuel liquids at ambient temperature and pressure; others are solids which could be turned into pellets. Proposed hydrides for use in a hydrogen economy include simple hydrides of magnesium or transition metals and complex metal hydrides, typically containing sodium, lithium and aluminium or boron. These materials have good energy density by volume, although their energy density by weight is often worse than the leading hydrocarbon fuels.

Solid hydride storage is a leading contender for automotive storage. A hydride tank is about three times larger and four times heavier than a gasoline tank holding the same energy. Lithium, the primary constituent by weight of a hydride storage vessel, currently costs over \$40 a pound (\$90/kg). Any hydride will need to be recycled or recharged with hydrogen, either on board the automobile or at a recycling plant. A metal-oxide fuel cell, (i.e. zinc-air fuel cell or lithium-air fuel cell), may provide a better use for the added weight, than a hydrogen fuel cell with a metal hydride storage tank.

Often hydrides react by combusting rather violently upon exposure to moist air, and are quite toxic to humans in contact with the skin or eyes, hence cumbersome to handle. For this reason, such fuels, despite being proposed and vigorously researched by the space launch industry, have never been used in any actual launch vehicle.

Few hydrides provide low reactivity (high safety) and high hydrogen storage densities (above 10% by weight). Leading candidates are sodium borohydride, lithium aluminium hydride and ammonia borane. Sodium borohydride and ammonia borane can be stored as a liquid when mixed with water, but must be stored at very high concentrations to produce desirable hydrogen densities, thus requiring complicated water recycling systems in a fuel cell. As a liquid, sodium borohydride provides the advantage of being able to react directly in a fuel cell, allowing the production of cheaper, more efficient and more powerful fuels cells that do not need platinum catalysts.

Recycling sodium borohydride is energy expensive and would require recycling plants. More energy efficient means of recycling sodium borohydride are still experimental. Recycling ammonia borane by any means is still experimental.

Hydrogen produced for metal hydride storage must be of a high purity. Contaminants alter the nascent hydride surface and prevent absorption.

1.2 Problem Statement

Study of the processes in the absorption and desorption of hydrogen in various metal hydrides used for hydrogen storage and transportation and identify the thermodynamic properties and the kinetic of the process.

While hydrogen has many obvious advantages, there remains a problem with storage and transportation. For transportation, the overarching technical challenge for hydrogen storage is how to store the amount of hydrogen required for a conventional driving range within the vehicular constraints of weight, volume, efficiency, safety, and cost. Durability over the performance lifetime of these systems must also be verified and validated, and acceptable refueling times must be achieved. Requirements for off-board bulk storage are generally less restrictive than on-board requirements; for example, there may be no or less-restrictive weight requirements, but there may be volume or "footprint" requirements. The key challenges include:

- **Weight and Volume.** The weight and volume of hydrogen storage systems are presently too high, resulting in inadequate vehicle range compared to conventional petroleum fueled vehicles.
- **Efficiency.** Energy efficiency is a challenge for all hydrogen storage approaches. The energy required to get hydrogen in and out is an issue for reversible solid-state materials. Life-cycle energy efficiency is a challenge for chemical hydride storage in which the byproduct is regenerated off-board. In addition, the energy associated with compression and liquefaction must be considered for compressed and liquid hydrogen technologies.
- **Durability.** Durability of hydrogen storage systems is inadequate. Materials and components are needed that allow hydrogen storage systems with a lifetime of 1500 cycles.
- **Refueling Time.** Refueling times are too long. There is a need to develop hydrogen storage systems with refueling times of less than three minutes over the lifetime of the system.

- **Cost.** The cost of on-board hydrogen storage systems is too high, particularly in comparison with conventional storage systems for petroleum fuels. Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost, high-volume manufacturing methods.

1.3 Objective and scope of study

To investigate the thermodynamics and the kinetic properties of absorption and desorption of hydrogen in metal hydrides. By reducing the particle size, the thermodynamic properties of material may be changed to a point where surface free energy can govern the reaction. Kinetics refers to the rates of hydrogen absorption and desorption. The kinetics of both absorption and desorption can be improved by an order of magnitude simply by reducing the grain size of the metal.

CHAPTER 2

LITERATURE REVIEW

- Hydrogen storage for mobile applications
- The ability of metal hydrides to store hydrogen
- The thermodynamic of the process
- Fuel Cell
- Van't Hoff Equation
- Rate Equation

2.1 Hydrogen Storage for Mobile Applications

Many scientists and engineers, some companies, governmental and non-governmental agencies and even finance institutions are convinced that hydrogen's physical and chemical advantages will make it an important synthetic fuel in the future. After the successful use of hydrogen for space technology, national hydrogen associations were created and joint ventures started. Examples are fuel-cell development projects, the International Hydrogen Energy Association and its technical-economic conferences, and solar hydrogen R&D programs. But are these ventures aimed at mobility?

There are essentially two ways to run a road vehicle on hydrogen. In the first, hydrogen in an internal combustion engine is burnt rapidly with oxygen from air. The efficiency of the transformation from chemical to mechanical through thermal energy is limited by the Carnot efficiency and is slightly higher for hydrogen–air mixtures (around 25%) than for petrol–air mixtures. When a lean mixture is used, the exhaust gas contains nothing but water vapor; richer mixtures also produce NO_x.

In the second method, hydrogen is 'burnt' electrochemically with oxygen from air in a fuel cell, which produces electricity (and heat) and drives an electric engine. Here, the efficiency of the direct process of electron transfer from oxygen to hydrogen is not limited by the Carnot efficiency; it can reach 50–60%, twice as much as the thermal process.

For on-board energy storage, vehicles need compact, light, safe and affordable containment. A modern, commercially available car optimized for mobility and not prestige with a range of 400 km burns about 24 kg of petrol in a combustion engine; to cover the same range, 8 kg hydrogen are needed for the combustion engine version or 4 kg hydrogen for an electric car with a fuel cell.

Hydrogen is a molecular gas. At room temperature and atmospheric pressure, 4 kg of hydrogen occupies a volume of 45 m^3. This corresponds to a balloon of 5 m diameter hardly a practical solution for a vehicle. In the following we will focus on the question of compacting hydrogen, looking at the materials, technology and safety aspects (Figure 1) [1].

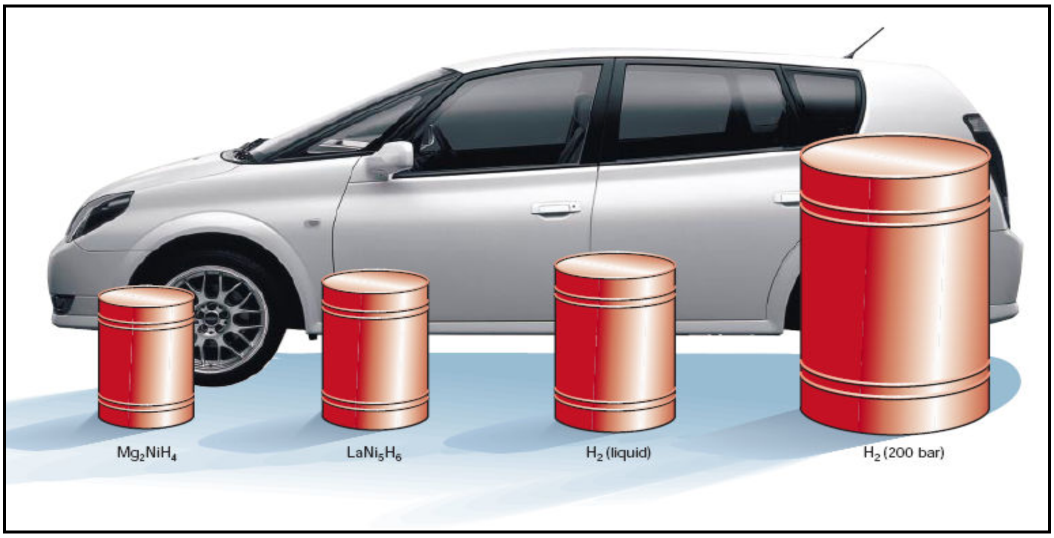


Figure 1: Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car

Table 1 below shows the properties of hydrogen, methane and petrol.

Table 1: Physical and chemical properties of hydrogen, methane and petrol

Physical and chemical properties of hydrogen, methane and petrol			
Properties	Hydrogen (H_2)	Methane (CH_4)	Petrol (–CH_2–)
Lower heating value (kWh kg^{-1})	33.33	13.9	12.4
Self-ignition temperature (^{o}C)	585	540	228–501
Flame temperature (^{o}C)	2,045	1875	2,200
Ignition limits in air (Vol%)	4–75	5.3–15	1.0–7.6
Minimal ignition energy (mW s)	0.02	0.29	0.24
Flame propagation in air (m s–^{1})	2.65	0.4	0.4
Diffusion coefficient in air (cm^{2} s^{-1})	0.61	0.16	0.05
Toxicity	No	No	High

2.2 The ability of metal hydrides to store hydrogen

Metal hydrides are powders whose particles are typically a few microns in size. When these metal powders absorb hydrogen to form hydrides, heat is released. Conversely, when heat is absorbed, hydrogen is released from the hydride.

In the absorption process, hydrogen gas molecules break down into hydrogen atoms and penetrate into the interior of the metal crystal to form a metal hydride. In the desorption process, hydrogen atoms migrate to the surface of the metal hydride, combine into hydrogen molecules and flow away as hydrogen gas, allowing the material to form the original metal structure

Many metals and alloys are capable of reversibly absorbing large amounts of hydrogen according to the reaction:

$$Me + x/2\ H_2 \ \square\ MeH_x$$

Here Me is a metal, a solid solution, or an intermetallic compound, MeH_x is the hydride and x the ratio of hydrogen to metal H/Me. In most, cases the reaction is exothermic and reversible. If we applied heat hydrogen is desorbed again.

Charging can be done using molecular hydrogen gas or hydrogen atoms from an electrolyte. If hydrogen is loaded from gas phase several reaction stages of hydrogen with metal occurred as it showed in the figure.

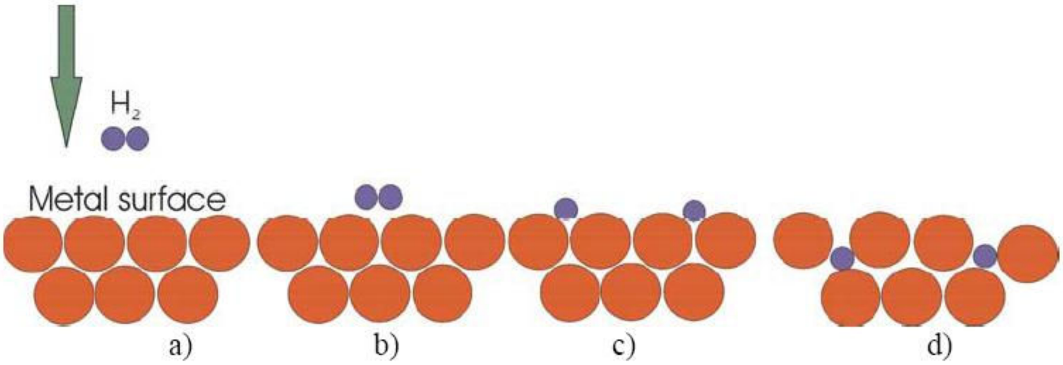


Figure 2: Reaction of H_2 molecule with a storage material

Today, the annual consumption of hydrogen in the United States alone is more than 90 billion m^3, mostly in refineries and chemical plants where it is produced. For such an application, storage has not been critical. However, for fuel usage in vehicles, storage has been the main technical challenge. Present storage techniques for hydrogen include compressed gas, cryogenic liquid, and absorption on solids. This part deals with the hydrogen storage using solid metal hydrides [2, 3]. For optimum hydrogen storage, the metal should have following desirable properties:

- High hydrogen capacity per unit mass and unit volume
- Low dissociation temperature
- Moderate dissociation pressure
- Low heat of formation to minimize the energy necessary for hydrogen release and
- low heat dissipation during the exothermic hydride formation
- Reversibility for limited energy loss during charge and discharge of hydrogen
- Fast kinetics
- High stability against O_2 and moisture for a long cycle life
- Cycle-ability
- Low cost of recycling and charging infrastructures and high safety

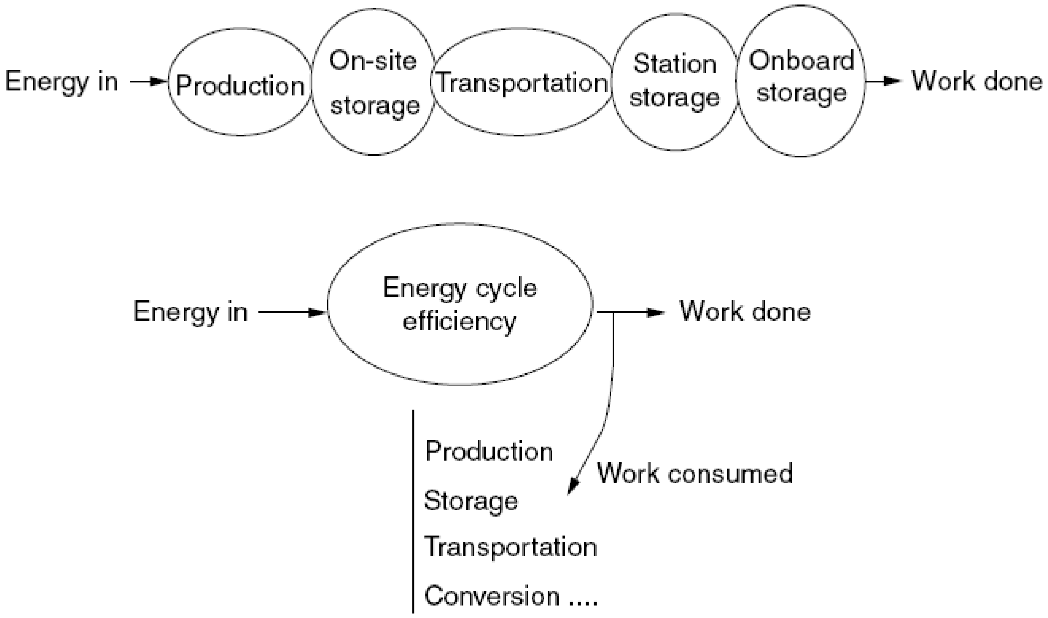


Figure 3: Importance of Hydrogen Storage

Current metal hydrides, suitable for automotive applications, typically store 0.5–2 wt% hydrogen [4]. Hydrides release heat when charged with pressurized hydrogen, and absorb heat to release hydrogen. More than 50 metallic elements of the periodic table can absorb hydrogen in good quantities; hence, the possible choices of hydride materials are enormous.

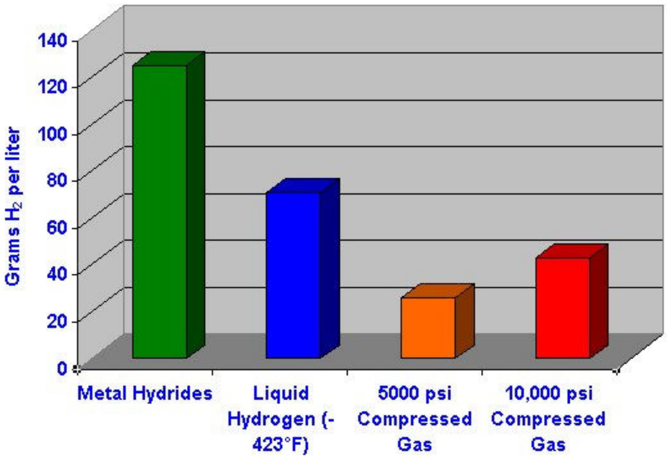


Figure 4: Capacity of metal hydrides to store H_2

But, only some of them are suitable for hydrogen storage at moderate temperatures and pressures. Practically, the temperature should not go above 100°C and below 10°C during charging and discharging, respectively. The choice is further narrowed by the need for a moderate charging pressure and a suitable discharging pressure [5].

Metal hydrides have a large capacity to store hydrogen compared to the other types of hydrogen storage techniques (Figure 4).

Hydrides such as MgH_2 are known as high hydrogen containing materials, it contains 7.66% by weight of hydrogen (Figure 5).

At 300°C decomposes to produce H_2 at 1 bar pressure, the high temperature required is seen as a limitation in the use of MgH_2 as a reversible hydrogen storage medium.

$MgH_2 \rightarrow Mg + H_2$

Its potential as a reversible "storage" medium for hydrogen has led to interest in improving the hydrogenation and dehydrogenation reaction kinetics.

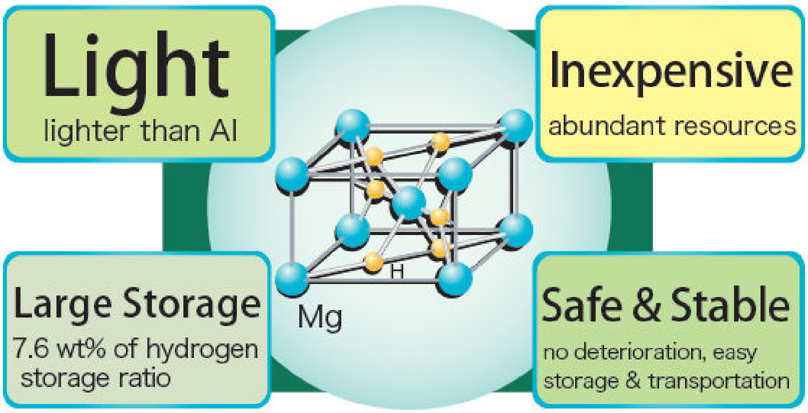


Figure 5: Advantages of MgH_2

2.3 The thermodynamics of the process

By reducing the particle size, the thermodynamic properties of material may be changed to a point where surface free energy can govern the reaction. For example, the improvement in the sorption properties of metal hydrides can be achieved by ball milling. Nanostructures metal hydrides address one of the key problems of hydrogen sorption kinetics: the diffusion of hydrogen within the metal leading to the formation of the hydride. Although the detailed mechanism of hydrogen diffusion in nanostructures metals needs to be in practically all metal hydrides, the kinetics of both absorption and desorption can be improved by an order of magnitude simply by reducing the grain size of the metal [6]. Figure 5 shows how the hydrogen molecules interact with the solid metal molecules

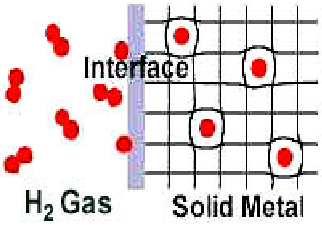


Figure 6: Interaction of H_2 molecules

Nanocomposites, where both nanostructure and nanocatalysis can be incorporated into a more complex system, are the next step in designing high-performance metal hydrides. The key feature of such nanocomposites is that the metal hydrides are intermixed on the nanoscale in such a way that they preserve their basic thermodynamic characteristics, but at the same time interact [7].

In order to maintain a low weight and volume of hydride, it is critical to maintain short cycle times for charging and discharging hydrogen. Heat transfer is the rate limiting process that controls hydrogen uptake or removal and is determined by the effective conductivity of the hydride bed. The dynamic response of a hydrogen storage system is important in the design of metal hydride based energy conversion. Hence it is necessary to predict transient heat and mass transfer in the metal hydride bed [8].

However, it is known that absorption and desorption of hydrogen are limited by the thermal conductivity of the metal hydride bed [9]. The effective thermal conductivity is a function of the conductivity of the hydride metal and interstitial hydrogen gas. The conductivity of hydrogen and its interstitial volume concentration are essentially constant. But the conductivity of hydride metal varies as a function of the concentration of the chemisorbed hydrogen. This means that the effective conductivity changes during the process.

The law of heat conduction, also known as Fourier's law, states that the rate, in time, of heat transfer through a material is proportional to the negative gradient in the temperature and to the area at right angles, to that gradient, through which the heat is flowing:

Fourier’s Law: $q \alpha K A \frac{\Delta T}{L}$

Based on Fourier’s law in the factors affecting the hydrogen absorption and desorption are:

1. Surface area (A)
2. Temperature Difference (ΔT)
3. Thermal conductivity (K)
4. Diffusion depth

- **Thermal Conductivity**

The thermal conductivity of a substance is defined as the heat flow per unit area per unit time when the temperature decreases by one degree in unit distance.
The change in the heat transfer rate causes the rates of storage/discharge of hydrogen to vary. The effective property of the powder bed can be measured, but modeling of the absorption/desorption times is complicated by the fact that the thermal conductivity of the hydride metal cannot be determined independently by experiment. The problem then is to devise suitable methods to calculate the variation in the hydride particle thermal conductivity as a function of the hydrogen concentration from the experimentally obtained effective conductivity of the powder [10].

Provides an indication of the rate at which energy is transferred by the diffusion process. It depends on the physical structure of matter, atomic and molecular, which is related to the state of the matter.

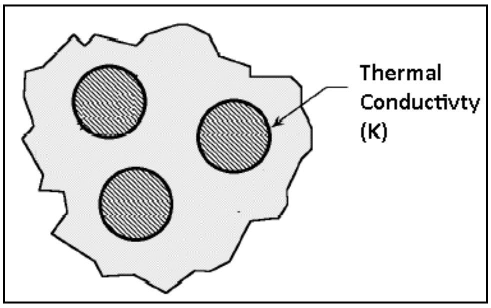


Figure 7: Thermal Conductivity

Raghavan and Martin [12] considered one-dimensional heat flow in a unit cube and showed that the Ohm’s law approach can be reconciled with the multidimensional field solution of Maxwell, by modeling the field distortions by means of distortions of the geometry. The ease of application of the unit cell and the exactness of approach of the field calculation are combined in this manner.

The effective resistance of the unit cube can be calculated by using either the parallel isotherms or parallel heat flow lines. The height 'h' of the inclusions shown in these figures is a quantity that can be varied or 'distorted' in accordance with all the factors that would cause a change in the effective conductivity of the medium. The result for equivalence of Ohm's law approach and Maxwell's approach is expressed by the remarkably simple relation:

$$h = \frac{3c}{2 + c}$$

This value of 'h' will be termed $h_{Maxwell}$. In the real material of finite concentration, the following formula applies as shown by Raghavan and Martin [12]:

$$K = 1 + \frac{c}{\frac{\alpha}{\alpha - 1} - h \times F}$$

Where F is a modifying function that accounts for the geometric distortions equivalent to the distortions in isotherms and heat flow lines.

$$F = 1 + \beta c(1 - c)[\frac{3Ao(1 - c)}{2 + A1c}]$$

Where α represent the ratio of conductivities, $\alpha = k_{MH}/ k_{H2}$, and $= \frac{\alpha - 1}{\alpha + 2}$.

It will have a value equal to unity when concentration tends to zero as in Maxwell's model.

The 'h' versus 'c' plot (Figure 8) is a useful new tool for the analysis not only of thermal conductivity models but models of transport properties in general. With only the assumption of macroscopic homogeneity and isotropy, the new approach described here leads to a simple and physically illustrative formula for calculating the conductivity of two-phase dispersions.

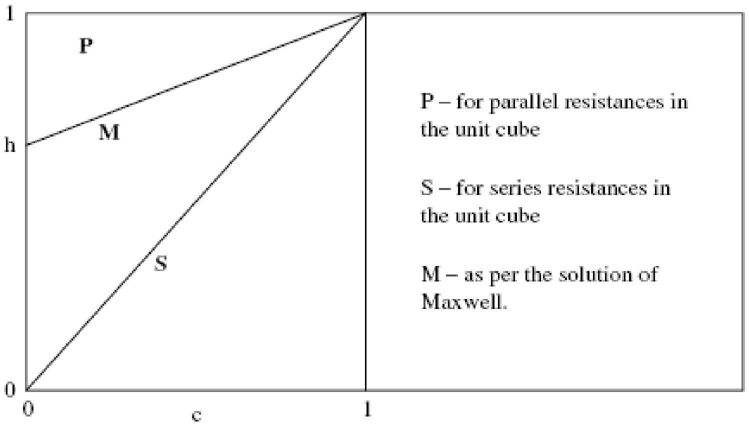


Figure 8: Dimensionless height ‘h’ as a function of volume

The thermal conductivity of hydrogen is lower than the thermal conductivity of metal hydride, i.e. the value of α is >1. For this ratio of a, the effective conductivity of metal hydride goes up as the concentration of hydrogen increases (Figure 9).

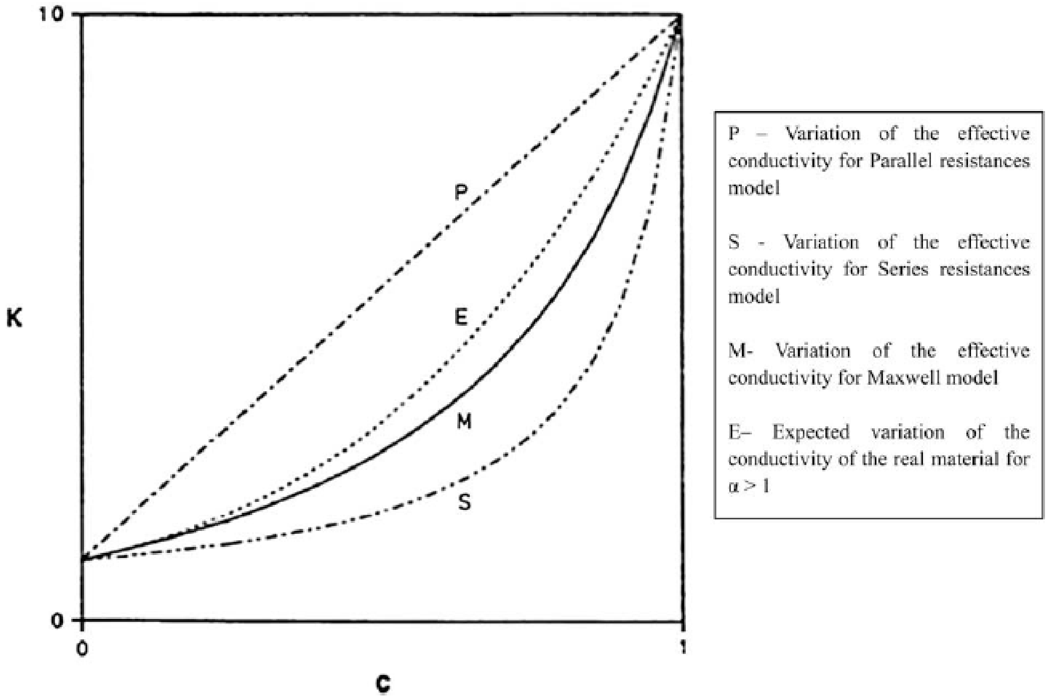


Figure 9: Conductivity K as a function of c for α=10

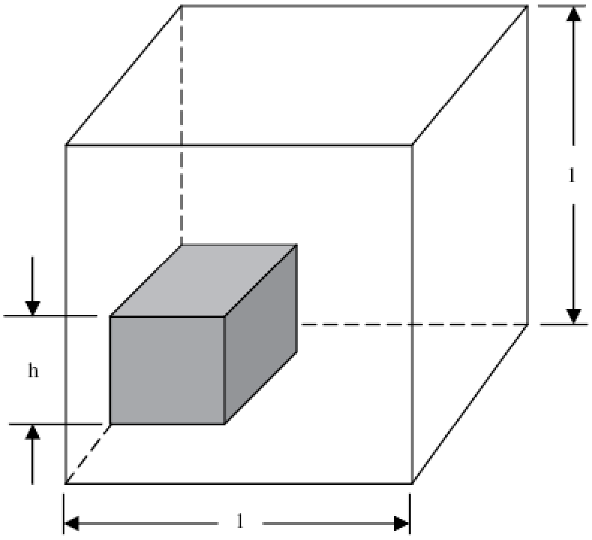


Figure 10: Schematic of the unit cube showing the height 'h'

Many studies have been made on the method of estimation of the effective conductivity of packed beds, but only a little information is available either on experimental data or on the estimating method for metal hydrides.

2.4 Fuel Cell

A fuel cell is an electrochemical cell that produces electricity from a fuel tank. The electricity is generated through the reaction, triggered in the presence of an electrolyte, between the fuel (on the anode side) and an oxidant (on the cathode side). The reactants flow into the cell, and the reaction products flow out of it, while the electrolyte remains within it. Fuel cells can operate virtually continuously as long as the necessary flows are maintained [14].

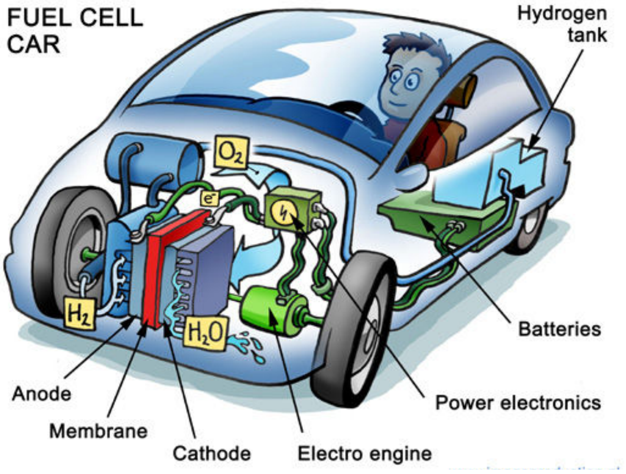


Figure 11: Configuration of components of fuel car cell

Instead of hydrogen combustion to produce the motive force to run the engine, the fuel cell that converts chemical energy of hydrogen directly to electrical energy to drive the car, is the preferred choice. Another advantage is that the conversion efficiency of a fuel cell is higher as energy generation in a fuel cell is not limited by the Carnot efficiency. Fuel cells can be powered by hydrogen–oxygen, hydrogen– air, and methane–oxygen or methane–air combinations. The highest efficiency is obtained from hydrogen fuel. Hence, solutions need to be found for carrying hydrogen in the automobile. One way is to liquefy hydrogen and fill up high-pressure cylinders with it, allowing the cylinder pressure to increase tremendously as it reaches ambient temperature.

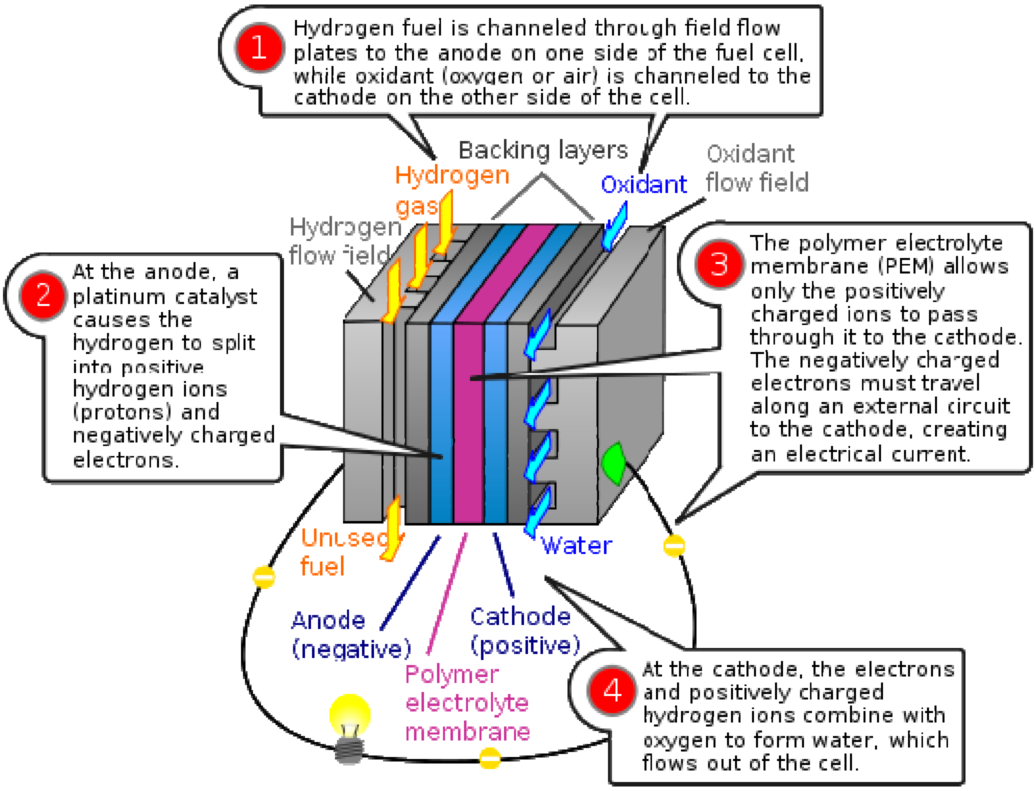


Figure 12: Proton Exchange Membrane Fuel Cell

A second, more practical method is to carry the hydrogen in the form of metal hydride at normal pressures and temperatures. The design of such a system and prediction of storage and discharge times in it requires knowledge of the thermo-physical properties of metal hydride and their variation with hydrogen content in the discrete particles [13] Fuel cells are very useful as power sources in remote locations, such as spacecraft, remote weather stations, large parks, rural locations, and in certain military applications. A fuel cell system running on hydrogen can be compact and lightweight, and have no major moving parts. Because fuel cells have no moving parts and do not involve combustion, in ideal conditions they can achieve up to 99.9999% reliability. This equates to around one minute of down time in a two year period [14].

Metal hydride fuel cells are a subclass of alkaline fuel cells that are currently in the research and development phase. A notable feature is their ability to chemically bond and store hydrogen within the cell. This feature is shared with direct borohydride fuel cells, although the two differ in that MHFCs are refueled with pure hydrogen. Though the absorption characteristics of metal hydrides (around 2%) is far lower than sodium-borohydrides and other "light" metal hydrides (around 10,8%), prototypes have been claimed to demonstrate a number of interesting characteristics:

- Ability to be recharged with electrical energy
- Low operating temperatures (down to -20°C)
- Fast kinetics
- Extended shelf life
- Fast "cold start" properties
- Ability to operate for limited periods of time with no external hydrogen source, enabling "hot swapping" of fuel canisters.

2.5 Van’t Hoff Equation

The van 't Hoff equation (also known as the van 't Hoff isochore) in chemical thermodynamics relates the change in temperature (T) to the change in the equilibrium constant (K) given the standard enthalpy change (ΔH) for the process. The equation was first derived by Jacobus Henricus Van’t Hoff.

$$\frac{\mathrm{dlnK}}{\mathrm{dT}} = \frac{\Delta H}{RT^2}$$

If the enthalpy change of reaction is assumed to be constant with temperature, the definite integral of this differential equation between temperatures T_1 and T_2 is given by

$$\mathrm{Ln}\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

In this equation K_1 is the equilibrium constant at absolute temperature T_1 and K_2 is the equilibrium constant at absolute temperature T_2. ΔH is the standard enthalpy change and R is the gas constant.

Since

$$\Delta G = \Delta H - T\Delta S$$

And

$$\Delta G = -RT\ln K$$

It follows that

$$lnK = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

Therefore, a plot of the natural logarithm of the equilibrium constant versus the reciprocal temperature gives a straight line. The slope of the line is equal to minus the standard enthalpy change divided by the gas constant, ΔH/R and the intercept is equal to the standard entropy change divided by the gas constant, ΔS/R. Differentiation of this expression yields the van 't Hoff equation [20].

2.6 Rate Equation

The rate law or rate equation for a chemical reaction is an equation which links the reaction rate with concentrations or pressures of reactants and constant parameters (normally rate coefficients and partial reaction orders). To determine the rate equation for a particular system one combines the reaction rate with a mass balance for the system. For a generic reaction mA + nB → C with no intermediate steps in its reaction mechanism, the rate is given by

$$r = k[A]^m[B]^n$$

Where [A] and [B] express the concentration of the species A and B, respectively (usually in moles per liter (molarity)); m and n are the respective stoichiometric coefficients of the balanced equation, otherwise they must be determined experimentally; and k is the rate coefficient or rate constant of the reaction. The value of this coefficient k depends on conditions such as temperature, ionic strength, and surface area of the adsorbent or light irradiation. For elementary reactions, the rate equation can be derived from first principles using collision theory. Again, m and n are not always derived from the balanced equation.

The rate equation of a reaction with a multi-step mechanism cannot, in general, be deduced from the stoichiometric coefficients of the overall reaction; it must be determined experimentally. The equation may involve fractional exponential coefficients, or it may depend on the concentration of an intermediate species [21].

2.6.1 First-order Reaction

A first-order reaction depends on the concentration of only one reactant (a unimolecular reaction). Other reactants can be present, but each will be zero-order. The rate law for an elementary reaction that is first order with respect to a reactant A is

$$r = -\frac{d[A]}{dt} = k[A]$$

Where k is the first order rate constant, which has units of 1/time.

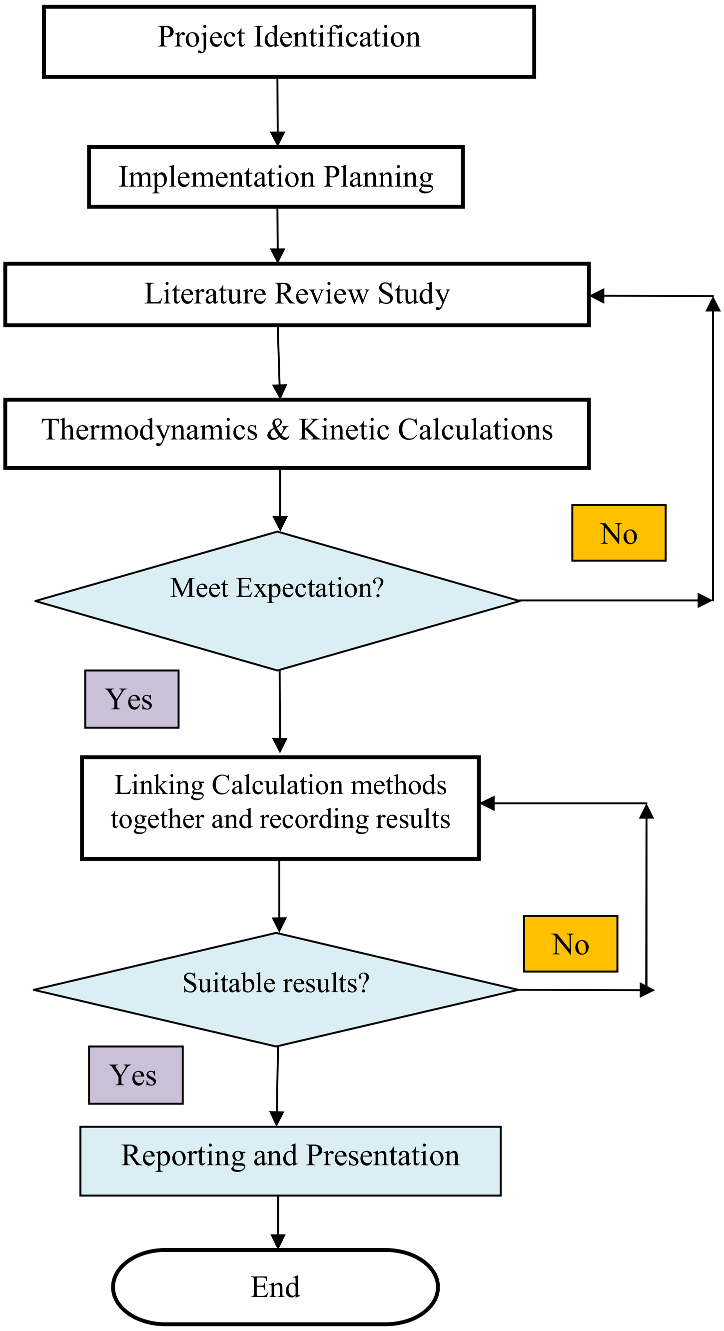
The integrated first-order rate law is

$$\ln[A] = -kt + \ln[A]_0$$

A plot of ln[A] vs. time t gives a straight line with a slope of –k [21].

CHAPTER 3

METHODOLOGY



3.1 Research Work

After reviewing several articles and journals, it has been clear that metal hydrides are the most advantageous and promising storage material because of its light weight and low cost.

The thermodynamic and the kinetics of the process of storing hydrogen in metal hydrides involve many different factors.

3.2 Data Analysis

- Identifying the required data for hydrogen storage.

- Material selection.
  Chemical hydrides such as MgH_2 are known as a potential hydrogen storage medium. It contains 7.66% by weight of hydrogen.

- Investigating the thermodynamics/kinetics properties for desorption of hydrogen in MgH_2.
  By using:
  1) Van't Hoff equation.
  2) Rate Equation.
  3) Fourier's law. To calculate the thermal conductivity of the hydride to apply it in Fourier's law.

- **Tools required:** No tools required – analytical research.

3.3 Gantt chart

	Details/Week	1	2	3	4	5	6	7	8	9		10	11	12	13	14
1	Van’t Hoff Equation [Research + Application]	🟥	🟥	🟥							Mid Semester Break					
2	Progress Report 1 submission				●											
3	Rate Equation [Research + Application]				🟥	🟥	🟥	🟥	🟥	🟥						
4	Seminar and Progress Report 2 submission								●							
5	Project work continues											🟥	🟥	🟥	🟥	
6	Preparation for the poster presentation											●				
7	Submission of final draft															●
8	Oral Presentation											**To Be Announced**				
9	Submission of Dissertation (Hard bound)											**7 days after presentation**				

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Rate of Heat Flow

Fourier's law, states that the rate, in time, of heat transfer through a material is proportional to the negative gradient in the temperature and to the area at right angles, to that gradient, through which the heat is flowing. Based on Fourier's Law, factors affecting the heat flow rate:

- High surface area
  - Smaller the particles, the higher the surface area
- Large ΔT
- Thermal conductivity

Fourier's Law: $$q = KA\frac{\Delta T}{L} \qquad \text{Equation (1)}$$

Where:

q: Rate of heat flow

K: Thermal conductivity

A: Cross sectional surface area

ΔT: Applied temperature differential

L: the heat diffusion distance

Assumption: A cubical hydride bulk, with a side length = 10cm,

Therefore, $A = (0.1\text{m}) \times (0.1\text{m}) = 0.01\text{m}^2$

$L = 0.1\text{m}$

$\Delta T = 250^{\circ}\text{C} = 523^{\circ}\text{K}$

The thermal conductivity can be calculated using Raghavan - Martin model.

$$K = 1 + \frac{c}{\frac{\alpha}{\alpha - 1} - h \times F} \qquad \text{Equation (2)}$$

K: non-dimensional conductivity k_{eff}/k_{cont}

c: volume concentration of the dispersed phase $0 < c < 1$.

The height 'h' of the inclusions shown in these figures is a quantity that can be varied or 'distorted' in accordance with all the factors that would cause a change in the effective conductivity of the medium. The result for equivalence of Ohm's law approach and Maxwell's approach is expressed by the remarkably simple relation:

$$h = \frac{3c}{2 + c} \qquad \text{Equation (3)}$$

The volume concentration c is between 0.4-0.6, so 0.5 will be chosen.

Hence,

$$h = \frac{3(0.5)}{2 + (0.5)}$$

$$h = 0.6$$

Where F is a modifying function that accounts for the geometric distortions equivalent to the distortions in isotherms and heat flow lines.

$$F = 1 + \beta c(1 - c)\left[\frac{3Ao(1 - c)}{2 + A1c}\right] \qquad \text{Equation (4)}$$

α represent the ratio of conductivities, $\mathbf{k_{MH}/k_{H2}}$, (k_{MH} = 5 W/mK, k_{H2} = 0.1805 W/mK)

α = (5 W/ mK)/ (0.1805 W/ mK)

α = 27.7

β represent the transformed ratio of conductivities, **(α +1) / (α -2)**,

β = (27.7 + 1)/ (27.7 – 2)

β = 0.899

$A_o = 1/3$ and $A_1 = 1/4$

Therefore, by substituting in (Equation 4);

$$F = 1 + (0.899)(0.5)(1-0.5)\left[\frac{3 \times 1/3(1-0.5)}{2 + (1/4 \times 0.5)}\right]$$

$$\boldsymbol{F = 1.0529}$$

Hence, the thermal conductivity *K*

c	α	h	F
0.5	27.7	0.6	1.0529

$$K = 1 + \frac{0.5}{\frac{27.7}{27.7 - 1} - (0.6) \times (1.0529)}$$

$$\boldsymbol{K = 2.232\ \mathrm{W/mK}}$$

The rate of heat flow is calculated by using Fourier's Law, recalling (Equation 1)

$$q = KA\frac{\Delta T}{L}$$

K	A	ΔT	L
2.232 W/ mK	$0.01m^2$	523^oK	0.3m

q = (2.232 W/ mK) ($0.01m^2$) (523^oK)/ (0.1m)

q = 116.73 W

The heat required to absorb by the metal hydride (MgH_2) in order to release hydrogen is **116.73 W.**

4.2 Van’t Hoff Equation

Van’t Hoff equation is an equation for the variation with temperature *T* of the equilibrium constant *K* of a gaseous reaction in terms of the heat of reaction at constant pressure.

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

In MgH_2 the required temperature for desorption to start is 250°C, while the values for the other parameters are given in Table 2.

Table 2: Values of MgH_2 properties

	MgH_2
Enthalpy (ΔH)	-73.1 KJ mol^{-1}
Entropy (ΔS)	-126 J K^{-1}mol^{-1}
Temperature (T)	250^{o}C, 523^{o}K
Gas constant (R)	8.314472 J□K^{-1}□mol^{-1}

Therefore the value the equilibrium constant *K* can be determined by substituting these values in Van’t Hoff equation.

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\ln K = -\frac{(-73.1)}{(8.314472)(253)} + \frac{(-126)}{(8.314472)}$$

$$\ln K = -15.18905023$$

The equilibrium constant K = 2.532090954x10^{-7} **s^{-1}**

4.3 Reaction Rate Equation

The desorption reaction equation is as follows:

$$MgH_2 \rightarrow Mg + H_2$$

This reaction is a first-order reaction, and to calculate the rate of this reaction the following equation will be used:

$$r = \frac{-d[A]}{dT} = k\,[A]$$

Where k is the reaction rate coefficient, [A] is the concentration of the product/reactant. The rate equation is an equation which links the reaction rate with concentrations of reactants and constant parameters (normally rate coefficients and partial reaction orders).

$$[MgH_2] = \frac{\text{number of moles}}{\text{volume}}$$

Since,

$$\text{The number of moles} = \frac{\text{mass}}{\text{molecular weight}}$$

And,

$$\text{Volume} = \frac{\text{mass}}{\text{density}}$$

By substituting eq. (3) and (4) in eq. (2)

Therefore,

$$[MgH_2] = \frac{\text{mass}/\text{MW}}{\text{mass}/\rho} = \frac{\rho}{\text{MW}}$$

Known that for MgH_2:

Molecular weight (MW) = 26.32088 g/mol,

The density (ρ) = 1.45 g/cm^3

Therefore, the concentration of $MgH_2 = \frac{1.45\ g/cm^3}{26.32088\ g/mol}$

$= 0.055089343\ mol/cm^3$

By substituting the concentration of MgH_2 in the rate equation (1)

$$r = k\,[A]$$

k (s^{-1})	**[MgH_2] (mol cm^{-3})**	**r (mol cm^{-3} s^{-1})**
$2.532090954 \times 10^{-7}$	0.055089343	$1.394912271 \times 10^{-8}$

By increasing the concentration, the hydrogen desorption rate will increase as well.

4.4 Hydrogen density

How to increase the stored hydrogen density is the most critical issue. Density must be considered both in weight and volume. A high weight fraction of hydrogen will do no good if the weight per volume is small. One most obvious example is hydrogen gas. It is 100% hydrogen but its weight per volume is uselessly small at ambient conditions. To put metal hydrides in perspective with other hydrogen containing materials, the hydrogen content in several common metal hydrides such as methane, propane, methanol, gasoline, gas and liquid hydrogen. Note that bulk density, which is about half of theoretical density for a solid is used to calculate the volumetric density of hydrogen. The reason is obvious.

One can in practice fill a tank to the bulk density of the material not to the theoretical density of the material. This figure brings out two very significant points. First, the present practical metal hydrides contain about 0.06 g/cc of hydrogen compared with 0.07 for liquid hydrogen and about 0.1 for the liquid hydrogen carbon fuels that include gasoline, methanol and ethanol.

Second, the light solids such as magnesium hydride and the sodium aluminum hydride increase the hydrogen weight ratio significantly but not the volumetric density. The volumetric density of sodium aluminum hydride is actually decreased. This information implies an important point: the bulk volumetric density of hydrogen storage is not likely to be more than 0.07 g/cc, certainly not 0.1 g/cc.

Recommendation

There are several techniques can be used in order to improve the absorption and desorption kinetics. By using ball milling, studies has shown that milling of MgH_2 improves the kinetics of the process over those of the unmilled MgH_2 because of the smaller crystallize size.

Adding catalyst to the hydride will also increase the reaction rate in both the forward and the reverse reactions by providing an alternative pathway with lower activation energy.

Decreasing desorption temperature of the hydrogen by changing the chemical properties of the hydrides.

CHAPTER 5

CONCLUSION

Hydrogen storage for vehicular applications is a major concern for the implementation of a hydrogen-based economy. When compared to storage in the pressurized tank, metal hydrides occupy much less volume. However, the weight of metal hydrides systems are still high and further improvement in the material will be needed. Once the weight is reduced by the discovery of new materials, their use in mobile applications will be practical. Owing to a high heat of hydrogen absorption/desorption, metal hydrides need an effective heat management system, which adds to the weight. The storage properties such as pressure, temperature, rate of absorption/desorption are being enhanced by adding catalyst and creating nanostructures.

The attractiveness of metal hydrides stems from their high hydrogen density per unit volume and their ability to release and absorb significant quantities of thermal energy during the hydride formation and the reversible reactions.

There are several factors affecting the desorption rate of hydrogen. Based on Fourier's law (A, ΔT ,L and K) are the factors affecting the heat flow rate.

Adding catalyst to the hydride will improve the hydrogen desorption rate of hydrogen by providing an alternative pathway with a lower activation energy.

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