The objective of this paper is to provide a brief overview of the possible onboard hydrogen storage options available today namely in fuel cell or ICE/electric hybrid vehicles. The issues associated with increasing the hydrogen volumetric densities via solid state materials storage and liquid carriers are the main focus with an overview of the current storage technologies. Possible onboard hydrogen production is discussed based on water splitting technologies.

**Introduction**

Decreasing greenhouse emissions has been a topic of interest in the recent decades. Key contributors to observable greenhouse effects are emissions from combustion of fossil fuel in industry and transportation sector. Developing a viable technology that could provide a clean energy source is of outmost importance for future generations. In addition to the environmental concerns, recent research and development of the smart grids and electric vehicles shows that the demand for electrification is on the rise. Hydrogen is viewed as a potential fuel of choice as it can be produced from renewable energy sources, is non-polluting and its combustion produces no (or very little) harmful by-products. Today most of the hydrogen is produced from syngas. Syngas (a mixture of various concentrations of carbon monoxide and hydrogen) is easily obtained since it can be produced from many non-petroleum resources such as natural gas, coal-bed gas, landfill gas, coal or biomass, through the processes of steam reforming, partial or autothermal oxidation.\(^1,2\)

Diversion from carbon-based hydrogen production which yields significant amounts of CO\(_2\) into a sustainable energy source utilizing wind or solar technology has been a focus of numerous studies.

The term hydrogen economy has been used as a way to describe an overall process of hydrogen utilization as an electricity source encompassing its production (from renewable resources), transportation, storage and electrical generation (Figure 1).\(^3\) The current state of technology has not reached levels where industrial commercialization is viable, as the challenges such as hydrogen generation, storage (onboard a vehicle, during delivery and in refueling stations) and high performance fuel cells still have to be addressed before H\(_2\) as a fuel can be fully integrated within the transportation sector. From a practical and economic point of view, an advantage of hydrogen fuel is that its incorporation into existing internal combustion engines would require only slight modifications. Fuel cells (ex. polymer electrolyte membrane) can convert chemical energy stored in hydrogen into electrical energy and water as the only products\(^4\) with a significantly higher efficiency (60%) compared to currently used internal combustion engines (around 20%). System design (Figure 2) can be tuned to control power of the vehicle by varying the size of the fuel cell while the amount of energy stored onboard can be controlled with the size of the fuel tank.\(^5\) While conceptually this design shows promise, the main challenge still remains of how to develop the technology if the root of the problem is in understanding and influencing the intrinsic properties of the fuel (hydrogen).

In its pure state hydrogen is a diatomic molecule that is transparent, odorless and nontoxic. It is a solid below 13.8 K and gas above 20.3 K with a very small liquid phase range.\(^6\) In gas phase it is flammable in a wide range of temperatures, has strong buoyancy and high volatility. Hydrogen is mainly found as a part of a compound (e.g. water, hydrocarbons), which implies that a method of H\(_2\) production will determine if the electricity is generated from the hydrogen cycle or from the carbon cycle. The detriment of hydrogen as a fuel is its low energy content by volume due to extremely low density under normal conditions, which causes a need for large onboard fuel tanks in order to provide for longer driving range capability. The benefit is high energy content by weight, with the heat of combustion for gas phase hydrogen being twice that of liquid gasoline (Figure 3). Research efforts are focused on tailoring the system to reduce the volumetric requirements while maintaining the gravimetric performance of hydrogen. These efforts are driven by the goal set by DOE (Department of Energy) to develop the storage capacity of 81 g H\(_2\)/L with 9 wt% by 2015.

To meet these goals requires advancement in the over-
all H₂ storage system (tank, storage media, safety system, valves, regulators, piping, mounting brackets, insulation, added cooling capacity, etc.), and in the performance characteristics such as refueling time, discharge kinetics and cycle life. Optimally, stored fuel should be under atmospheric pressure and ambient temperature. However, most mature hydrogen storage technologies require either high pressures (pressurized cylinders) or very low temperatures (liquefaction). Newer directions focusing on the interaction between H₂ and the material as a means of storage and transportations (adsorption, absorption, physisorption, liquid carriers, etc.) are challenging with respect to thermodynamic and kinetic restrictions upon the reaction between the nanostructured storage material and hydrogen. Currently these materials need further research and development to increase their porosity, tuning of pore sizes, optimization of adsorption potentials, and enhancement of volumetric capacities. This review will provide an overview of the most promising, renewable energy technologies for hydrogen generation with an emphasis on the most recent advancements in hydrogen storage via chemisorption and physisorption of pure hydrogen and with liquid carriers.

Hydrogen Production

As previously mentioned, industrially hydrogen is produced from syngas. New directions for an effective and clean way to produce H₂ are being explored. Some selected technologies that exhibit potential for onboard H₂ production systems are water splitting via photoelectrochemical solar energy conversion and via electrolysis. Hydrogen generation from solar energy conversion via photochemistry processes, specifically solar water splitting, has shown great promise. In general, using catalyst, water is split into hydrogen and oxygen via an oxidation-reduction reaction. This is achieved when the incoming energy is high enough to excite an electron from the valance band into the conduction band. A requirement for the photo-catalyst is to have a bandgap higher than 2.43 eV, which is the energy needed for the splitting of water. The speed of the reaction is the main determinant in this process which could be addressed by reducing the bandgap to a wavelength where the intensity in sunlight is very high. Further improvements in the efficiencies are necessary, with the research also focusing on the charge transfer ability and surface catalytic reactivity for half-reactions. In order for solar energy to be the major contributor to the generation of hydrogen, the efficiencies of solar water-splitting devices need to be improved.

The electrolyzer systems use electricity to produce hydrogen from water. Recently, electron-coupled-proton buffers (ECPBs) have been developed that allow decoupling of the half-reactions of electrolytic water splitting (H₂ and O₂ evolution proceed at separate times). The process uses a redox mediator that is reversibly reduced during the oxidation step, upon which it is transferred to a separate compartment for catalytic H₂ evolution. This system exhibits potential for onboard H₂ production as the electrochemical step is performed at atmospheric pressure while the H₂ evolution would be performed in a different higher pressure compartment. Also, no H₂ is produced in the electrolytic cell, H₂ evolution would not be directly coupled to the rate of water oxidation, and the hydrogen produced has the potential to have an inherently low O₂ content.

Hydrogen Storage

Hydrogen storage is an important component in the ongoing development and commercialization of hydrogen and fuel cell technologies. Safe and economically feasible hydrogen storage technology needs to be developed in order to compete with current fossil fuels driven economy. Storage is required onboard the vehicle, in production sites, during transportation and in refueling stations. Challenge for onboard storage is to safely store enough fuel to enable a driving range in excess of 300 miles which usually corresponds to 47 kg of hydrogen. This requires a significant increase in H₂ energy density within the storage media. This is further complication by ambient temperature and atmospheric pressure conditions desired.
for this process. In general, the density of a gas can be increased with very low temperatures (below critical point), by applying work to compress gas or by interaction with second material. When the second material is utilized, uptake and process reversibility also become important. Based on these requirements, hydrogen can be stored as pure H\textsubscript{2} via compression or liquefaction,	extsuperscript{12,13} in solid state materials via chemisorption in metal hydrides and complex (meal-hydrogen) hydrides\textsuperscript{14–18} and physisorption,\textsuperscript{19–21} or utilizing a liquid as a carrier.

**Pure Hydrogen Storage**

**Compression**

High pressure gas cylinders are the most mature technology for pure H\textsubscript{2} storage, currently exhibiting the highest storage capacity and best overall performance compared to other storage methods.\textsuperscript{12,13} Significant increase in energy density is achievable; however, a drawback is the reduction in gravimetric density under high pressure due to the increasing thickness of the cylinder walls. Additionally, safety concerns associated with pressurized hydrogen gas are significant.\textsuperscript{22} Full cylinder contains 4\% by mass hydrogen at 450 bar which can autoignite at ambient temperature, requiring additional safety measures for thickness of the cylinder wall. This further increases the size of the storage tank which is currently too large to accommodate the entire hydrogen storage unit capable of providing a desired driving range. Cylinders are usually produced from materials such as austenitic stainless steel, copper or aluminum alloy which are nonreactive with hydrogen and have high tensile strength.\textsuperscript{23}

**Liquefaction**

Liquefaction is a physical storage of cryogenic hydrogen in isolated tanks at -253 °C and the pressures of 6-350 bar. This process requires large amount of energy for liquefaction and the continuous boil-off due to heat leaks which would not be practical or economically sustainable in the transportation sector.\textsuperscript{12,13}

**Solid State Materials**

Hydrogen storage based on solid state materials exhibits potential to significantly increase the volumetric density of stored hydrogen under low pressure and ambient temperature conditions. The process involves surface H\textsubscript{2} dissociation and consequent diffusion of H atoms into the bulk structure (absorption) or by surface diffusion only (adsorption). The type of storage is determined by the strength of interaction between hydrogen and the solid material. Van der Walls forces lead to the initial physisorption state of the hydrogen molecule, upon which the molecule has to overcome a dissociation barrier. Once a bond with surface metal is formed (chemisorption) hydrogen atom can either diffuse across the surface or into the bulk. Inherent complexity associated with storage in solid state materials is the heat produced during the refilling process. Therefore, thermodynamic restrictions may be difficult to overcome.\textsuperscript{22}

**Physisorption**

Physisorption is an adsorption process that binds hydrogen weakly to the surface. This process has shown to exhibit excellent kinetic properties utilizing highly porous materials (high surface area). Determinant to physisorption are low temperature (< 273 K for carbon based materials) requirements for the Van der Waals forces have any substantial effect on the process, which implies low hydrogen adsorption unless the process can be catalytically improved. Hydrogen storage on high surface area materials generally exhibits excellent kinetic properties.

Carbon-based porous materials have been identified as promising candidates for hydrogen storage via physisorption due to high surface area, large pore volume and good chemical stability. The strength of the hydrogen carbon interaction at room temperature can potentially be improved by doping activated carbons with nanoparticles of elements that dissociate hydrogen easily, most predominantly researched element being platinum. The kinetics are improved via the spillover mechanism wherein at room temperature, hydrogen dissociates on Pt and diffuses onto the surface. The results show significant hydrogenation and reversible dehydrogenation of a carbon support suggesting routes to design improved catalysts for hydrogenation and fuel cell applications.\textsuperscript{24} Surface diffusion from the catalyst to its support was shown to occur via a mobile chemisorbed phase and the reverse mobility occurred by diffusion back to the catalyst. Significant research still needs to be performed, as the exact spillover mechanism and the reaction rate limiting step are still unknown.

**Metal hydrides**

Metal hydrides have been extensively studied as a possible hydrogen storage medium due to high hydrogen content by weight and a potential for high adsorption capacity under desired reaction conditions. The absorption process involves surface dissociation of H\textsubscript{2} and its consequent diffusion into the metal or metal alloy to form metal hydrides. At ambient temperatures metal hydrides tend to exhibit low gravimetric densities due to very weak atomic hydrogen bonding (ex. AlH\textsubscript{3}, VH\textsubscript{2}), while metal hydrides exhibiting acceptable gravimetric densities tend to bind atomic hydrogen very strongly (ex. LiH, MgH\textsubscript{2}).\textsuperscript{25} Further improvements to reaction thermo-
dynamics (enthalpy) are required. The aim is to decrease the current 300-350°C reaction temperature.

Complex hydrides

Light metals (e.g., Li, Mg, B, and Al) give rise to a large variety of complex metal hydrides. The goal is to form alloys using elements capable of affecting the hydrogen dissociation rate. Metallic alloys have been shown to have high hydrogen storage capacity in addition to good dehydrogenation properties allowing for the reversible process. These compounds exhibit the highest gravimetric hydrogen densities at room temperature, the most predominant being LiBH₄, with 18% by mass gravimetric density and 121 kg m⁻³ volumetric density. However, the compounds are highly stable requiring temperatures in excess of 650 K to release H₂. Subsequent research has provided a new crystalline phase that contains two polymorphs -LiHB (-Li₂H₂BH₃) at low temperature and -LiHB at high temperatures. This material is more reactive and less stable upon heating than the parent HB.

Complexes of rare-earth and d-transition metals such as LnₓMHₓ have demonstrated unique synergy that exhibits increased hydrogen adsorption. These hydride clusters are of particular interest as molecular models for hydrogen storage alloys. However, well-defined rare-earth/d-transition metal polyhydride complexes are currently very rare due to the lack of a strategy for efficient synthesis and difficulty in catalyst characterization.

Liquid Carriers

Recent advances have been made in developing liquid energy carriers, utilizing molecules containing a high percentage of hydrogen. The most promising non-fossil resources are alcohols (e.g., ethanol, methanol) because in the presence of water and, at relatively low temperatures, hydrogen-rich mixtures can be produced. Steam reforming of methanol (CH₃OH + H₂O → CO₂ + 3H₂) as a process for onboard H₂ production is of special relevance. Liquid methanol has high energy density (under standard conditions), low boiling point, has no C-C bonds and contains 12.6% by mass of hydrogen. These properties indicate that under relatively mild reformate reaction conditions H₂ generation can be viable through a process that does not contribute to a net addition of CO₂ to the atmosphere.

Ruthenium complex catalysts have been shown to exhibit potential for aqueous-phase methanol dehydrogenation and reforming at atmospheric pressure and low temperatures (65 - 95°C). Full conversion of all available hydrogen has been observed (Figure 4) with the 3:1 ratio of H₂ to CO₂. Incorporation of this technology into fuel cell vehicle design could provide an extremely high energy density (3 times that of lithium ion batteries) and for an extremely low (1 ppm) CO and CH₄ concentration in product. Additional research is needed to prevent the deactivation of the catalyst because the base used for activation of the process is preventing deprotonation of methanol and formic acid (reaction intermediate species). Therefore, the nature of the base and its concentration, the water content and the temperature require further optimization.

![FIG. 4: Schematic pathway for a homogeneously catalyzed methanol reforming process via three discrete dehydrogenation steps. Adapted from Reference 29.](image)

Conclusion

This review has looked at some new promising technologies that exhibit potential for onboard hydrogen production and storage, and technological issues that still need addressing before full integration into the transportation sector is viable. Onboard H₂ production systems such as water splitting via photoelectrochemical solar energy conversion or electrolysis offer an alternative that could potential make for an easier transition into the hydrogen economy. Hydrogen storage based on solid state materials shows potential to substantially increase hydrogen density in storage materials and improve the kinetics of hydrogen uptake and release under the low pressure and room temperature conditions. Unlike the pure hydrogen storage technologies (compression and liquefaction) which are commercially available today, these technologies still require significant research to further understand the reaction mechanisms as well as to design a concept that can be fully integrated into an electric vehicle design. However, storage materials such as complex metallic hydrides and liquid energy carriers offer a safe and effective way to store hydrogen which can be a way towards substantial increase in hydrogen based fuel cell electric vehicles on the roads.

4 L. Klebanoff, Hydrogen Storage Technology: Materials and Applications (Taylor and Francis Group, LLC, 2013).
18 J. Graetz, Chemical Society Reviews 38, 7382 (2009).
20 A. C. van den Berg and C. O. Arean, Chemical Communications 6, 668681 (2008).