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Advanced Storage Technologies for Hydrogen and Natural Gas

On August 1, 2012, The National Petroleum Council (NPC) in approving its report, *Advancing Technology for America's Transportation Future*, also approved the making available of certain materials used in the study process, including detailed, specific subject matter papers prepared or used by the study's Task Groups and/or Subgroups. These Topic Papers were working documents that were part of the analyses that led to development of the summary results presented in the report's Executive Summary and Chapters.

These Topic Papers represent the views and conclusions of the authors. The National Petroleum Council has not endorsed or approved the statements and conclusions contained in these documents, but approved the publication of these materials as part of the study process.

The NPC believes that these papers will be of interest to the readers of the report and will help them better understand the results. These materials are being made available in the interest of transparency.

Advanced Storage Technologies for Hydrogen and Natural Gas

Introduction

On-board fuel storage continues to be one of the key technical challenges to the widespread commercialization of natural gas and hydrogen-fueled vehicles. Natural gas and hydrogen fuels are both flammable gases with lower volumetric energy densities than gasoline or diesel, their similarities mean storage technologies and issues are also very similar. Current storage applications rely on compression or liquefaction, both of which have some important cost and performance barriers. This has led to dedicated research into alternative, low-pressure gas storage technologies which aim to meet performance and cost targets to support widespread hydrogen and natural gas vehicle deployment.

Current Technologies

The current primary storage technologies are compressed gas and liquefied gas storage tanks.

Compressed Gas – Gaseous storage of hydrogen and natural gas requires high-pressure tanks to achieve workable energy densities for transport. Current hydrogen vehicle tanks operate at 5,000 or 10,000 psi, while compressed natural gas (CNG) is usually stored at 3,600 psi. The technology for these tanks has evolved to allow higher storage pressures, however this would require greater gas compression which increases operating costs and technical challenges around refuelling. Latest Class IV tanks are made with an impermeable plastic liner, which holds the gas, completely wrapped in a carbon fiber shell. The shell provides the structural strength against internal pressures and external shocks.

Liquefied Gas – Liquefaction is more common in natural gas than in hydrogen onboard storage. Liquefied natural gas (LNG) has 2.4 times the energy density by volume of CNG, meaning it is a preferred solution for heavy-duty and long-haul vehicles which have lower fuel efficiency and require greater range, justifying the higher costs of liquefaction over compression. Hydrogen liquefaction for onboard fuel storage is almost non-existent as fuel cell technologies are less widespread in heavy duty vehicles and as hydrogen liquefaction requires a lower temperature than natural gas (-252°C/-423°F vs. -162°C/-260°F) and therefore more energy and cost to produce.

Cryo-compression, which combines compression and liquefaction by using moderate pressures to raise the liquefaction temperature, is currently being assessed and could provide a better overall combination of the benefits and challenges of both storage methods.

Problems with Current Technologies

Although the current storage methods are technically feasible, and are economically viable for certain markets, there are some significant issues which limit their value in widespread deployment.

Energy density by volume – Both hydrogen and natural gas cars are currently able to achieve ranges of over 300 miles, however such ranges require compressed gas tanks which take up more space within the car than gasoline tanks. In particular, hydrogen's lower density requires considerably larger tanks. LNG has higher density but still offers ranges below those targeted by long-haul trucking fleets.

Tank Cost – Pressurized or cryogenic tanks are significantly more expensive than gasoline or diesel tanks. The main driver of current compressed gas tank costs is the requirement for large volumes of carbon fiber, which can represent over 75% of the overall tank cost and drive costs to over $2,000 per tank (over $10/kWh). For LNG tanks, the additional costs of stainless steel, multiple containers and creating a vacuum between layers to manage cryogenic liquids, raises costs above a simple low-pressure, non-cryogenic tank.

Gas Production Cost – Compression and liquefaction are costly and energy intensive activities which must be performed to provide feedstock for these storage technology pathways. Liquefaction of hydrogen can require 30% of the input energy. There are also considerable LNG handling costs and challenges relating to managing LNG venting and fire safety regulations. Compression of natural gas or hydrogen is costly and adds to the equipment and site requirements for compressed fuel dispensing.

Research into higher strength metallic materials and new composites could allow incremental increases to storage pressures and therefore energy density. However, these will not necessarily improve tank costs and increasing pressures would drive increases in gas compression costs. There is therefore significant research occurring into disruptive technologies which could allow storage at higher densities, lower pressures and lower total costs. Such low-pressure storage technologies are viewed as key facilitators of widespread hydrogen and natural gas vehicle use.

Disruptive Technology Goals and Research

At present, the majority of fuel storage research is focused on hydrogen; however many of the technologies could also significantly improve natural gas vehicle storage range and costs. Natural gas-focused R&D funding is also increasing, such as through ARPA-E's natural gas program[i]. The Department of Energy has set goals for hydrogen research which would result in vehicles with a driving range of more than 300 miles (500 km) while meeting space, packaging, cost, safety, and performance requirements to be competitive with current vehicles.

Key Hydrogen Storage Technology Goals:

- System Energy Density (Volumetric) – 40 g/L (2015); 70 g/L (ultimate)
- System Energy Density (Gravimetric) – 5.5 wt% (2015); 7.5 wt% (ultimate) (wt%=kg H_2/kg H_2+system)
- Storage Costs – $2/kWh
- Operating Conditions – Performs at reasonable temperatures and pressures
- Kinetics – Ability to quickly store and release fuel
- Deliverable hydrogen capacity – Ability to release a significant portion of the stored fuel

Methane R&D at the federal and state level (through groups such as the California Energy Commission) has worked toward the following targets for natural gas storage.

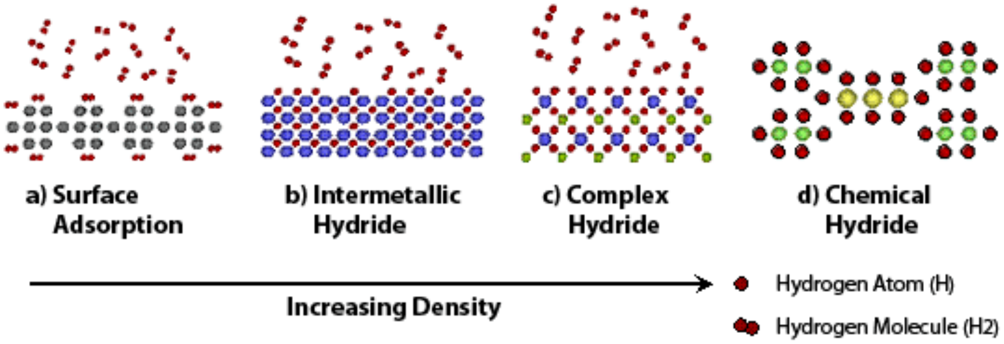
Key Natural Gas Storage Technology Goals[ii]:

- System Energy Density (Volumetric) – 118 g/L @ 25^0C and 1 bar
- CNG stores 190 g/L @ 25^0C and 250 bar, LNG stores 423 g/L @ -161^0C and 1 bar

Since FY 2005, public US hydrogen storage research has been conducted under the framework of the National Hydrogen Storage Project. This effort includes DoE EERE support for independent projects and Centers of Excellence (CoEs) in applied hydrogen storage, and DOE Office of Science support for basic research projects for hydrogen storage. A new effort, started in FY 2009, is the Hydrogen Storage Engineering CoE that provides a coordinated approach to the engineering R&D of on-board materials-based systems. The Engineering CoE is planned as a five-year effort and may produce up to three sub-scale prototype systems (based on the most promising materials under consideration) as its final output (subject to go/no-go decision points). Crosscutting efforts on system analysis and material chemical and environmental reactivity are also included in the National Hydrogen Storage Project. The three current materials-development CoEs have been focused on specific hydrogen storage material classes: hydrogen adsorbents, metal hydrides, and chemical hydrogen storage materials.

Disruptive Technology Pathways

Disruptive storage technologies seek to bypass the pressure and thermal challenges of traditional storage technologies by utilizing the chemical and physical properties of certain materials to store gas at low pressure and moderate temperatures. The common approach involves holding the hydrogen or methane atoms or molecules in storage materials which allow a greater density of fuel by adsorbing onto the material surface, absorbing into the material, or storing the fuel as a chemical compound. Using such technologies for hydrogen, it is possible to achieve volumetric and gravimetric storage densities rivaling liquid hydrogen because the H_2 molecule is dissociated into atomic hydrogen within the material, such as a metal hydride. A range of materials are currently being assessed across these storage pathways. The gas is loaded into and forced out of the material by applying changes to pressure or temperature, or through a chemical reaction. Storage in materials offers great promise, but additional research is required to better understand the storage mechanism under practical operating conditions and to overcome critical challenges related to capacity, the uptake and release of the stored gas (i.e., kinetics), management of heat during refueling, system costs, and life cycle impacts.



Adsorption Materials – Combining materials capable of achieving high surface area per unit mass with highly adsorbent chemicals is considered an attractive way to produce materials with high storage densities for gases, including hydrogen and methane. Research is pursuing a range of potential materials, including carbon nanostructures, metal organic frameworks, polymers, and other new materials.

Carbon nanotubes have demonstrated the potential to store material volumes of hydrogen, with results ranging from 3 to 10 wt% at room temperature. However achieving consistency in these storage densities and replicable manufacturing capability is still a major challenge in developing reliable carbon nanotube storage materials. Doping of the carbon with metals has shown some potential to improve performance. Carbon for methane storage has also seen significant research with activated carbon being formed into a range of structures to maximize porosity for adsorption. Research into adsorbent carbon pellets and briquettes has shown great promise, achieving Department of Energy technical goals by delivering 132 g/L (110% of target), but still requires cost reductions and tank design improvements.

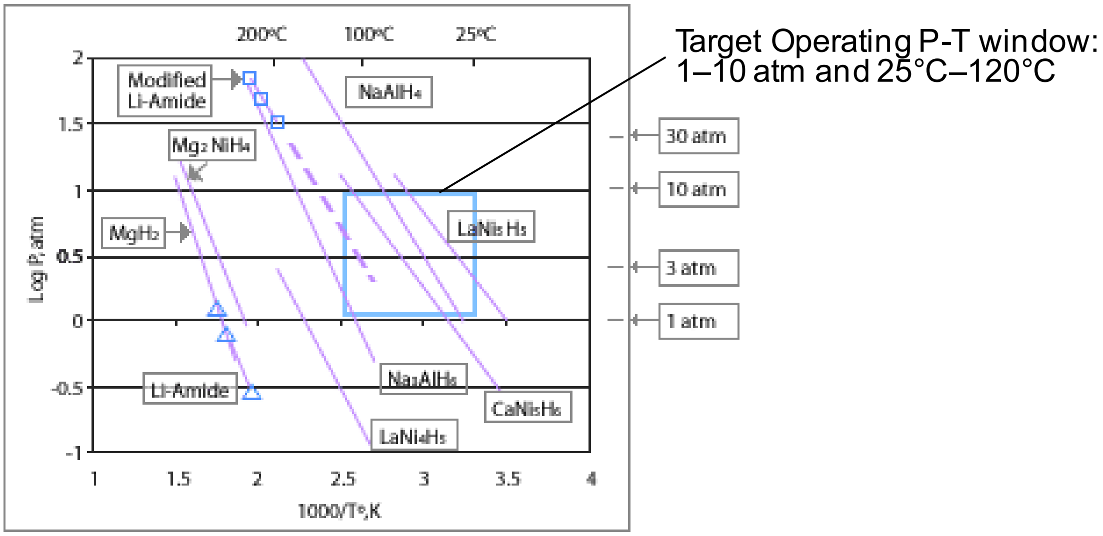
Metal organic frameworks (MOFs) are highly crystalline inorganic-organic hybrids, constructed by assembling metal-containing clusters into a three dimensional structure. MOFs are capable of achieving surface areas of 6,000m^2/g allowing them to efficiently trap large volumes of various gas molecules[iii]. MOFs are able to achieve gravimetric and volumetric energy densities in the range of department of energy targets, however they require cryogenic temperatures of around -195C to achieve such strong results. At room temperatures, even under high pressure, the thermal energy of the hydrogen impedes uptake of the gas. Research into high density adsorption at atmospheric temperatures is ongoing but is still in early stages of development and study. Research into MOFs for methane storage have shown positive results but are less developed than hydrogen storage research.

In recent years, porous aromatic frameworks (PAFs) with diamond-like structures have also emerged as a highly promising storage material, with theoretical hydrogen uptakes of 6.53 wt% at 25C and 100 bar. PAFs demonstrate pronounced stability relative to other permanently porous materials as a result of their diamond-like topography, and also exhibit surface areas as large as 7,100m^2/g. Simulations of diamond-like PAFs have demonstrated hydrogen uptakes equivalent to high-surface area MOFs. Studies have therefore commenced, exploring various methods of functionalizing PAF structures for hydrogen storage by attaching various organic moieties, such as metal alkoxides, to the framework surface.

Other materials such as clathrates and polymers are being studied for their potential but have yet to develop significant research to assess their potential.

Metal Hydrides – Metal hydrides are metal-hydrogen compounds, such as MgH_2, which are able to absorb and desorb high volumes of hydrogen. Metal hydrides can be simple, involving a single metal, or complex, using a combination of metals bonded with hydrogen. These complex metal hydrides can balance the properties of different metals into a superior material, such as Na_3AlH_6. Different combinations of metals alter the energy density and also the temperatures and pressures required to absorb and release the hydrogen.

At present, advanced materials are able to achieve certain performance targets but are unable to meet all targets in a single material. In particular, there is a trade-off between energy density and ability to absorb/desorb within target operating conditions. Laboratory materials have been developed which can achieve wt% energy densities of up to 12 wt% for the material (compared to the 7.5 wt% system target)[iv], however reversing storage of such dense materials requires pressures of 950 bar and temperatures of 400^{0}C. To be commercially attractive these hydrides must be able to store sufficient hydrogen but also reverse absorb/desorb along a pressure-temperature coefficient within the targeted operating window (see chart).



DOE: http://www1.eere.energy.gov/hydrogenandfuelcells/storage/metal_hydrides.html

Ongoing research continues to assess new combinations of materials, as well as the structure of these materials, in order to push for a material which meets all storage targets in a cost-effective and durable material. A handful of stationary metal hydride storage pilots are occurring in Germany at refueling station pilots.

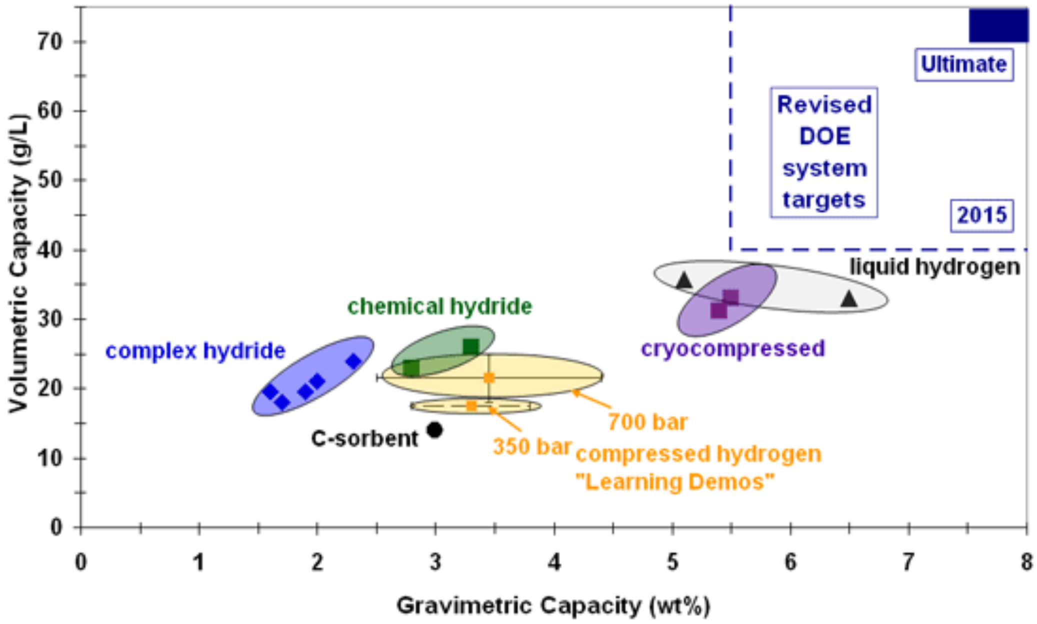
Chemical Storage Technologies – Chemical storage technologies capture and then release stored hydrogen through a chemical reaction, most commonly reactions of hydrogen-containing chemicals with water (or other compounds such as alcohols). A major differentiation from the storage techniques above is that the storage is not usually reversible within the tanks, meaning a liquid storage medium would be added and removed from the vehicle storage tanks for offboard hydrogen regeneration. The chemical reactions used for this production method are oxidation reactions which replace the hydrogen in the storage chemical with oxygen, releasing hydrogen gas.

The chemical being studied most-widely is sodium borohydride ($NaBH_4$), which reacts with water to release hydrogen. In operation, sodium borohydride is held in an inert stable liquid in the fuel tank; water is added to the storage medium causing it to release hydrogen ($NaBH_4 + 2H_2O = NaBO_2 + 4H_2$). The reaction rate can be controlled in via pH or a catalyst. The technology is attractive as the chemical provides high hydrogen densities and hydrogen is rapidly released; however, the cost and complexity of 'refueling' the tank and regenerating the sodium borohydride requires research. Working systems using this technology are being used in the field, and a commercial product does exist with a claimed gravimetric capacity of 4 wt%[v]. However current early use is primarily in non-transport applications.

Conclusion

Despite significant improvements to compressed and liquefied gas storage capabilities, storage remains a critical challenge to widespread deployment of gaseous transport fuels. A number of potential storage technologies are being assessed which offer high potential energy densities at lower pressures, however none are yet able to meet all the performance targets specified by the DoE for a competitive technology. At present metal hydrides are achieving a lot of attention but, as the chart below suggests, the technologies will still require improvements at the lab scale before they are able to compete in the field.

Hydrogen Storage Technologies (Energy Densities vs. DoE Targets)



In assessing disruptive storage technologies, a systems approach must be taken looking at all benefits and costs. In the case of natural gas for example, an indirect effect would be that lower pressure storage hinders the ability to use emerging high-pressure direct injection engine technology which has the potential to improve engine efficiency. In addition, if significant infrastructure is built out for high-pressure or liquefied fuel supply chains, transformation costs and support for legacy systems must be considered.

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[i] http://arpa-e.energy.gov/media/news/tabid/83/vw/1/itemid/44/Default.aspx

[ii] http://www1.eere.energy.gov/cleancities/pdfs/ngvtf11_pfeifer.pdf

[iii] http://www.chem.tamu.edu/rgroup/zhou/PDF/075.pdf

[iv] http://www.hydrogen.energy.gov/pdfs/progress11/iv_0_hydrogen_storage_overview_2011.pdf

[v] http://www1.eere.energy.gov/hydrogenandfuelcells/storage/chem_storage.html