SUSTAINABLE HYDROGEN

LAST ACTS

Final report of the ACTS-programme Sustainable Hydrogen

The Hague, November 2013
I am proud to present to you the final publication of the Sustainable Hydrogen programme of ACTS (Advanced Chemical Technologies for Sustainability). You will find an overview of eleven years of efforts that have considerably contributed to a strong foundation of sustainable hydrogen technology in the Netherlands. We will also look ahead to the future.

Environmental issues associated with the use of fossil fuels and the dependency on nature for the production of alternative, fully renewable energy sources have triggered a quest for a robust, cost-effective and efficient technology for energy transportation and storage. Hydrogen has the potential to become a sustainable and universal energy carrier. To be able to explore future implementation of hydrogen as a pivotal energy carrier in its full spectrum, the Sustainable Hydrogen programme focused on fundamental scientific questions, technological aspects as well as the social-economic impact of hydrogen as a clean energy carrier. These features make it a unique programme.

On route towards the ‘sustainable hydrogen economy’, a large number of innovative solutions and improvements should be generated. In the Sustainable Hydrogen programme, we focused on developing such solutions and technologies. We invested in research on the technological aspects, such as hydrogen production, detection, and storage, e.g., for implementing hydrogen to power automobiles. The advantages of hydrogen – no exhausts, availability, affordability, options for CO₂ free production, and easy transportation – brought together five companies and M€ 18.2, yielding 34 projects, covering a wide range of research themes: hydrogen production from fossil and renewable sources, separation technologies to produce clean hydrogen, better hydrogen storage solutions, hydrogen sensors and hydrogen-powered energy saving devices, integration pathways for hydrogen into the energy supply that allow for a gradual transition to a fully sustainable energy system, technologies and management approach for the integration of hydrogen storage solutions in future energy systems, societal governmental and environmental issues concerning hydrogen as a part of the energy infrastructure.

This dynamic and versatile programme turned out to be one of the largest and scientifically most successful of the ACTS programmes, as a recent CWTS study has shown. The programme has proven the possibility to do state of the art scientific work, providing industry with a long term compass to navigate on.

I believe that hydrogen technology definitely has established its role as an important tool for a sustainable future. I am sure that after reading the results of the Sustainable Hydrogen programme you will feel the same, and I hope that you will be inspired to contribute to more effective and sustainable chemistry.

Dr Louis B.J. Vertegaal
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• Prof. dr. ir. H. van Lente: Measuring expectations of hydrogen energy systems

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The hype has gone but the ambition remains

“In the second half of the 1990s the development of fuel cell cars for emission-free electric transmission took off. The ambition was 100,000 fuel cell cars in 2005”, remembers Herman Kuipers. Such a development required a new fuel.

Herman Kuipers, former member of the Sustainable Hydrogen Programme Committee and Senior Principal Researcher at Shell: “At Shell we had discovered the Catalytic Partial Oxidation technology (CPO) to convert natural gas into synthesis gas. We subsequently found that CPO also works for liquid fuels, such as petrol. This made it possible using a ‘small chemical factory’ to convert petrol into a hydrogen-rich gas on board a car. This so-called ‘reformer’ can subsequently serve as an input for a fuel cell. As a result you can use an existing fuel and associated infrastructure to make the step to fuel cell cars. For the supply of a medium-sized car, a CPO reactor the size of a coffee cup was found to be big enough. Daimler-Chrysler was busy with the conversion of methanol into hydrogen. That is a bit easier but requires the development of an enormous methanol synthesis infrastructure. With the use of a CPO reformer ordinary petrol can be used. Within a relatively short period of time we demonstrated the feasibility of this technology in collaboration with Daimler-Chrysler.”

Fundamental approach
Companies often built upon knowledge previously developed at universities but there was not really enough fundamental knowledge. “So together with NWO we set up a broad programme with partners, under the ACTS umbrella, to develop fundamental knowledge for the future that included aspects such as the production, storage, and embedding in infrastructure but also the safety and public acceptance of hydrogen. The slogan for the entire ACTS programme was ‘ACTS means business’, but that applied less to our long-term programme ‘Sustainable Hydrogen’. “We mainly focussed on laying a foundation of knowledge”, says Kuipers. Sytze B. van der Molen, former member of the

“It was a fantastic programme that attracted many good scientists.”
Sustainable Hydrogen Programme Committee on behalf of ECN: “Back in 2000 many European research projects focused on hydrogen. For example, on fuel cell busses, in cities like Amsterdam, the virtual power plant with interconnected household fuel cell applications, and ‘Hyways’, research into the introduction of hydrogen along motorways. With Sustainable Hydrogen the Netherlands followed in these footsteps. That was realised, for example, by training young scientists for a future in the hydrogen activities of Shell Hydrogen, Gasunie, Nuon, BTG, ECN and other parties. The NWO research programme had two phases. The first, fundamental phase was aimed at discovering bottlenecks for the introduction of hydrogen as an energy carrier and for finding approaches to solving these challenges.”

Achieved Objectives
Kuipers: “It was a fantastic programme that due to its ‘clean’ and technologically challenging character attracted many good scientists. The programme had enthusiastic PhDs and great workshops and a real family feeling developed within it. I am therefore still proud of the programme. The fundamental phase also covered the crucial factor of public acceptance. Researchers from the social sciences and humanities ultimately made a number of impressive contributions to the programme in this area.”

The second phase was to consist of partnerships with industry to support application-oriented technological developments. Van der Molen: “In the first phase a lot was done on storage, production, integration, sensors and socioeconomic embedding. The objectives were achieved and a lot of knowledge was acquired, for example through PhD research at universities (theses).” According to Van der Molen, the second phase of the project became more challenging when almost all large industrial parties deprioritized their hydrogen activities. Fluctuating company strategies are a known phenomenon in large and long running PPP-programmes. Nowadays, companies like Shell are redirecting their efforts toward hydrogen again.

Continuity or knowledge destruction
That Shell turned away from hydrogen was mainly because the collaboration with Daimler-Chrysler ended, says Kuipers. The costs of developing two parallel options for a fuel cell car, one based on methanol and the other on petrol, proved to be very high. Daimler-Chrysler therefore decided to demonstrate the earlier developed methanol version and to consider the development of a petrol version at a later stage. For both parties that was the reason to part ways. Shell Hydrogen set up a CPO fuel-reformer company, Hydrogen Source, with the experienced American partner UTC. The aim was to offer this technology to all manufacturers of fuel cell cars. Unfortunately, after two years it transpired that both government bodies in the United States as well as the majority of car manufacturers preferred to use a stored form of hydrogen for the fuel cell car. So although the joint venture was impressive from a technical perspective, the market chose otherwise.

Such swings are probably an inherent aspect of breakthrough technology. Van der Molen: “The long development time required can cause some parties to lose interest, in contrast to Asian countries where the long-term development simply continues. This is something of a Dutch problem: we try something for four years and then stop again. If the continuity is missing then you risk destroying the knowledge acquired. Fortunately there are still some enthusiastic industrial parties active who are united in the Dutch Hydrogen Association. Therefore the time is ripe for the second phase: helping to realise product development and applications. A possible follow-up of the programme should, in my opinion, focus on technology development in close collaboration with the somewhat smaller parties. Knowledge acquisition therefore needs to go hand-in-hand with training. Besides university training there is a need for technicians trained at various vocational levels.” The founding of Nationaal Regieorgaan Praktijkgericht Onderzoek SIA at NWO offers interesting opportunities in that direction.
Fits seamlessly
Van der Molen: “At present the ‘battery car’ is a popular topic in plans to reduce local emissions in town centres. That’s fine: the fuel cell fits seamlessly in the hybrid systems that all car manufacturers are currently busy with. Whereas purely electric cars will always be limited in their action radius, the problem for fuel cell cars is the setting up of the hydrogen infrastructure. That is far easier to realise for a local system, such as a municipal transport company, than it is for private cars. The city of Arnhem is leading the way in terms of industry and local organisation. The Hyways study pointed to Rotterdam with its large local hydrogen production as the first ideal location in the Netherlands. We will have to wait and see where the rollout of hydrogen from a local to a national level will take place.”

Kuipers also has no doubts about the ultimate success: “It will always be a problem to achieve a large action radius with affordable batteries. In the 1990s everyone was ambitious with hydrogen. We still are, but the hype is less. Now 700 Bar hydrogen storage has been accepted. The yield of the reformer plus the fuel cell for electric transmission can still match that of the combustion engine despite the spectacular progress made in that area. The hybrid with the fuel cell as a range extender is a good option for the future. We have the largest hydrogen fuel station capacity in the world but we can only sell it if there is demand. But there is interest in hydrogen and the knowledge is available. If the willingness in society increases and the partners come forward then we are ready. That proved to be the case when it was announced in October that Shell plans to build 400 hydrogen fuel stations in Germany together with a number of partners.”
This will enable a successful mass introduction of a Hydrogen driven electrical car. “Lenin said: ‘the future is electric’ and I still think that is the case.”
To store hydrogen in metals, we need to find light-weight materials which desorb hydrogen at low temperatures (<100 °C). Using thin films as a model system, the interaction of the metal hydride with its surroundings was investigated. A surprising result was that the nucleation and growth behaviour of 10 nm thin Mg films could be visualized using a simple optical technique. It was found that the nucleation of the metalhydride in the metal phase is an important factor governing the kinetics of hydrogen absorption. The general conclusion is that the effect of the matrix on the hydrogenation properties of metallic nano-particles is governed predominantly by the plastic deformation which is due to the 30% volume expansion of the metal on absorption of hydrogen.
Schoot Uiterkamp: In her doctoral thesis about the history of hydrogen from 1970 to 2010, Marloes Dignum reveals strong ups and downs in interest during that period. The 1970s began enthusiastically but at the end of the decade the interest in hydrogen waned. At the start of the 21st-century interest peaked again, only to fall when the Bush administration made way for Obama. The United States and Japan play a decisive role and the future is difficult to predict.

The Sustainable Hydrogen programme covers the entire life cycle of hydrogen from production and storage to distribution. It was set up before the hybrid battery breakthrough. There was a strong focus on mobile hydrogen storage applications because at the start of the programme that was where the main challenges lay. And still lie because the ideal storage material has not yet been found. At least now we know where we have to look. Hydrogen enters carbon nanotubes easily but does not come out again. We are looking for a system that works like Post-Its: easy to stick and remove again. The thin-layer materials offer such a perspective.

Non-mobile storage applications have also been investigated in relation to the current issue of ‘power to gas’. In off-peak periods with a lot of wind, wind turbines produce large amounts of ‘excess’ electricity. This excess could be used to produce hydrogen that is stored in the gas network. Research revealed that several percent of hydrogen – with a high energy density – can be mixed with natural gas. That might be interesting for the Netherlands as a gas distributor.

Surprising outcomes

Frans Berkhout, Sustainable Hydrogen Programme Committee member, explains: “For Sustainable Hydrogen, not just the technical component but also the societal embedding of the energy transition was examined. Sociologists, economists and political scientists have carried out fantastic studies into the energy-economic, societal and political aspects surrounding the transition processes. If it is to achieve a breakthrough then hydrogen must be able to fill a clear economic and technological niche. Within such a niche learning processes can take place that lead to usable and competitive technologies. The search for a clear and stable niche for hydrogen in the energy system is far from over.”

Schoot Uiterkamp: “Later on in the programme the aspect of leaking hydrogen was also included as this...”
could have a potentially harmful effect on the ozone layer. Fortunately that effect was not serious. This research into the atmospheric aspects, the question how ecosystems deal with hydrogen, had surprising outcomes. Processes in the soil and the sea were found to absorb and release hydrogen in annual cycle that is the opposite of the carbon dioxide cycle. This was previously unknown. The actual relevance of this might only become clear much later but I am very enthusiastic about it.”

**Sailing ship effect**

Berkhout: “One of the most important aspects in the energy transition is the replacement of the oil market. PhD researcher Samuel Okullo has produced a new model for the world oil market that includes the role of hydrogen in competition with oil. Oil was found to be a very robust market. A market in which combustion engines, batteries and fuel cells compete alongside each other will probably emerge for a long time. The ‘sailing ship effect’ could occur, named after the rapid innovation of the sailing ship when competition with the steamship occurred. Competition releases innovative forces and if there is choice on the market then genuine competition occurs. An important conclusion for future policy is therefore to invest in as many options as possible. Even if an option loses in the end, the investment was not wasted money. Losers make the winners better and help them to make faster progress.”

Schoot Uiterkamp: “You can clearly see that effect. Partly due to the emergence of hydrogen, battery manufacturers have worked hard on improving the battery and rapid charger technology. That has made electric (hybrid) cars so popular now. This popularity is challenging Shell, which does not have an interest in electric cars, to turn back to hydrogen. Unlike electricity, hydrogen can be spread through their distribution network. If the interest becomes big enough then the company will write off the initial losses for the distribution.

Besides more rapid innovation in the intended technology this also leads to surprising spinoffs.

An example is a hydrogen leakage study at Delft University of Technology within the Sustainable Hydrogen programme that has led to a possible medical application: in breath analysis the hydrogen level provides useful information about a patient’s state of health. There are also applications in chemical and biological reactors. Some of the expected objectives have not been reached but some unexpected objectives have been. That is the beauty of science and of this programme: it remains exciting. I am very satisfied, especially about the many young scientists who have gained their doctorates in the area of hydrogen and about the communal atmosphere that developed within the programme. Furthermore, bibliometric research has shown that in terms of number of publications and citations, Sustainable Hydrogen scores the highest of the four ACTS programmes recently investigated.”

A clear sign that public-private partnership programmes are very capable of generating both useful and highly qualitative scientific research.

**Profiling**

Berkhout: “The necessary competition in the energy mix was one reason for investing in a large hydrogen programme such as Sustainable Hydrogen. It profiles hydrogen as an important technological option. This does not require one million cars on the road. The technology advances as a result of the programme but the programme has an even bigger impact still. It influences the behaviour of large market players such as Shell and it has an impact on decisions concerning infrastructure. It will also determine, in part, how banks and other financiers will manage their investment portfolios.”

Schoot Uiterkamp: “The government has an important role too. The fuel cell car is already available. It boils down to a chicken-and-egg question: first the car or first the fuel distribution? California has already opted for hydrogen in addition to other fuels. The Netherlands ought to do the same.”
For the implementation of hydrogen as a sustainable fuel, the development of hydrogen sensors is essential. Metal hydride based optical sensors were developed, because of the large optical signals that can be obtained. Optical signals are preferred over electrical ones, since they present less danger to act as a trigger for explosion. Thus, a way was found to use so-called Surface plasmon resonance changes as a means to detect the presence of hydrogen. Also, several Pd alloys were found with a continuous change in optical properties as a function of the hydrogen pressure. A tape sensor was made from which the hydrogen pressure can be read from the distance over which the coloration has proceeded. As a result a hydrogen ‘thermometer’ was obtained.
Ronald Griessen, former member of the Sustainable Hydrogen Programme Committee and professor at VU University, says: “The ACTS programme was therefore aimed at those challenges and not at improving specific products. With input from chemists, physicists, social economists and industry, the programme had a very broad basis which made it both refreshing and exciting and gave it a clear added value. Programme members were also involved in interesting European programmes focused on physics and materials science. Interestingly, the industrial partners had every confidence that the programme committee would select the best projects. The breadth is apparent from the funding of the selected proposals: 50% concerned hydrogen storage and 20% hydrogen production. Social acceptance, integration and sensors were good for another 10% each.” Independent studies showed that the Sustainable Hydrogen Programme is scientifically very strong.

In-depth investment
“The fundamental character ensured that new knowledge was the main objective of the programme. In fundamental research surprises can happen during the quest for new knowledge. For example: prior to the programme my own group, as the result of an “accidental” discovery, switched almost entirely from high-temperature superconductivity to ‘switchable metal-hydride mirrors’. These are thin metallic layers that become transparent when brought in contact with hydrogen. They were later found to be also attractive for thin batteries. This was another surprising development. The Sustainable Hydrogen programme has yielded a wealth of new insights. The programme also brought together people and disciplines who would otherwise never have met. This led to intensive interactions during the regular conferences and workshops and to joint publications. The programme has considerably strengthened the

“Hydrogen has a promising future.”
infrastructure for hydrogen research; it was a valuable in-depth investment.”

**Promising future**

“Unfortunately, good young scientists from the programme often went abroad. Shell has still not become a hydrogen company and there is no automobile industry in the Netherlands developing a hydrogen car. At the start of the programme my group was one of the few with experience in metal-hydrogen systems in our country. Now, thanks to outstanding publications from many groups, the Netherlands has gained a clear international reputation in hydrogen research.

Personally I am proud of the discovery of ‘Hydrogenography’ in my group. Using this optical method, the hydrogen absorption in thousands of alloys can be determined simultaneously under exactly the same conditions. This facilitates greatly the search of suitable alloys for hydrogen storage or membranes. The patents for safe hydrogen detection via optical fibres are also of added value for the programme. The hydrogen economy has not yet been realised. Will it become a reality in the coming decades? The nickel-metal hydride battery, famous from the Toyota Prius and many other products, was a successful application of a metal-hydrogen system. And in the United States a Toyota fuel cell sedan car that will cost 50,000 dollars has already been announced for 2015. This is half the price of an electric Tesla. Hydrogen has a promising future.”
Hydrogen may well be the fuel of the future. It is not a direct greenhouse gas itself, and it burns cleanly to produce only water as an exhaust. Hydrogen emissions are not, however, without potential consequences for climate, atmospheric chemistry and – via formation of water vapor – for stratospheric ozone. Four Dutch major players in atmospheric and energy research – IMAU (Utrecht University), MAQ (Wageningen University), TNO and ECN – combined their expertise in atmospheric measurements and modelling to improve our understanding of the atmospheric hydrogen cycle and on Dutch emissions of this trace gas. This improved understanding allows a much better assessment of the potential chances and risks of a hydrogen economy.
“Since the combustion properties of natural gas change when hydrogen is added to it, caution should be exercised about admixing hydrogen in the natural gas grid, as has been outlined by the Dutch government. In my opinion, optimum use of sustainably produced hydrogen in the energy infrastructure requires a broad perspective. For example, the conversion of hydrogen into methane, the main component of natural gas, makes it easier to use hydrogen in the natural gas network and it also makes the decentralised use of the gas possible with existing gas utilisation equipment. In addition, the decentralised use of hydrogen in equipment specifically developed for hydrogen can be considered, such as in local transportation.”

Howard Levinsky (DNV KEMA)

“I was involved in the programme committee during the first phase of the programme”, says Howard Levinsky, former Sustainable Hydrogen Programme Committee member on behalf of GasUnie. “While I was in the committee I saw a lot of very useful fundamental research. That included research into safety aspects and the possibilities/limitations of materials for hydrogen storage in mobile applications. In the meantime a new theme concerning hydrogen storage is on the agenda: power-to-gas. In that context, storage in the natural gas network is also being considered.”

Excellent research
“I’ve seen a lot of excellent fundamental research in the programme. This has also revealed intrinsic limitations of hydrogen. Companies no longer do such fundamental research. Gaining insight into fundamental limitations is important: it can save ten years of fruitless empirical research. Obtaining clarity about what you can do and, for example how you can improve materials, is therefore a necessary step. What has the programme yielded for the parties involved? Access to all project results offers a big advantage. The parties gain a wealth of information for a fraction of the cost. One should also keep in mind that participation in the programme creates opportunities for collaboration and possibilities for support/consensus among different stakeholders.”
Hydrogen as an energy carrier is a promising option, but its eventual success will depend on the expectations of many potential user groups, such as car owners, environmentalists or engineers. Therefore, a project was started that provides a sophisticated understanding of the perceptions of stakeholders of hydrogen energy systems and helps to avoid the pitfalls of exaggerated expectations. Innovation research has pointed to the importance of visions, expectations and promises in technological development. Visions of the future are part of developing strategies many actors have. An evaluation was made of the technical, economic and other arguments used to defend or to criticize hydrogen projects by expanding the approach of learning curves.
Until three years ago he was a member of the programme committee on behalf of ECN. He left the programme committee in 2010 when he moved to become technology director at fuel cell producer Nedstack in Arnhem, a company not directly involved in the programme. “Shell already knew a lot about hydrogen production and ECN possessed the knowledge for fuel cell technology. Hydrogen storage was identified as a technical bottleneck, on which there was a lack of knowledge in the Netherlands. It was seen as good opportunity for the Sustainable Hydrogen Programme to focus the programme on this area.”

Further development
In a scientific research programme aimed at PhD studies, the programmatic outline is fixed for a long period of time. “Companies certainly have limited possibilities to adjust the course they have set out at the start. Now from a company perspective I would say: you are better off closely supervising three PhDs directly than looking at the work of almost thirty PhDs just twice per year. And my message to the government is: do not try to force industry to be involved in fundamental research. The gap to bridge is simply too large, especially for smaller companies. They have a greater need for applied scientific research that they can quickly deploy in their product and in improving the processes.”

In March 2011, De Bruijn organized a congress. “At that review moment you could see that the research was of a high level and that the programme had yielded a lot of scientific knowledge, especially about hydrogen storage. The Netherlands has gained recognition in this area. Patentable discoveries have also been made in the area of hydrogen sensor technology.” According to De Bruijn, the foundation has been laid for the next challenge: further
commercial development in hydrogen storage, also through spinoffs.

**Vision needed**

Although Nedstack only focuses on fuel cells for telecom applications that are already competitive, De Bruijn also has a clear vision for hydrogen mobility. “Why are we still playing around with the electric car despite its limited range? All prototypes for fuel cell cars have a 700 Bar fuel tank that is good for a range of 400 to 700 kilometres. They provide space for five people and the only reason why they are still too expensive is the known laws of scaling up. So the technology is already there. The only remaining obstacle is the filling station logistics. Consumers will not take to hydrogen cars unless thirty percent of filling stations sell hydrogen. Such coverage will not be realised without intervention from the government because the oil companies will not invest billions before the sale of fuel cell cars has taken off. Only the government can break through this chicken-and-egg problem. A clear vision is needed with respect to this.”
Hydrogen, if produced from renewable sources, is attractive as fuel for cars. However, efficient, compact and safe storage of hydrogen is a challenge. It can be stored as a solid: certain light metals can take up (and release upon heating) considerable amounts of hydrogen gas. Methods were developed to decrease the grain size in the powders to a few nanometres (using carbon sponges) which results in easier and faster hydrogen can be release at more moderate temperatures and pressures. Especially for complex metal hydrides, which have high storage capacities, the cycling stability was greatly improved. Also the fundamental understanding of these complex but important materials was enhanced.
Facts & Figures

Number of projects

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Participating companies

- Shell
- Nuon
- ECN
- GasUnie
- Biomass Technology Group
Members of the Programme Committee

On behalf of Shell*: Herman Kuipers, Hans Geerlings, Gert Jan Kramer
On behalf of Nuon*: Menno van Groeningen (Chair 2002-2007), Kay Damen
On behalf of ECN*: Sytze van der Molen, Frank de Bruijn, Wim Haaij
On behalf of GasUnie: Howard Levinsky
On behalf of Biomass Technology Group: Bert van de Beld

Academic members: Frans Berkhout (VU), Bernard Dam (TUD), Ronald Griessen (VU),
Petra de Jongh (UU), Joop Schoonman (TUD), Ton Schoot Uiterkamp (RUG, Chair 2007-2013),
Rob van Veen (TUe), Pier Vellinga (VU).

Programme managers on behalf of NWO-ACTS*: Theo Barenbrug, Robert van der Drift,
Susanne van Weelden, Irene Hamelers, Marieke van Santen, Marijn Hollestelle

* in subsequent order

Patent applications

1. Optical switching device, Bernard Dam (VU), Ronald Griessen (VU), Wiebke Lohstroh (VU),
   Mathieu Pasturel (VU), Martin Slaman (VU)
2. Protective coating for metalhydride based devices, Bernard Dam (VU), Mathieu Pasturel (VU),
   Martin Slaman (VU), Herman Schreuders (VU)
3. Process for preparing carbon and magnesium comprising composites, carbon and magnesium
   composites thus prepared, use of such composites and a hydrogen storage system,
   Rudy Wagemans (UU), Bibiana Dauvillier (UU), Petra de Jongh (UU), Adrianus van Dillen (UU),
   Krijn de Jong (UU)
4. Hydrogen storage material, electrochemically active material, electrochemical cell and electronic
   equipment, Peter Notten (Philips Research, TU/e), E. van Thiel (Philips Research),
   Paul Vermeulen (TU/e)
5. Inrichting en werkwijze voor het optisch detecteren van gas, Martin Slaman (VU)

Project meetings

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SUSTAINABLE HYDROGEN Projects
Metal-hydride thin films as a tool to find new/improved light weight storage materials

The essence of this work has been the development of a thin film combinatorial technique to study the thermodynamics and kinetics of the hydrogenation of metals.
Results

To extend the range of an electric car, we need a hydrogen storage system that is both light and compact. A safe way to store hydrogen is to incorporate it in a solid. The best metalhydrides available commercially today are still too heavy (typically 430 kg for the 6 kg of hydrogen necessary for a medium-sized car with a 400 km range) although the volume (68 litre) is acceptable. Magnesium-based hydrides would be significantly lighter but, due to their stability, it is difficult to desorb the hydrogen from these materials. Recent discoveries of catalysed alanates (compounds containing AlH₄ building blocks) and lithium nitrides with high hydrogen densities, have made it clear that there are completely new classes of hydrogen storage materials waiting to be explored. The search for new hydrogen storage materials and the appropriate catalysts is a work of titans if carried out on bulk samples. This is the reason why we developed a completely new combinatorial technique based on gradient composition thin film samples. By using simultaneously several sources in a suitable configuration one produces large area films (typically 7 cm in diameter) with large spatial variations in composition. The hydrogenation of such a matrix-film with hydrogen can then be observed with a video system. Here we use the fact that hydrogen absorption leads to large changes in the optical properties. With this technique it is possible to monitor typically hundreds of samples simultaneously under exactly the same conditions. We found that we can analyse both the thermodynamics and kinetics of the hydrogenations of metals. While the ideal storage material was not found, we did find a material with the required enthalpy of formation. However, due to an unexpected correlation with the entropy, the equilibrium pressure of this material appeared to be not high enough for practical applications.

Project leader
- Prof. dr. B. Dam (TUD)

Co-applicant
- Prof. dr. R. Griessen (VU)

Researchers
- Andreas Borgschulte (VU)
- Robin Gremaud (VU)
- Herman Schreuders (VU)

Duration
- 2003 - 2009

Budget
- € 284

Highlights
- We derived a combinatorial thin film technique to analyse the equilibrium pressure of hundreds of different compositions simultaneously. Our technique (hydrogenography) is now used at Ilika Inc (GB).
- This technique can also be used to calculate the enthalpy and entropy of hydrogenation in a combinatorial way.
- The optical technique can also be used for interstitial metal hydrides. We use this to verify the validity of the techniques and the conditions within which it can be applied.
Novel Nanostructured Light Metal Hydrides for Hydrogen Storage. Fundamentals and Application

Research on nanostructured metal hydride enabled us to realise absorption and release of hydrogen at much milder conditions.
Results
Renewable energy resources can be replaced, and will not run out, like sunlight, wind and water. Global energy consumption of, as an example, solar energy demands new energy storage and transport management. Hydrogen stands as a promising alternative energy source since it is clean-burning, the only byproduct is water and heat, both of which can be recycled. Key challenges for hydrogen storage include safety standards, efficiency and low-cost materials and components. Research has shown that the results of chemical bonding of hydrogen gas (H\(_2\)) with a metal forming metal hydrides are very promising. The primary focus of research has been on Magnesium (Mg) to react with H\(_2\) to MgH\(_2\). While MgH\(_2\) is too stable, leading to increasing desorption temperatures, we have focused on destabilising MgH\(_2\) by allowing thin films of Mg to become amorphous or targeting highly energetic particles. Alternatively, we could produce small particles of Mg measuring 1-10 nm (1 nm = 1 billionth metre). These tiny particles should have the potential to release H\(_2\) at lower temperatures.

Project leader
- Prof. dr. ir. K.P. de Jong (UU)

Co-applicant
- Prof. dr. F.H.P.M. Habraken (UU) †

Researchers
- Kees Baldé (UU)
- Govert Kruijtzer (UU)

Duration
- 2004 - 2008

Budget
- k€ 605

Highlights
- Nanoparticles of complex metal hydrides are deposited on carbon nanofibres via an impregnation method. A relationship was found between the size of the particles and the activation energy for desorption of H\(_2\). For nanoparticles of NaAlH\(_4\) decomposition takes place in a single step and no intermediate hydride is formed, as is the case with bulk compounds.
- These developments coincided with some expectations but the implementation required a lot due to sensitivity of nanoparticles for oxygen and water. Nevertheless, our results have been guiding for further research and have received substantial international attention.
We model hydrogen storage materials on an atomic scale using solid-state electronic structure calculations. Our central objective is to unravel the relation between structure and chemical composition of alloys, and thermodynamic, kinetic and optical properties of their hydrides.
> Results
Metals and metal alloys can absorb hydrogen in large quantities. The hydrogen is dissolved in atomic form in the crystal lattice of the metal. Minimizing the weight requires using lightweight metal alloys that adsorb and desorb hydrogen fast and at a low energy cost. We model such metal alloys on an atomic scale using solid-state electronic structure calculations. The central objective is to gain an understanding of the relation between structure and chemical composition of alloys, and thermodynamic, kinetic and optical properties of their hydrides.

We focus on magnesium-aluminium-transition metal alloy hydrides. Magnesium-aluminium-hydride, Mg(AlH₄)₂, is found to be too unstable as a hydrogen storage material, whereas magnesium-titanium-hydrides, MgₓTi(1-x)H₂, are found to be too stable. Adding Al or Si to Mg-Ti, or substituting Ti for V or Cr, destabilizes the hydrides. Controlling the structure of the atomic lattice then allows for final tuning of the hydrogen desorption energy in the required range for applications.

Thin films of metallic Mg-Ti are reflecting, but films of the corresponding hydrides are black. The contrast between these two optical states is used for hydrogen sensing purposes, for instance. Calculating the optical properties from first-principles we show that the black state is an intrinsic property of these hydrides. It is caused by interband transitions between states in a wide band around the Fermi level with significant Ti d character.

The search for lightweight materials includes first row elements, such as boron. We optimize the complex structures of a range of borohydrides. From total energy calculations, incorporating vibrational contributions at finite temperature, we show that Mg(BH₄)₂ has a favourable hydrogen desorption enthalpy. However, the reaction kinetics of borohydrides is slow and irreversible. Storage of hydrogen in molecular form might overcome these problems. We explore options such as the adsorption of hydrogen molecules on lithium-decorated boron sheets.

> Project leader
• Prof. dr. G.H.L.A. Brocks (UT)

> Co-applicants
• Prof. dr. P.J. Kelly (UT)
• Dr. ir. G.A. de Wijs (RUN)
• Prof. R. A. de Groot (RUN)

> Researchers
• Süleyman Er (UT)
• Michiel van Setten (RUN)

> Duration
• 2004 - 2010

> Budget
• k€ 26

> Highlights
• Electronic structure and optical properties of lightweight metal hydrides; van Setten, M. J.; Popa, V. A.; de Wijs, G. A.; Brocks, Geert; PHYSICAL REVIEW B 75, 035204 (2007).
• A density functional study of alpha-Mg(BH(4))(2); van Setten, Michiel J.; de Wijs, Gilles A.; Fichtner, Maximilian; Brocks, Geert; CHEMISTRY OF MATERIALS 20, 4952-4956 (2008).
• Tunable hydrogen storage in magnesium-transition metal compounds: First-principles calculations; Er, Suleyman; Tiwari, Dhirendra; de Wijs, Gilles A.; Brocks, Geert; PHYSICAL REVIEW B 79, 024105 (2009).
• DFT Study of Planar Boron Sheets: A New Template for Hydrogen Storage; Er, Suleyman; de Wijs, Gilles A.; Brocks, Geert; JOURNAL OF PHYSICAL CHEMISTRY C 113, 18962-18967 (2009).
New light-weight, Mg-based, hydrogen storage materials have been developed. It was shown that compared to the conventional rutile-structured Mg-hydride compounds, these new fluorite-structured Mg-alloys including Ti reveal remarkably facile hydrogen transportation properties. This new class of materials therefore offer great potential for both gas phase and electrochemical storage.
> Results
The application of LaNi₅-type hydrogen storage materials in rechargeable NiMH batteries has become a great commercial success in the last decade. Almost half of the small rechargeable battery market is currently devoted to this battery system, while the potentials in Hybrid Electrical Vehicles (HEV) are even greater. In addition, efficient hydride-forming materials are crucial in future Fuel Cells. A new class of materials has recently been discovered, revealing very high hydrogen storage capabilities. At the Philips Research it has been found that a specific fluorite-type of Mg-based compounds can store up to 4 times the amount of hydrogen compared to that of the conventional LaNi₅, making these new materials very attractive for extremely high energy storage devices and offering serious potentials to meet the target of 6.5 wt.% hydrogen storage set by the US Department of Energy. It has been argued that the crystallographic structure seems to play a crucial role in the favourable transportation properties. Apart from this high hydrogen storage capacity (I), other requirements have to be fulfilled, such as (II) optimum thermodynamics, i.e. more favourable hydrogen pressures, (III) the rate at which hydrogen can be absorbed and desorbed and (IV) resistance against corrosion upon repeatedly absorption/desorption. The impact of the materials composition on all these aspects is of crucial importance and will be investigated on both thin film electrodes and powder materials. The developed materials can be used for hydrogen storage in both gas phase driven and electrochemically driven energy storage devices. The developed materials can, in the bulk form, directly be implemented in both rechargeable NiMH batteries and Fuel Cells. It is to be expected that this new class of materials will strongly contribute to the development of lightweight energy storage devices and hence to the future hydrogen economy.

> Project leader
- Prof. dr. P.H.L. Notten (TUE)

> Researchers
- Peter Kalisvaart (Philips Research Europe - Eindhoven)
- Paul Vermeulen (Philips Research Europe - Eindhoven)

> Duration
- 2004 - 2009

> Budget
- k€ 517

> Highlights
- Both fluorite-structured meta-stable thin film (sputter-deposition) and bulk powders (mechanical alloying) have been designed and developed.
- Si and Al were shown to destabilize the hydride formation process in thin films.
- Extremely high scientific output as laid down in numerous publications among which the articles below can be considered as highlights:
Effects of hydrogen addition on the flame chemistry related to NOx and soot formation in gaseous hydrocarbon fuels

The research aimed to assess and understand the potential of hydrogen addition to reduce pollutant emissions for specific flame conditions relevant for practical industrial combustion systems.
Results
In the transition to a sustainable-energy future, in which hydrogen will most likely play an important role, the amount of hydrogen available will grow progressively with time. The integration of hydrogen as a fuel into the energy supply can be greatly facilitated by incorporating hydrogen into the existing infrastructure for hydrocarbon fuels. This mode of integration will be even more successful if there is some intrinsic benefit to be gained by burning hydrogen with hydrocarbon fuels, such as a reduction of pollutant emissions in the energy-intensive industry. The research program explored the potential for control of pollutant formation, specifically NOx and to a lesser extent soot, in hydrocarbon combustion by the addition of hydrogen. Towards this end, important chemical intermediates that are determining factors in pollutant formation, such as the CH radical in NOx formation, were measured in well-defined, oxygen-deprived flames burning methane as a reference fuel at low pressure. To avoid disturbing the flame processes by the use of intrusive probes, these species were measured using laser-spectroscopic methods. The results were compared with those obtained from numerical simulation of flame structure using detailed chemistry and transport, to obtain insight into the mechanistic origins of the observed behaviour. The results using 25% hydrogen in the fuel showed that under oxygen-poor situations (occurring at least locally in many industrial situations) hydrogen addition led to a significant reduction in NO formation. However, the results suggest that reduction in NOx emissions arising from hydrogen addition, at least at the hydrogen fraction studied, is limited. Further, advances were made in analysing laser-induced fluorescence to measure acetylene (a major soot intermediate) in flames. The intrinsically weak fluorescence signal at high temperatures, the high "background" signal, and substantial energy transfer in the excited state make the measurement of "native" acetylene with this technique in flames problematical.

Project leader
- Prof. dr. H.B. Levinsky (RUG)

Co-applicant
- Dr. A.V. Mokhov

Researcher
- Alexey Sepman (RUG)

Duration
- 2003 - 2007

Budget
- k€ 219

Highlights
- The research showed the mechanistic origins of changes in NO formation upon hydrogen addition.
- The research showed the importance of considering NO-precursors in the total nitrogen balance.
- The research was presented at a number of national and international (European and American) Scientific Symposia.
Pure hydrogen production out of biomass derived fuel using the steam-iron process

An important advantage of the steam-iron process over other known methods for hydrogen production is that the process can produce sufficiently clean hydrogen for use in any kind of fuel cell.
> Results

The steam-iron process is one of the oldest methods for hydrogen production. In principle, it is a cycle process for water cleavage, whereby coal is consumed. Three steps could be distinguished in the process. In the first step, coal is gasified with steam and air to produce a reducing gas containing carbon monoxide and hydrogen. This gas is reacted with iron oxides (Fe$_3$O$_4$ and FeO) in the second stage to produce reduced forms of iron oxides (FeO and Fe respectively). The reduced species are then reoxidised in the third step of the process with water to form the original oxides at the same time producing hydrogen. An important advantage of the steam-iron process over other known methods for hydrogen production is that the process can produce sufficiently clean hydrogen for use in any kind of fuel cell.

From different renewable feedstocks which can be used for the steam-iron process pyrolysis oil seems very attractive because it is a liquid and can be stored until required or readily transported to where it can be most effectively utilized, thus it can be produced at places where the biomass is cheap and abundantly available. Moreover, pyrolysis oil does not contain any contaminants present in the original biomass and it can easily be injected into a conversion system at high pressures. The overall aim of the project was to develop a process for production of pure hydrogen based on the cycle including oxidation of a “catalyst” (iron/nickel/molybdenum) with steam and its reduction with pyrolysis oil. The produced hydrogen was readily used for small and medium scale heat and power generation involving fuel cells and other advanced systems based upon hydrogen fuels.

> Project leader

- Prof. dr. H.J. Veringa (TUE)

> Co-applicants

- Prof. dr. ir. L. Lefferts (UT)
- Prof. dr. ir. W.P.M. van Swaaij (UT)

> Researchers

- Johan Agterhorst (UT)
- Mariken Bleeker (UT)
- Daryl Cusack (UT)
- Benno Knaken (UT)
- Berta Matas Guèll (UT)
- Guus van Rossum (UT)

> Duration

- 2003 - 2009

> Budget

- m€ 1
Governing the transition to a hydrogen economy: evaluation of competing hydrogen strategies from a multi-level perspective

By facilitating a science-stakeholder dialogue, tools were found to identify criteria for governing the transition to a hydrogen economy.
Results
The project focused on the feasibility of hydrogen strategies, i.e. strategies of interaction between hydrogen technologies with public acceptance, economics and international politics. Research has shown us that stakeholder participation is playing a major role for good governance, therefore consensus building is key. By facilitating a science-stakeholder dialogue, tools were found to identify criteria for governing the transition to a hydrogen economy. The project was organised into two studies. Study 1A facilitated a science-stakeholder dialogue, which integrates the five projects in the programme. Stakeholders and scientists selected technological images and trajectories. They step by step transformed these technological scenarios into competing hydrogen strategies, which was analysed in the context of the findings of the projects 2 - 4 (on public acceptance, economics and international politics). Study 1B analyses competing scientific theories with respect to the effectiveness of governance strategies. Next, an in-depth analysis of three cases highlights factors of success and failure in the implementation of (Dutch) energy innovations.

Project leader
- Dr. M. Hisschemöller (VU)

Researchers
- Ries Bode (VU)
- Marleen van de Kerkhof (VU)
- Tjeerd Stam (VU)
- Bas de Vries (VU)

Duration
- 2004 - 2009

Budget
- k€ 380
Results

Solar energy is one of the few truly sustainable and abundant sources of energy. However, since the sun does not always shine (day/night, clouds), we need a way to temporarily store the sun’s energy for later use. One way to achieve this is by converting solar energy into chemical bonds, for example in the form of hydrogen. A promising route towards this ‘solar fuel’ is to split water into hydrogen and oxygen gas in a photo-electrochemical cell. In this project, we explored new photoelectrode materials for such a device. These photoelectrodes need to combine good chemical stability in water with high conversion efficiencies. Our efforts focussed on thin film Fe$_2$O$_3$ and BiVO$_4$ photoanodes for oxygen evolution. We found that for both of these materials, a thin interfacial layer of SnO$_2$ between the photoanode and the conducting substrate strongly reduced recombination by acting as a so-called ‘hole-mirror’. In-depth electrochemical studies revealed that electron transport limits the charge separation efficiency in Fe$_2$O$_3$ and BiVO$_4$. We solved this by doping these materials with Si and W, respectively, which further improved the efficiency. These combined strategies resulted in quantum efficiencies higher than 50% for BiVO$_4$, which sets a new record for this material. Another important challenge is the external bias potentials that these materials need in order to split water. To overcome this, we constructed an n-Si/n-Fe$_2$O$_3$ heterojunction...
tandem photoanode. The n-type Si provided a bias voltage of 0.3 V, which is sufficient to make bias-free water splitting thermodynamically possible with this tandem photoelectrode. Although the efficiency was still modest, we showed that photoelectrochemical water splitting with low-cost metal oxide-based photoelectrodes is a promising route towards the sustainable production of hydrogen.

> Project leader
- Prof. dr. R. van de Krol (TUD)

> Co-applicants
- Prof. dr. M. Bonn (UL)
- Prof. dr. A.W. Kleijn (UL)
- Prof. dr. G.J. Kroes (UL)

> Researchers
- Mattijs Koeberg (UL)
- Yongqi Liang (TUD)
- Joost Middelkoop (TUD)
- Zheng-Wang Qu (UL)

> Duration
- 2003 - 2009

> Budget
- k€ 257

> Highlights
- Three of the 6 papers from this project have been cited more than 25 times:

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Optical fibre hydrogen sensors

We demonstrated an optical fibre based hydrogen detector with a threshold pressure well below the lower explosion limit of hydrogen in air.
Results

Safety is essential for the implementation of a future hydrogen based economy. For the operation of hydrogen powered devices there is a great need for sensitive, selective, fast, reliable, stable and cheap hydrogen sensors. Most of the sensors available commercially are based on electrical measurements at the sensing point. This is undesirable in potentially explosive environments. Furthermore, they are often expensive and not stable over long periods of time. These disadvantages can be circumvented by using optical detectors in which the end of an optic fibre is coated with a hydrogen sensitive layer. The changes induced in the optical properties of this layer during absorption of hydrogen are detected optically at the other end of the fibre. This type of sensors is easily scaled up to large numbers of fibres converging to a unique detector. We demonstrated the use of Mg-based alloys as the sensing layer for such an optical fiber hydrogen sensor. The great advantage of our Mg-based materials is that the optical changes occur at low concentrations of hydrogen and that diffusion of hydrogen in the sensor is sufficiently fast over a large temperature range (-40 °C to +90 °C). In this project we demonstrated the design of such a sensor. It proved vital to add not only a catalytic Pd layer, but also a protective coating to make the sensor work reliably in a humid environment.
Mechanisms of hydrogen storage in alanates; a first principles approach

This research focussed on storage of hydrogen in alanates. Alanates are compounds that contain aluminium, (stored) hydrogen, and a metal like sodium or lithium. Our investigation focussed on NaAlH₄.
> Results
In the hydrogen economy, hydrogen is used as a fuel. When energy is extracted from hydrogen, no carbon dioxide is emitted, avoiding further global warming. However, breakthroughs are needed in the area of hydrogen storage in cars to realize the hydrogen economy. Hydrogen tanks take up too much volume, or are overweight. The past 4 years computational research was performed in Leiden on hydrogen storage in sodium alanate, a compound in which hydrogen can be stored with a weight of 5.5%. In order to ensure that the hydrogen is taken up rapidly enough, a catalyst is required, such as titanium. Calculations show that a difference between “good catalysts” and “bad catalysts” is that the good ones can penetrate the surface of the sodium alanate in such a way that sodium ions are pushed out of the material. Thus, a start of a separation between sodium and aluminum ions is achieved, necessary to achieve the releasing of hydrogen. The results suggest that further experiments on catalysts with precisely this feature are necessary, in order to develop improved materials for hydrogen storage.

> Project leader
- Prof. dr. G.J. Kroes (UL)

> Co-applicants
- Prof. dr. E.J. Baerends (VU)
- Prof. dr. J.J.C. Geerlings (Shell)
- Prof. dr. G.J. Kramer (TUE)

> Researchers
- Christian van der Burgh (VU)
- Ali Marashdeh (UL)
- Julius Ojwang (TUE)
- Filipo Zuliani (VU)

> Duration
- 2004 - 2009

> Budget
- k€ 574
Lithium-silicon-nitrides: a promising class of novel hydrogen storage materials with storage capacities larger than 10 wt.%

Hydrogen storage is one of the remaining issues to enable the future hydrogen economy, Nitrides show high potential as they can store more than 10 wt.% hydrogen.
Results
As fossil fuels contribute to the green-house effect, originate from political unstable regions and their resources become exhausted, a worldwide conversion to sustainable energy technologies is required. In the near future hydrogen can take over the role of sustainable energy carrier provided some specific problems are solved. One of the issues is storage of hydrogen in a safe, economically attractive and technically feasible way. A promising option in this respect is hydrogen storage in solid state materials. So far most attention has been paid to hydrogen storage in metals, which however is limited to about 7 weight % hydrogen. In particular for mobile applications materials with higher storage capacities are searched for. Nitride materials show high potential in this respect as they can store more than 10 wt.% hydrogen. In this project a novel class of nitride materials is proposed, which are modified by deliberate substitutions to improve the reversible hydrogen storage kinetics at ambient temperatures.

Project leader
- Dr. H.T.J.M. Hintzen (TUE)

Co-applicants
- Dr. P.C.M.M. Magusin (TUE)
- Drs. R. Mallant (ECN)
- Prof. dr. P.H.L. Notten (TUE)

Researchers
- Joanna Bendyna (TUE)
- Chien-Yueh (Harrison) Tung (TUE)
- Marcel Vliex (TUE)

Duration
- 2008 - 2013

Budget
- k€ 703

Highlights
- The materials morphology rather than catalysts has a big impact on the (de)hydrogenation kinetics.
- Promising light-weight Mg-based nitrides with interesting storage properties are prepared.
Destabilized, multi-component, Mg-based hydrogen storage materials

The eventual goal of the work is to develop light-weight, bulk storage materials with near-atmospheric equilibrium pressure in the working range of fuel cells.
> Results
Hydrogen has been proposed as emission-free energy carrier in the future hydrogen economy, e.g. in fuel-cell powered cars. One of the major challenges to be overcome in realizing such hydrogen economy is finding an efficient and safe hydrogen storage medium. Mg can store 7.7 wt% hydrogen but suffers from slow absorption/desorption rates and low equilibrium hydrogen pressure. The kinetic shortcomings can be overcome by alloying Mg with Sc/Ti, which induces a change in the crystal structure from rutile to favourable fluorite. New ternary and quaternary Mg-Ti alloys will be proposed to raise the equilibrium pressure while preserving the crystallographic structure. By adopting a combinatorial electrochemical approach, new materials will be investigated to quickly scan suitable alloying elements. Subsequently, promising new compositions will be ‘translated’ into bulk materials. The eventual goal of the work is to develop light-weight, bulk storage materials with nearatmospheric equilibrium pressure in the working range of fuel cells.

> Project leader
- Prof. dr. P.H.L. Notten (TUE)

> Co-applicants
- Prof. dr. B. Dam (VU)
- Dr. E.M. Kelder (TUD)

> Researchers
- Anneke Delsing (TUE)
- Thirugna Gobichettipalayam Manivasagam (TUE)
- Kamil Kiraz (TUE)

> Duration
- 2009 - 2013

> Budget
- k€ 678
Search for new light-weight hydrogen storage materials using Hydrogenography

This work shows that the thermodynamics and kinetics of hydrogenation is strongly depending on the matrix which embeds the metal.
Results

The storage of hydrogen in metals is determined by thermodynamics. We need to find light-weight materials which desorb hydrogen at low temperatures (<100 °C). One approach to adjust the desorption temperatures is to make small nano-particles and embed them in a matrix. Both the size of the particles and their interaction with the matrix will determine the hydrogen desorption pressure.

In this project, using thin films as a model system, we investigated the interaction of the metal hydride with its surroundings. We find that the contribution of the interface energy on the desorption pressure will be small, not exceeding much more than one order of magnitude in pressure. A much larger effect is found to be due to the plastic and elastic interactions that occur due to the large lattice expansion of the metal on hydrogenation. These effects, however, mainly affect the hydrogen absorption rather than the desorption pressure. A surprising result of our study was that we could visualize the nucleation and growth behaviour of 10 nm thin Mg films, using a simple optical technique. From these experiments we learned that the nucleation of the metal hydride in the metal phase is an important factor governing the kinetics of hydrogen absorption. The general conclusion of our study is that the effect of the matrix on the hydrogenation properties of metallic nano-particles is governed predominantly by the plastic deformation which is due to the 30% volume expansion of the metal on absorption of hydrogen.

Project leader
• Prof. dr. B. Dam (TUD)

Co-applicant
• Prof. dr. R.P. Griessen (VU)

Researchers
• Lennard Mooij (TUD)
• Andrea Baldi (VU)
• Matteo Filippi (TUD)
• Martha Gonzalez-Silveira (VU)
• Yeukekiy Pivak (TUD)

Duration
• 2008 - 2013

Budget
• k€ 892

Highlights
• We demonstrated the effect of interface energy on the hydrogenation pressure of Magnesium.
• We visualized the nucleation and growth behaviour in 10nm thin Magnesium films.
• From the nucleation and growth behaviour we calculated the plastic deformation involved in the hydrogenation process.
In situ NMR analysis of hydrogen storage materials

The design and optimization of hydrogen storage materials requires detailed microscopic insight in the local structure, disorder and dynamics. In this project we developed new thin film NMR methods for in situ measurements on these materials with exceptionally high sensitivity. An example is the first observation of low concentration mobile hydrogen in photochromic YHxOy films.
Results
The design and optimization of hydrogen storage materials requires detailed microscopic insight in the local structure, disorder and dynamics. NMR is potentially the most powerful technique to give this information. A possible route to find suitable materials is “combinatorial chemistry” which means that the composition of materials is varied systemically. Compositions that show favourable performance can then be further optimized. Using thin films of material this can be done with a very low consumption of base materials and essentially zero waste production. Traditional NMR is well established for crystals, powders and liquids, but not for thin film configurations. In this project we have developed a new setup for thin film NMR. The result is an NMR probe with exceptionally high sensitivity, sufficient to monitor hydrogen storage materials with a thickness of about 1 micron in near real time. An example is the observation of low concentration mobile hydrogen in photochromic oxygen containing Yttrium Hydride films. These results are compared with NMR measurements of powders or jelly-roll films with high resolution MAS-NMR as function of temperature and hydrogen content. This combination provides microscopic insight in the nano-structure and hydrogen dynamics that is crucial for future applications. For the alanates we have shown that nanostucturing on a carbon matrix can favourably change the kinetics and thermodynamics of reversible hydrogen storage. For borhydrides we can monitor the diffusion and rotational mobility of the various nuclei and molecular complexes as function of composition and temperature.
A new concept for NMR imaging, comparable with medical MRI but with superior sensitivity, resolution and spectral specificity is introduced. Proof of principle is given and compatibility with thin film geometries is demonstrated. The main advantage is that the imaging modality does not use switched magnetic field gradients and spectral resolution is not compromised.

Project leader
• Dr. P.J.M. van Bentum (RUN)

Co-applicant
• Prof. dr. A.P.M. Kentgens (RUN)

Researchers
• Jacob Bart (RUN)
• Vinodchadran Chandrasekharan Nair (RUN)

Duration
• 2009 - 2013

Budget
• k€ 331

Highlights
• New probe technology developed for thin film NMR.
• New NMR imaging methodology with RF gradients.
• NMR insight in the effect of nanostucturing on kinetics and thermodynamics.
• NMR insight in the mechanism for photochromic effects in YHxOy.
Hydrogen surface adsorption in porous crystalline materials

Hydrogen storage characteristics of highly porous Metal Organic Frameworks (MOFs) were studied. These materials are built from organic linkers that bind metal ions in a three dimensional crystalline porous structure.
Hydrogen storage is a major bottleneck for the implementation of a hydrogen based renewable energy economy. In this project we studied the hydrogen storage characteristics of highly porous Metal Organic Frameworks (MOFs). These materials are built from organic linkers that bind metal ions in a three dimensional crystalline porous structure. The structure is so porous that it contains a large internal surface on which small molecules like hydrogen (H\textsubscript{2}) can be adsorbed and thus stored for later use. Since the adsorption interaction is fairly weak these materials need to be cooled to temperatures typically around 80 K, and also a hydrogen pressure needs to be applied to keep the hydrogen in. An advantage of the weak interaction is that loading and unloading of hydrogen can be performed rapidly (within minutes) in large quantities without heating or mechanical problems.

In this project we determined the influence of the chemical structure of the MOF’s on the adsorption characteristics of hydrogen in the pores, and for that purpose designed and synthesized various MOF’s. One approach has been to modify the chemical linkers in the MOF’s by adding side groups to it. The so called MOF-5 material was used as a model system since this MOF has a record uptake capacity at 77K and 100Bar. With respect to the adsorption interaction it appeared that a large number of methoxy groups can increase the adsorption interaction in MOF-5, while other types of side groups show hardly an effect (e.g. Br or Cl ions). A most interesting observation is that adding methyl side groups to the benzene linkers of MOF-5 has a beneficial effect on the stability of the structure against moisture. This is relevant when applications of MOF-5 as hydrogen gas storage are considered since any moisture in the hydrogen should not disturb the operational characteristics over long time use.

New types of linkers were considered and synthesis efforts performed, either shorter linkers to make the pores smaller or less bulky ones to observe the effect of pore shape. The lessons learned here are that the small linkers prevent the removal of solvent molecules and result in poorly crystalline materials. The less bulky linkers also showed limitations in the sense that they enable interpenetration of two MOF crystals where one MOF grows through the pores of the other, and again too small pores result for solvent removal. Both types of MOFs did not show improved hydrogen sorption characteristics.
Nanostructured hydrogen storage materials: the benefits of particle size effects and support interaction

If you squeeze metal hydrides, important materials for reversible storage of hydrogen as an energy carrier, into a very small space (nanoconfinement) this dramatically changes the fundamental properties of these materials. As a result hydrogen can be release and absorbed much faster, and capacity losses during cycling can be minimized.
Results

Hydrogen, if produced from renewable sources, is attractive as fuel for cars, or as renewable electricity storage option, as it does not lead to the emission of polluting or greenhouse gases at the point of use. However, efficient, compact and safe storage of hydrogen is a challenge. Hydrogen gas is voluminous and difficult to compress, while liquefaction takes much energy. To solidify hydrogen is no option, but it can nevertheless be stored as a solid: certain light metals can take up (and release upon heating) considerable amounts of hydrogen gas.

Many metal hydrides are being considered, but non satisfies all requirements such as fast hydrogen uptake and release, mild uptake and release conditions, and cycle ability. We investigated the possibility to improve the properties of known light metal hydrides by making use of size and confinement effects. We studied the processes during cycling with hydrogen, in an approach that combined the study of model systems, thin films, and theoretical calculations, to better understand these systems. We developed methods to decrease the grain size in the powders to a few nanometres (using carbon sponges) which results in easier and faster hydrogen release at more moderate temperatures and pressures. Especially for complex metal hydrides, which have high storage capacities, the cycling stability was greatly improved.

We also published the first diagram showing how nanoconfinement changes the stability of the phases, adding to the fundamental understanding of these complex but important materials.

Project leader

- Dr. P.E. de Jongh (UU)

Co-applicants

- Dr. J.H. Bitter (UU)
- Prof. dr. B. Dam (VU)
- Prof. dr. ir. K.P. de Jong (UU)
- Prof. dr. G.J. Kroes (UL)
- Dr. R.A. Olsen (UL)

Researchers

- René Bogerd (UT)
- Francesca Costanzo (UL)
- Peter Ngene (UT)
- Ilaria Pino (UL)
- Rien van Zwienen (UU)
- Jinbao Gao (UU)
- Qiang Zheng (TUD)

Duration

- 2008 - 2013

Budget

- k€ 1092

Highlights

- Confinement of NaAlH₄ in nanoporous carbon: impact on H₂ release, reversibility and thermodynamics

- Nanosizing and confinement: new strategies towards meeting hydrogen storage goals

- Nanoscale composition modulations in MgₓTi₁₋ₓHₓ thin film alloys for hydrogen storage

- Hydrogen dissociation on small aluminum clusters,
  Pino, I., Kroes, G.J., Van Hemert, M.C., 2010, Journal of Chemical Physics 133 (18), art. no. 184304
Atomistic modelling of advanced hydrogen storage materials

We model hydrogen storage materials using first-principles calculations in order to advance their development by understanding the relation between their chemical composition and atomistic structure, and their thermodynamic, kinetic, and spectroscopic properties.
Results
We model hydrogen storage materials using first-principles calculations to advance their development by understanding the relation between their chemical composition and atomistic structure, and their thermodynamic, kinetic, and spectroscopic properties. Metal alloys can absorb hydrogen in large quantities, but are often too heavy for a practical hydrogen storage medium. Combinations of lightweight metals and first-row elements as boron and nitrogen can chemically bind large amounts of hydrogen, and are sufficiently light. However, the chemical reactions involved in hydrogen absorption and desorption of these materials tend to be slow and hardly reversible. Such reactions require mass transport through bulk solids, which proceeds by means of lattice defects. The study of the structure and abundance of such defects gives insight in the reaction mechanisms. We find that in alkali borohydrides and nitrohydrides the most prominent mass transporting defects are simple charged vacancies (missing ions). Hydrogen desorption reactions inside the bulk materials imply creating defects with a large formation energy. Such reactions are much more likely to proceed at the surfaces of hydride particles. The beneficial effect of adding alkaline earth or transition metals or compounds results from promoting surface reactions or from modifying surface morphology.

From explicit studies on lithium borohydride nanoparticles we conclude that downsizing the particles does not decrease the reaction enthalpy of hydrogen desorption in these compounds, suggesting that the experimentally observed improvement of (de)hydrogenation properties of nanoparticles can be attributed to improved reaction kinetics. Embedding the particles in a nanoporous graphitic host only mildly influences the reaction thermodynamics, mainly because of the intercalation of the reaction product lithium in the host material.

Nuclear magnetic resonance (NMR) is an important experimental technique to obtain structural information on small particles. We model cluster motion and chemical shifts in alkali aluminium- and boro-hydrides to help elucidate NMR experiments.

Project leader
- Prof. dr. G.H.L.A. Brocks (UT)

Co-applicants
- Prof. dr. R.A. de Groot (RUN)
- Prof. dr. P.J. Kelly (UT)
- Dr. ir. G.A. de Wijs (RUN)

Researchers
- Süleyman Er (UT)
- Ebrahim Hazrati (RUN)

Duration
- 2008 - 2013

Budget
- k€ 561

Highlights
- Native Defects and the Dehydrogenation of NaBH₄; Cakir, Deniz; de Wijs, Gilles A.; Brocks, Geert; JOURNAL OF PHYSICAL CHEMISTRY C 115, 24429-24434 (2011).
- First-Principles Study of LiBH₄ Nanoclusters and Their Hydrogen Storage Properties; Hazrati, Ebrahim; Brocks, Geert; de Wijs, Gilles A.; JOURNAL OF PHYSICAL CHEMISTRY C, 18038-18047 (2012).
- Carbon Support Effects on Confined LiBH₄ Nanoparticles: A First-Principles Study; Hazrati, Ebrahim; Brocks, Geert; de Wijs, Gilles A.; JOURNAL OF PHYSICAL CHEMISTRY C, to be submitted.
Realisation and application of in-situ TEM of hydrogen storage materials at 1-10 bar hydrogen pressure and 200°C

Breaking the pressure boundary in electron microscopy.
Results

The objective of the project was to realise a set of tools that would allow for the in-situ study in a transmission electron microscope of the (de)hydrogenation of hydrogen storage materials on a nanometre scale. The main scientific result is that we realised a holder/nanoreactor combination that does allow in-situ (de)hydrogenation in a transmission electron microscopy (TEM) up to at least 4.5 bar, which has never been shown before. It is a remarkable result because the TEM requires an very high vacuum and only by applying very thin electron transparent membranes (typically 10-20 nm) and a very short gas column one can realise this pressure around the sample and still have a low enough scattering of the membranes and gas column to allow TEM imaging. We expect that this approach will become an important milestone in the route to all kinds of in-situ TEM experiments.

Other results of the project are: a) the modelling and testing of several shapes to realise thin membranes that allow for a high pressure difference (up to 10 bar), b) a study of the (de)hydrogenation of Pd up to 4.5 bar, whereby the (de)hydrogenation of individual Pd nanoparticles could be followed, c) an in-situ TEM study of the oxidation and reduction of Pd at temperatures up to 600°C and pressures up to 1.5 bar. Furthermore apart from the sample holder and nanoreactors, an alignment tool for alignment of the two MEMS parts of the nanoreactor with micrometre precision have been realised.

Project leader
- Prof. dr. H.W. Zandbergen (TUD)

Co-applicants
- Dr. ir. J.F. Creemer (TUD)
- Prof. dr. J.J.C. Geerlings (Shell)
- Dr. P.J. Kooyman (TUD)

Researchers
- Eef Graffhorst (TUD)
- Meng-Yue Wu (TUD)
- Tadahiro Yokosawa (TUD)
- Tuncay Alan (TUD)

Duration
- 2008 - 2013

Budget
- k€ 684

Highlights
- We have realised a holder/nanoreactor/micro-manipulator combination that does allow in-situ (de)hydrogenation in a transmission electron microscopy (TEM) up to at least 5 bar, which has never been shown before.
- The (de)hydrogenation of Pd up to 5 bar, whereby the (de)hydrogenation of individual Pd nanoparticles could be followed, with a good comparison with other techniques, but now on a nanometer scale.
- The size and shape of electron transparent thin membranes was modelled and tested allowing us to go to 10 bar.
Promoted hydrogen storage in nanoporous clathrate hydrate materials with enhanced storage capacity

The van der Waals interaction between hydrogen molecules and promoter is specific enough to the promoter molecule to influence the order of stability of the hydrates.
Results
The overall aim of the joint project was to find a promoter that stabilises a sH clathrate hydrate storing 5 weight percent of hydrogen, focusing on promoter molecules that would stabilise the medium-sized cage. Quantum dynamic calculations were performed of the translation-rotation (T-R) energy levels of one molecule of p-H\textsubscript{2}, o-H\textsubscript{2}, o-D\textsubscript{2}, p-D\textsubscript{2} and HD inside the small, medium and large cages of the sH clathrate hydrate using the MCTDH method.
Calculations of 2 hydrogen molecules inside the cages of the sH hydrate clathrate have also been done. We have performed 10-dimensional quantum dynamic calculations of the translation-rotation energy levels of two molecules of p-H\textsubscript{2}, o-H, o-D\textsubscript{2}, p-D\textsubscript{2}, and HD inside the small, medium, and large cages of the sH clathrate hydrate using the MCTDH method.
Molecular dynamics simulations at constant temperature and pressure have been performed to study the stability of pure sII clathrate hydrates (8 promoter organic molecules per 136 water molecules) and binary sII clathrate hydrates (8 promoter organic molecules and 16 hydrogen molecules per 136 water molecules). The TIP5P potential was used to describe the interaction between the water molecules, whereas promoter-promoter and water-promoter interactions were described by a GAFF potential.
The effect of microscopic properties of promoter molecules on the macroscopic properties of the pure and binary hydrates was investigated through computation of guest-water interactions as well as hydrogen bonding occurrences, guest-guest interactions, distortion of the beta-lattice of water molecule and volume. The validity of our simulations was checked by comparison with experimental results from the literature. The van der Waals interaction between hydrogen molecules and promoter is specific enough to the promoter molecule to influence the order of stability of the hydrates. Our study suggests the following rules for selecting promoters for hydrogen storage in clathrate hydrates: (A) Promoter molecules forming energetically stable pure clathrate hydrates likely form energetically stable binary hydrates with H\textsubscript{2}, and (B) promoter molecules containing protruding sp\textsuperscript{2} atoms or many halogen (F) atoms are likely to yield binary hydrates with further improved energetic stability due to their favourable interaction with H\textsubscript{2}.

Project leader
- Prof. dr. ir. C.J. Peters (TUD)

Co-applicant
- Prof. dr. G.J. Kroes (UL)

Researchers
- Jiancheng Chen (UL)
- Alondra Torres Trueba (TUD)
- Sebastien Rives (UL)
- Alvaro Valdés de Luxán (UL)

Duration
- 2009 - 2013

Budget
- k€ 572
Hydrogen sensors and safety detectors for the hydrogen economy

Sensing technology is one of the enablers of the implementation of hydrogen technology. For this technology cost reduction, reliability, and safety are of the utmost importance. Our optical technology is inherently safe and contributes to the portfolio of techniques that is needed in this field.
Results

For the implementation of hydrogen as a sustainable fuel, the development of hydrogen sensors is essential. We choose to develop metal hydride based optical sensors, because of the large optical signals that can be obtained. Optical signals are preferred over electrical ones, since they present less danger to act as a trigger for explosion. We obtained the following results:

1. We found a way to use so-called Surface plasmon resonance changes as a means to detect the presence of hydrogen. With this technique several points of measurement may be obtained in a single fibre. For this technique part of the fibre cladding is removed and a Au/SiO₂/Pd layer stack is deposited. The optical changes in Pd due to hydrogenation, are then monitored by a change in the resonance wavelength. In principle, the same layout can be used replacing Pd with, for example, a Mg/Pd stack. The equilibrium pressure of the MgH₂ then largely determines the optical response, which results in a hydrogen detector operating at lower hydrogen pressures.

2. We found several Pd alloys not having a defined plateau pressure. In these materials we find a continuous change in optical properties as a function of the hydrogen pressure. The optical contrast of this material is large enough to act as a sensor over 1-2 orders of magnitude in pressure. The absence of a hysteresis implies that this sensor can be used under conditions in which the pressure oscillates.

3. We made a tape sensor from which the hydrogen pressure can be read from the distance over which the coloration has proceeded. This is based on a so-called wedge layer of Mg. Due to the plastic interaction with the Pd-caplayer, the hydrogenation pressure depends strongly on the Mg thickness. As a result we obtained a hydrogen ‘thermometer’. Unfortunately, it is for single use only! However, it reliably indicates the maximum pressure obtained.
Catalytic hydrothermal generation of hydrogen from aqueous biomass streams: Integration with a crude oil refinery

Efficient catalytic reactor technology for the valorisation of low or no value aqueous waste biomass stream via its conversion to hydrogen.
> Results
Hydrogen is an energy carrier on which future energy applications of mobile (e.g., automobiles) or stationary (electricity generators) situations can be met in the future. The Aqueous Phase Reforming process in general and the integration of the APR process in a bio-refinery to produce hydrogen from waste, e.g. aqueous waste biomass streams, allows for a completely green fuel development. Current non-catalytic challenges with APR of the aqueous fraction of pyrolysis oil prevent feasible exploitation of this process. However, it is projected that the catalytic APR technology developed in this project is applicable for reforming of such aqueous bio/organic aqueous waste streams and also others that are produced in large quantities including in the paper and food production industry.

The main achievements of the project, involved the development of a stable catalyst support for APR in sub- and supercritical water, which formed the basis for the design of an efficient APR catalyst for reforming of challenging model compounds.

The developed Ru/CNT catalyst did not only show remarkable stability for supercritical water APR of acetic acid but also showed commercially relevant reforming rates. Reforming of real aqueous waste streams revealed that the process is subjected to engineering challenges which should first be overcome before the developed catalyst can be further assessed.

> Project leader
- Prof. dr. K. Seshan (UT)

> Co-applicants
- Prof. dr. S.R.A. Kersten (UT)
- Prof. dr. ir. L. Lefferts (UT)
- Dr. ir. G. van Rossum (UT)

> Researchers
- Bert Geerdink (UT)
- Dennis de Vlieger (UT)
- Jitendra Kumar Chinthaginjala (UT)
- Erna Fränzel-Luiten (UT)
- Henk Naafs (UT)

> Duration
- 2008 - 2013

> Budget
- k€ 607

> Highlights
- Design of catalysts that can cope with acidic and fouling conditions present for the efficient conversion of oxygenates present in aqueous biomass streams.
- Stable catalysts based on Ni-Pt/CNT, (Caron Nano Tubes) developed gives, high hydrogen yields with minimal methane/alkanes formation (< 2%) and use of Ni which also allows use of cheaper catalyst.
- Reactor design for a heat integrated hydrogen production process in hot compressed water at elevated temperatures (<350°C) and pressures (<450 bars) in which continuous operation is feasible for feeds with no or minor homogeneous coking tendency.

We have demonstrated that from a long-term techno-economic perspective hydrogen may well prove the optimal transport fuel during the 2nd half of the century - electricity could dominate if electric car costs go down by more than an extra 40%.
> Results
The political ambitions to move away from the present fossil fuels based energy system towards a more sustainable energy system are high. Energy security and climate change are the key driving forces. The use of hydrogen as an energy carrier is often viewed as a key solution for such a sustainable energy future. However, it is highly unlikely that hydrogen technologies will be able to compete with fossil fuel alternatives in the near future, while in the long run they may have trouble competing with alternative technologies based on solar, nuclear or biomass. From an economic perspective the prospects for a hydrogen economy are strongly dependent upon major cost reductions of hydrogen technologies combined with considerable price escalations of conventional fossil fuels. The present study explores the future environmental promise of hydrogen technology in the light of both potential cost reductions of hydrogen technology in Europe and potential price escalations on global fossil fuel markets. To this end we use a detailed model of European energy system transitions in combination with a comprehensive model of global fossil fuel depletion. Thus we can obtain a more accurate picture of the economic conditions required for the hydrogen economy as a sustainable solution and the consequences such conditions may have for R&D and deployment policies for hydrogen technology.

> Project leader
- Dr. B.C.C. van der Zwaan (ECN)

> Co-applicants
- Prof. dr. J.J.C. Bruggink (VU)
- Dr. R.B. Dellink (VU)
- Prof. dr. M.W. Hofkes (VU)
- Drs. H. Rösler (VU)

> Researchers
- Samuel Okullo (VU)
- Frédéric Reynes (VU)
- Hilke Rösler (ECN)
- Ikka Keppo (ECN)

> Duration
- 2008 - 2013

> Budget
- k€ 579

> Highlights
- In our approach transportation decarbonizes later than e.g. power production.
- Hydrogen becomes the dominant transport fuel during the 2nd half of the century.
- Electricity dominates if electric car costs go down by more than an extra 40%.
- This holds even if H₂ infrastructure proves much more costly than assumed today.
Socio-economic modelling and simulation of hydrogen infrastructure development strategies

In the transition towards a sustainable transport system different alternative vehicle technologies compete, such as hydrogen and electric cars, to replace the dominant internal-combustion-engine vehicles. We study the interplay between car manufacturers producing vehicle technologies, consumers adopting these vehicle technologies and policy instruments implemented by governments in order to accelerate the diffusion of more environmentally friendly technologies.
Results
The transition to a more sustainable transport system requires the replacement of current vehicle technologies by more environmentally friendly vehicle technologies, such as hydrogen fuel-cell vehicles. This substitution process is very difficult and time consuming due to the lock-in into fossil fuel-based technologies. Overcoming lock-in of these existing technologies is hard due to several reasons, such as a lack of refueling stations and high initial prices of hydrogen vehicles. An additional barrier for substitution to occur that we found in this research is the competition between hydrogen, electric and other vehicle technologies. This research project focuses on the transition towards a more sustainable transport system in general and greening of the market for passenger cars in particular. We address the replacement of current vehicle technologies by more environmentally friendly vehicle technologies that have either a radical or incremental nature. We study the interplay between car manufacturers producing vehicle technologies, consumers adopting these vehicle technologies and policy instruments implemented by governments in order to accelerate the diffusion of more environmentally friendly technologies. We found that governments can accelerate this transition with policy instruments. Governments should select a limited range of alternative vehicle technologies that receive specific support. The selected technologies need to be sufficiently different in terms of technology to increase the opportunity to pick a successful one. When technologies are more similar it is important that they have a common infrastructure to benefit from network externalities. When governments want to support the technologies with various instruments simultaneously careful evaluation is necessary.

The direct costs of different support instruments can rise quickly without generating significant additional benefits. It is important that policy instruments target both sides of the coin: encourage the adoption of hydrogen vehicles and discourage the usage of polluting technologies. For manufacturers we found that frontrunners in CO₂ reduction experienced the highest relative increase in sales in the Netherlands.

Project leader
• Prof. dr. M.P. Hekkert (UU)

Co-applicants
• Dr. F. Alkemade (UU)
• Prof. dr. H.M. Amman (UU)
• Dr. P.J. Engelen (UU)
• Dr. T.B. Klos (CWI)
• Prof. dr. C.J.M. Kool (UU)
• Dr. T. Poot (UU)
• Prof. dr. J.A. la Poutré (CWI)
• Prof. dr. ir. R.E.H.M. Smits (UU)

Researchers
• Ye Li (UU)
• Alexander van der Vooren (UU)
• Aschwin Engelen (UMC Utrecht)

Duration
• 2008 - 2013

Budget
• k€ 425

Highlights
Articles:
• A. van der Vooren, F. Alkemade, and M.Hekkert (IN PRESS). Environmental Performance and Firm Strategies in the Dutch Automotive Sector. Transportation Research part A.
The impact of a future hydrogen economy on atmospheric composition and climate

We investigated the global cycle of atmospheric hydrogen with particular emphasis on using the isotopic composition.
Hydrogen may well be the fuel of the future. It is not a direct greenhouse gas itself, and it burns cleanly to produce only water as an exhaust. Hydrogen emissions are not, however, without potential consequences for climate, atmospheric chemistry and – via formation of water vapour – for stratospheric ozone. Unfortunately, those consequences can only be estimated roughly because the atmospheric cycle of hydrogen has been studied little in the past. In the present project four Dutch major players in atmospheric and energy research combine their expertise in atmospheric measurements and modelling to improve our understanding of the atmospheric hydrogen cycle and on Dutch emissions of this trace gas. This improved understanding will allow a much better assessment of the potential chances and risks of a hydrogen economy.

> Project leader
- Prof. dr. T. Röckmann (UU)

> Co-applicants
- Prof. dr. ing. J.W. Erisman (ECN)
- Prof. dr. M.C. Krol (WUR)
- Dr. M. Schaap (TNO)
- Ir. A.T. Vermeulen (ECN)
- Dr. E. Weijers (ECN)

> Researchers
- Anneke Batenburg (UU)
- Maarten Krol (UU)
- Elena Popa (UU)

> Duration
- 2008 - 2013

> Budget
- € 466

> Highlights
- Results from our group (and other groups internationally) on the atmospheric hydrogen cycle have resulted in a considerably improved understanding of the global budget, which is apparent from our global model study (Pieterse et al., 2013). Many individual processes have been characterized better, recently also the contribution from the present vehicle fleet (Popa et al., 2013). The variability of hydrogen at the tall tower in Cabauw has been characterized in considerable detail, including the isotopic composition (Popa et al., 2011, and Batenburg et al., 2013). The variability of the isotopic composition on the European and Global scale was determined for the first time over several annual cycles (Batenburg et al., 2011). The results from the regional model on the implications for a future hydrogen economy on the European scale are expected soon.
Storage of hydrogen as clathrate hydrate: kinetic and storage capacity aspects

This was an exploratory study, leading to the research “Promoted hydrogen storage in nanoporous clathrate hydrate materials with enhanced storage capacity”.
Results
The kinetics of formation and decomposition of hydrogen clathrate hydrate is studied for the first time. Experimental data on hydrogen hydrate formation kinetics in a pressure range from 5.5 to 15.0 MPa are reported. Experiments were carried out for the binary system $\text{H}_2 + \text{THF}$, which forms structure sII clathrate hydrate. The effect of initial pressure on the induction time, the rate of hydrate formation, the number of gas moles consumed and the temperature at which the hydrate formation takes place was evaluated and the results obtained suggest that higher pressures are favorable for the occurrence of hydrogen clathrate hydrate. The findings of this study provide most valuable information with respect to the applicability of hydrogen clathrate hydrates as a storage medium in the transportation sector.
Novel Mg-containing nanocomposites for reversible hydrogen storage under mild conditions

This was a short extension of the project described on page 59, to explore whether a technique to produce small Mg particle is promising enough to consider a patent application.
Results
A simple method has been identified to prepare MgH₂ crystallites with a size of only a few nanometers. Regarding applications optimisation is still needed to further increase the Mg loading of the samples, and to decrease the amount of bulk Mg. A patent application has been filed to protect the invention.

Project leader
- Dr. P.E. de Jongh (UU)

Co-applicants
- Prof. dr. ir. K.P. de Jong (UU)

Researchers
- Rudy Wagemans (UU)

Duration
- 2006 - 2006

Budget
- k€ 50

Highlights
Intermetallic nanopowders for hydrogen storage produced via Spark Discharge Generation

Novel metal alloys for use as hydrogen storage materials have been produced with two advanced methods, i.e. spark discharging magnesium-titanium electrodes fabricated via magnetic pulse compaction.
Catalysed storage of hydrogen gas in light metals or alloys (intermetallics) is an important field of research for obtaining safe storage systems. Magnesium-titanium alloys were already identified as potential candidates, but were difficult to produce as thin films. Here we have fabricated Mg-Ti alloys via so-called spark discharge generation (SDG), so as to synthesize these thermodynamically instable materials.

The principle is as follows: two electrodes made of selected materials are separated by a few millimetres and then subject to an adjusted voltage so to create a spark discharge. The materials are then melted and brought into the gas phase as nanoparticles. The frequency of the discharges determines the production rate. The discharge takes a few seconds and the temperature can reached about 20000 K. Cooling down of these generated particles goes by 10^10 K/s. The used mixed electrodes were fabricated via a non-conventional densification method referred to as Magnetic Pulse Compaction. The main goal was to synthesize a Mg-Ti alloy with well-defined composition that has a storage capacity of 1500-2000 mAh/g. Using SDG we were able to produce nano-crystalline Mg-Ti powders as measured with electron microscopy. The actual composition was difficult to established, but contained mainly Mg and Ti, but also oxygen as a result of partial oxidation. This oxidation behaviour is also an indication of the pyrophoric behaviour of the nano-particles.
Hydrogen indicator tape

We developed a hydrogen tape sensor which indicates the presence of lactose intolerance by a change in colour when exposed to exhaled breath.
Results
Currently the introduction of hydrogen applications is hampered by many of its properties. Hydrogen is a colourless, light-weight, odourless and extremely flammable gas. Unlike natural gas, it is not possible to add a odorant to indicate its presence. Current hydrogen detection systems are expensive, require electronic readout systems and are large in volume. In this project we developed a “hydrogen indicator tape”. This tape will warn through a colour change that a tube, seal, or tank, is leaking hydrogen. Due to the small size, the low cost and the lack of electronics, other hydrogen related applications are envisaged as well. I.e. the presence of hydrogen producing bacteria can be detected in food, resulting in a “freshness” indicator and hydrogen present in the breath of a patient can help doctors diagnose lactose in-tolerances.

Project leader
• Prof. dr. B. Dam (TUD)

Co-applicant
• Ing. M.J. Slaman (VU)

Researchers
• Peter Ngene (TUD)
• Tsveta Radeva-Mandzhukova (TUD)

Duration
• 2011 - 2013

Budget
• k€ 280

Highlights
• We found that Yttrium can be used as a sensing material to monitor lactose allergy through measuring the hydrogen concentration in breath.
• We developed a catalyst which allows hydrogen detection at high humidities.
• We found a way to enhance the colour contrast such that an eye-readable tape sensor is obtained.
Melt infiltration of porous matrices with light metals, alloys or hydrides, to prepare nanostructured materials for energy storage

Sometimes making advanced materials can be simple. In this project we explored a novel approach to make nanocomposites: simply melting one of the components into a second component that acts as a sponge. The resulting materials, in which the two components are intermixed on a nanoscale, show advanced energy storage properties.
Results
An interesting challenge with renewable energy resources such as sunlight and wind is that we cannot control them. Typically the electricity production from these resources does not match the electricity need of the consumers. Hence large scale cost-effective energy storage is crucial, and novel nanostructured materials, preferably composed of light and earth-abundant elements, have to be designed and produced to facilitate this. Electricity can be efficiently stored in batteries. Using electricity to produce hydrogen from water is an alternative. In this project we explored the potential of a new method, melt infiltration, for the production of light, nanostructured materials for energy storage.

Project leader
- Dr. P.E. de Jongh (UU)

Co-applicant
- Dr. W.G. Haije (ECN)

Researchers
- Christina Bossa-Knöfel (UU)
- Tamara Eggenhuisen (UU)
- Suwarno Suwarno (UU)
- Rien van Zwienen (UU)

Duration
- 2011 - 2013

Budget
- k€ 234

Highlights
Measuring expectations of hydrogen energy systems

This project measures expectations about future technical and market possibilities of hydrogen as an energy carrier, and shows how expectations determine investments and directions of research, as well as decisions to adopt new technologies.
Hydrogen as an energy carrier is a promising option, but its eventual success will depend on the expectations of many potential user groups, such as car owners, environmentalists or engineers. It will also depend on how these user groups will respond to unavoidable disappointments and exaggerated expectations. New technologies are vulnerable, due to these “waves” of expectations that generally occur. To measure these expectations is the first step to be made, the first challenge of this project. As expectations are about future technologies, that is, about issues that do not yet exist, simple methods to measure them cannot be used. What is needed in particular is a method that can account for the varies degrees of knowledge and interests amongst potential user and stakeholder groups. Expectations have been measured by carefully following different actor constituencies, such as researchers of metal hydrides, car manufacturers and an US evaluation committee of hydrogen energy programs. The second step of the project was to analyse how the expectations are related to actual research and development work. This has been assessed by considering patents filed by car manufacturers and more than 200 prototypes, which are both proofs of technical achievements and claims of future developments. New insights are that decisions of researchers, firms and government actors are coordinated by expectations. It is also shown that expectations about future technologies compete: which one is the most promising? This project provides a sophisticated understanding of the perceptions of stakeholders of hydrogen energy systems and helps to avoid the pitfalls of exaggerated expectations.

**Project leader**
- Prof. dr. ir. H. van Lente (UU)

**Co-applicants**
- Dr. A.R.T. Donders (UU)
- Prof. dr. M.P. Hekkert (UU)
- Prof. dr. M.T.H. Meeus (UU)

**Researcher**
- Sjoerd Bakker (UU)

**Duration**
- 2006 - 2011

**Budget**
- k€ 194

**Highlights**
- Publication in Research Policy:
  Bakker, S., Van Lente, H., Meeus, M.T.H.
Towards a Winning Hydrogen Economy?
The Dynamics of a Techno-Institutional Co-evolution

This research is about designing an institutional arrangement that might help a government to initiate a transition towards a hydrogen economy. We show that a suitable application of mechanism design, a game in which strategic moves are translated into technology choices, provides the best chance for a hydrogen technology transition.
Results

The main objective of our project is to define a possible institutional arrangement that might help a government to initiate a transition towards a hydrogen economy. In our evolutionary game-theoretic model we acknowledge that the emerging hydrogen market is not perfectly competitive and is dependent on ‘learning by doing’. We have characterised a technology lock-in as a situation in which producers of a certain good (e.g., cars, heating systems) could potentially benefit from switching to the hydrogen-based technology, but only if production costs are sufficiently low, most likely conditional on all producers switching. The government could initiate the development of a ‘critical mass’ by coordinating the decisions of the producers. However, it should do so carefully, allowing producers to pursue their self-interest still, arriving at a hydrogen economy only if feasible. The government therefore faces the task of designing a ‘mechanism’ that supports coordination among producers, without prescribing choices.

In our mechanism the government’s main role is to act as a mediator. Producers are invited to disclose their intention to switch (or not), but indirectly, by selecting an option in the mechanism or game. The options are part of the ‘rules of the game’, and can be labelled e.g. ‘one’, ‘two’ and ‘three’, or ‘a’, ‘b’, ‘c’. The government translates the options in technology choices in a transparent way. The producers are guided in selecting the optimal solution, by selecting the options in the mechanism, without being declined to choose their technology of choice. The mechanism is shown to be robust for different levels of development of the hydrogen-based technology. This means that the government does not need to be aware of the state of the technology and can rely on the assessment of the industry. Only if a hydrogen-based technology is feasible, it will be selected.

Project leader
- Dr. E. Woerdman (RUG)

Co-applicant
- Dr. Frans P. de Vries (University of Stirling)

Researcher
- Wilbert Grevers (RUG)

Duration
- 2007 - 2009

Budget
- k€ 120

Highlights
- Presentation USA 2008: Grevers, W., ”Soar-RL and Agent-based Computational Economics”, 28th Soar Workshop, Ann Arbor, USA (4-7 May).
- Innovative project results: Based on an evolutionary game-theoretic model, in which elements from mechanism design are integrated, we demonstrate that the government can optimally support the transition to a hydrogen-based economy by acting as a mediator among producers. A ‘mechanism’ is offered – presented as a game – that translates choices within this game in technology choices. The mechanism is transparent and invites the producers to act strategically. Adopting this mechanism, the government does not need to be aware of the state of the technology and can rely on the assessment of the industry. A hydrogen-based economy will then only be selected if feasible.
Public Evaluation of Hydrogen: The Role of Worldviews and Adequate Information

It is studied whether the relationship between informational provision and support for hydrogen technology is not equally strong for every social category in Dutch society. It shows that, pending on their cultural predispositions, some may even dismiss favourable information about hydrogen technology and grow to dislike it more.
Results
In this project we analyse support for hydrogen technology in the Dutch population. This is important because a successful introduction of this technology will be problematic without the consent of the Dutch public. Therefore, in this project we try to understand how positive and negative evaluations of this new technology come about. Why do certain groups of people tend to disapprove of new technologies such as hydrogen technology, while others tend to approve? To answer this question we investigate how adequate knowledge leads people to adjust their evaluations of technology. By giving some people correct information about hydrogen technology and withholding other people that information we build in an ‘experimental’ condition, allowing us to study whether knowledge about hydrogen really leads people to redirect their thoughts about hydrogen. With this information policymakers can provide the public with the right type of information in order to promote hydrogen technology applications, which contribute to a sustainable, environment friendly, development. Furthermore, we investigate how shared beliefs between groups of people (worldviews) that seem to underlie much of the recent critiques of technological innovation relate to support for hydrogen technology. Again, this gives policy-makers and other stakeholders more insight in how positive evaluations of technology in general and hydrogen technology in particular come about, and how these evaluations can be influenced by giving the public with these worldviews correct information about hydrogen technology.

Project leader
- Prof. dr. D. Houtman (EUR)

Co-applicants
- Dr. P.H.J. Achterberg (EUR)
- Dr. S.D. Aupers (EUR)
- Prof. dr. W.A. Hafkamp (EUR)
- Prof. dr. ir. J. Rotmans (EUR)

Researchers
- Samira van Bohemen (EUR)
- Katerina Manevska (EUR)
- Lieve Salomé (EUR)

Duration
- 2006 - 2011

Budget
- k€ 110

Highlights
Creating long term support for hydrogen: the role of visions

This research has been on the opportunities and barriers in the social and economic embedding of a new energy system, based on hydrogen.
Results

The first Part (ECN) focused on the role of hydrogen infrastructure in a future hydrogen economy. The construction of large pipeline infrastructures for H₂ transportation usually constitutes a major and time-consuming undertaking, because of safety and environmental issues, legal and (geo)political siting arguments, technically un-trivial installation processes, and/or high investment cost requirements. The main finding is that the economics of H₂ transportation through pipelines are volatile. Cost data of individual pipeline projects may strongly deviate from the global average because of national or regional effects, such as related to varying costs of labour and fluctuating market prices of components like steel. Only in an optimistic scenario we may observe learning effects for H₂ pipeline construction activity in the future, but there are currently insufficient data to fully support the limited evidence for this claim.

The second part (TU/e) focused on the role of the Hydrogen Economy vision, an example of a Large Technological Vision (LTV). In order to be able to assess the performativity of the Hydrogen vision, a framework has been developed. The longitudinal focus of the case studies provided insight in the dynamics and performativity of LTVs over an extensive period of time, creating insight in the long term nature of hype disappointment dynamics of the LTV. An important observation was that an LTV can be easily preserved over such a longitudinal time span. The attractiveness of an LTV contributes to this persistent character. When the context changes and becomes right for the vision to become more widely carried, the vision spreads and becomes omnipresent. This effect is stronger when community formation took place preceding the developments that created the opportunity for the wide-scale acceptance for the vision. In this sense, an LTV can be said to be patient: it waits for the right opportunity to arise.
Support mechanisms for technology learning of hydrogen based applications

In this project we have researched the use and limitations of learning curves for describing technological progress and formulating energy technology policy, both in theoretical terms through an innovative component-learning hypothesis and by developing the first ever learning curves for solid oxide fuel cells.
Results

Major barriers will have to be surmounted in order to achieve a transition towards a hydrogen-based energy system. Not only costs of the hydrogen-related technologies have to go down, but also the value added of the desired transition has to be proven. Reductions of investment costs of hydrogen-based technologies are essential. These cost reductions can be achieved by (increasing) R&D efforts as well as through technology deployment. It is of primary relevance that R&D and deployment efforts are well balanced. However, this balance is expected to vary for different types of technologies, and may vary over time as the hydrogen technology under consideration passes through the various stages of technical maturity. For large technologies that are built in only a limited number, i.e. large hydrogen production plants, the focus might be on R&D rather than on deployment. For fuel cells, deployment might be the key driver for cost reductions. This research project aims to investigate the mechanisms that determine cost reductions. Based on this, a prediction of future cost reductions will be developed (so-called learning curves). Insights obtained from this research have to contribute to closing the gap between technology development and technology deployment, taking into account the specific features that characterise hydrogen technology market deployment in the Netherlands.
Colophon

Editors (NWO)
Ursula Bihari
Marijn Hollestelle
Marieke van Santen
Pam Schouten
Maarten de Zwart

Interviews
Bureau Lorient Communicatie
Native Speaker Translations

Design
WAT ontwerpers, Utrecht

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Photo Louis Vertegaal: Ries van Wendel de Joode

Print
Zalsman Kampen
Advanced Chemical Technologies for Sustainability (ACTS)

Visitor’s address
Anna van Saksenlaan 51
The Hague
The Netherlands

Postal address
P.O. Box 93223
2509 AE The Hague
The Netherlands

Telephone
+31 (0)70 344 07 40

www.nwo.nl/acts
acts@nwo.nl