SUPERGEN DoSH$_2$

Delivery of Sustainable Hydrogen

Foreword

The term "hydrogen economy" was first used by John Bockris in 1970 in a talk given at General Motors. Forty years later the term is still very powerful, but means different things to different people. It is clear however, that hydrogen technologies have greatly advanced and in 2011 it is possible to buy hydrogen vehicles and to heat and power homes and businesses with hydrogen. Most importantly hydrogen is widely recognised to have the potential to be able to unlock the capability of clean and renewable generation technologies to address the problems of global warming and energy security. It achieves this as it is a vector that readily translates between electricity, heat, transport and chemicals. Whilst incumbent technologies continue to improve, hydrogen technologies are now sufficiently developed, robust and reliable that it is now a matter of when they see mass market penetration rather than if.

EU, US and Japanese motor manufacturers are building up production capacity in preparation for the bulk manufacture of hydrogen-fuelled passenger vehicles for 2015. The public transport sector as an early adoptor is seeing increasing numbers of hydrogen (fuel cell) buses appearing globally, while public/private partnerships are beginning the roll out of large scale infrastructure. This is all driven by societal need and economic opportunity not because of a desire to create a "hydrogen economy" with global sector investment now into the multi-billions of dollars.

The Supergen Delivery of Sustainable Hydrogen (DoSH$_2$) project addresses next generation production of hydrogen. Today's hydrogen production is dominated by large-scale plant and such plant will be required to help supply tomorrow's hydrogen, but the sector is set to become far more diverse and the opportunities are immense for smaller scale and/or modular production technologies capable of turning local primary energy into what is likely to become a universal fuel and energy storage vector.

The Delivery of Sustainable Hydrogen project has an emphasis on the new challenges posed by efficient small-scale production technologies - recognising that hydrogen is not the most convenient of fuels to transport and foreseeing its eventual wide-scale distributed production contributing to our energy security. Alternative approaches to steam reforming are considered, addressing a wider range of primary hydrocarbons, including many currently considered as problem wastes, in order to source new distributed hydrogen. Project topics address tuning processes that deal with unusual primary feed stocks whether by reforming or through very different processes. The project also addresses the utilisation of electricity surplus to demand through electrolysis, improved gas separation membranes, more efficient liquefaction, the storage of hydrogen as ammonia and the overarching sociotechnical aspects.

The project involves 12 Universities, commenced in September2008 and has about 1 year to run. This booklet presents a summary of research progress that has most relevance to applications. It is hoped that those interested in in working with the project partners to take these advances forward commercially will find this document of particular benefit. Needless to say the partners would welcome any further discussions or questions you may have.

John Irvine
Ian Metcalfe
Martin Smith

SUPERGEN DoSH$_2$ Project Consortium

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Introduction

The Supergen Delivery of Sustainable Hydrogen (DoSH2) project was constructed to address gaps in the overall Supergen portfolio of R&D in the hydrogen sector. As such, its R&D topics are more diverse than are found in most of the other Supergen Projects. 14 separate researcher groups from 12 leading UK universities each bring their own hydrogen production-related research to the project.

A recent US DOE call for proposals sought the construction of a biomass combustion plant capable of dealing with more than 100 000 tons of biomass per year – thought quickly gives rise to some serious questions on the source(s) of this mass. Would there be anything green remaining anywhere nearby? And how much energy would be used transporting that weight of fuel from far away? Clearly not all bio and other fuel/energy production can be on such a scale.

The researchers in $DoSH_2$ chose to focus mainly on potential technologies suited to widely-distributed local production of hydrogen, e.g. mainly on smaller scale technology.

Smaller-scale does generally mean higher capital investment per unit output, however "value" rather than capital cost is surely the key issue. Additional value will be found in smaller-scale plant where hydrogen is produced primarily from local feedstock(s) and mainly for local use [minimal or no transportation costs]. And despite capital investment levels that might be unacceptable to large-scale industry. It is worth remembering that not all businesses are restricted to short ROI periods. Agriculture is one of the best examples of this, where farmers often invest with a view to a decade or more ahead rather than on expected returns from next year's harvest. Indeed agriculture with its long term horizons, local availability of waste biomass, land for the production of wind/hydro energy, its huge need for fuel and equally large need for hydrogen-based agrochemicals is possibly one of the most exciting areas for emerging hydrogen and related technologies. There is undoubtedly a very significant potential market in agriculture alone – one that has so far received very little attention.

Some of the project technologies are modular in nature or are otherwise very scalable, so although smaller-scale has been the project focus, by no means is all of the project technology restricted to only small scale application.

The project breaks down into 7 recognisable topic areas:
1. Cycling to Sustainable Hydrogen
2. Catalysts and Improved Materials for Catalysis
3. Reactors
4. Hydrogen Separation Technologies
5. The Renewables Interface
6. Hydrogen as Energy Storage
7. Socio-Technical Analysis

Some of the technologies addressed are not best suited for the large-scale continuous production of hydrogen, for instance those that are intrinsically batch processes. This however reflects the view that hydrogen will eventually come from many local sources of varying scale as well as mass production to provide for conurbations. It also reflects that in some cases the feed stock supply itself may be intermittent in nature. The accumulation of sufficient waste oil in a large food production context may take some time - and so there will be businesses for which a batch process is more suitable, especially if that process can be tuned specifically to deal with that particular business' waste processing needs. Equally agro feed stocks will change with the season.

The idea of tuning a hydrogen production technology to meet the needs of a specific business or feedstock is particularly interesting. The latter will often require the development and tuning of a particular catalyst and process operating parameters. Many of the project elements deal with or involve catalysis in some manner.

Intermittency of renewables like wind and wave and the consequent requirement for energy storage has obvious and massive potential for hydrogen technologies. Not surprisingly perhaps this is reflected in project topics that include high temperatures electrolysis (of water and CO_2), the effect of wide-scale electrolysis on the grid, a more efficient means of liquefying hydrogen and the potential to make ammonia (electrochemically) as a hydrogen storage vector amongst other potential uses.

Though seldom thought about by the public, ultimately all of life is underpinned by energy and our ability to harness and use it. But how we do that has consequences that ripple through almost every aspect of life and no energy-related research can sensibly afford to ignore the human consequences of changes in energy technology. The $DoSH_2$ project is usefully extended from the purely technical domain into socio-technical research by the inclusion of groups from Cardiff and Imperial College London. Direct interplay between technical and socio-technical researchers does much to focus the work of each, to iron out potential communications issues and these socio-technical research groups have much to offer the wider sector.

Bringing together such a diverse group of researchers is interesting/useful in its own right and has yielded valuable cross-fertilisation of thinking across the whole group. In some cases this has led to developments within the project itself, in others to less-related external collaborations. The project has also formed a special environment in which around 40 early stage researchers (PhD students and post-docs) are exposed not only to the detail of their own work but also to that of the larger group. At various events the early stage researchers have been presenting and selling project work overall rather than simply their own. This type of activity lends itself towards developing the project's human capital more widely than would the case were the research items tackled in isolation. And hence looks to more rounded future professionals in this and the wider energy sector generally.

Finally, the project is presented with a view to finding industrial/commercial partnering for the further development of these technologies and research work. Some are more ready than others to take the step out of purely academic development, but even those at an earlier stage can benefit from external involvement of one type or another. Any form of partnering suggestion will be received with interest – main researcher contact details are given with each of the profiles. As with all things R&D, risk is part of the package, but equally the consequences of nothing ventured are known well enough.

Dr. M. J. Smith, October 2011.

Technology Profiles

Novel Process for Pure Hydrogen Production using Syngas and Water, with Inherent Separation, using Chemical Looping

Researchers at Newcastle University, led by Prof. Ian Metcalfe, have developed a novel technology, using a process called chemical looping, for the production of two pure AND separate streams of hydrogen and syngas directly from natural gas and water. The syngas produced by this process can be used as a reactant for methanol or ethylene synthesis. In an auto thermal chemical looping process, a solid metal oxide such as iron oxide is utilised to transfer oxygen between two or more gaseous streams without allowing the streams to mix. Being autothermal, the process avoids the need for additional energy input.

Innovative aspects:
A novel iron-containing perovskite material has been shown to operate for a higher number of chemical looping cycles than the previous best known materials. The inclusion of an air step, provides heat to the system from the further oxidation of the metal oxide. Potentially, useful additional heat is made.

Main advantages:

- The proposed process eliminates any separation steps, as the hydrogen and syngas streams are inherently separated.
- Processing costs are lowered by removing the requirement for a separation process.
- The system can produce pure hydrogen and syngas from natural gas, water and air alone, in an overall exothermic system. Thus, useful products are synthesised from cheap reactants with the possibility of producing useful heat.
- The syngas produced is in the molar ratio of 2:1 (hydrogen to carbon monoxide); perfect for Fischer Tropsch reactions to produce useful products such as methanol and ethylene.
- The advantage of performing this step compared to other combustion techniques is that the carbon dioxide will be ready for carbon capture and storage following a simple condensation step.

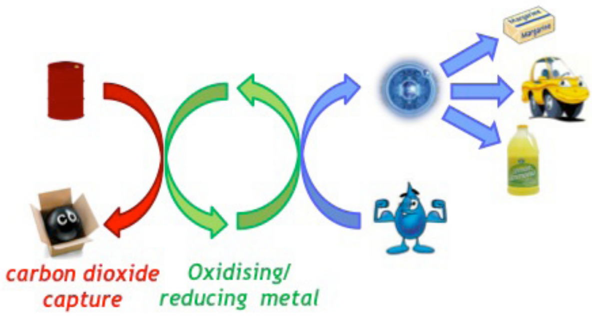
Notes

Current stage of development and outlook:
A major barrier to this type of technology previously has been the inability of earlier oxygen carrier materials* to undergo repeated cycling without mechanical collapse. A perovskite-type mixed metal oxide has shown no loss in performance over 150 cycles and has out-performed the current best oxygen carrier material. The production of other useful products (e.g. ethylene) is also being investigated.
*(iron oxide-based)

Industrial collaboration sought:
So far, work has involved the use of a microreactor and gas analysis systems to accurately measure production rates, but the process can be used in either a packed bed or circulating fluidised bed as a small unit (in a hydrogen fuelling station) or a large unit (in an industrial process). Collaboration with an experienced industrial partner is required to further understand the requirements and procedures for up-scaling.

Contact:

Professor Ian Metcalfe
ian.metcalfe@newcastle.ac.uk



Hydrogen from Bio-oils

Dr Valerie Dupont's group at Leeds have investigated bio-oils derived from pine and empty palm bunch fruits (EPBF)) as resources for hydrogen production, via sorption enhanced steam reforming and chemical looping reforming, using standard catalysts such as Nickel. Such bio-oils have low calorific values and are complex mixtures of organic compounds including acids, aldehydes, ketones, esters and phenolic compounds, and thus have limited applications for combustion in boilers and turbine engines. Many agricultural and forestry wastes can be recycled into bio-oils.

Innovative aspects:
This group is the first to demonstrate the use of bio-oils in sorption enhanced steam reforming and chemical looping reforming. The complexity of the mixture of bio-oil is difficult to deal with (e.g. left-over tar from reactants and deposited on catalysts etc) however, by thermodynamic modelling of each compounds and identifying the optimal operating conditions, this group are able to modify the process parameters and reactor design to enable hydrogen production. Furthermore, this work can be extended to work with the aqueous phase of bio-oil with methane (or any HC), to produce hydrogen, using sorption enhanced steam reforming and chemical looping reforming.

Main advantages:
- Utilisation of waste oils and conversion into hydrogen as an energy carrier
- Utilisation of aqueous phase of bio-oils, which are waste products during upgrade of bio-oils to bi-fuels, to convert into hydrogen as an energy carrier.
- Low temperature processes and other optimised parameters lead to high energy efficiencies

Notes

Current stage of development and outlook:
Hydrogen production from bio-oils using pine and EPFB has already been demonstrated. The group is now looking to work with the aqueous phase of bio-oil

Industrial collaboration sought:
The group is looking to collaborate with industrial partners interested in hydrogen production from sustainable sources and companies producing bio-oils who are interested in the upgrade of bio-oils to bio-fuels.

Contact:

Dr Valerie Dupont
V.Dupont@leeds.ac.uk

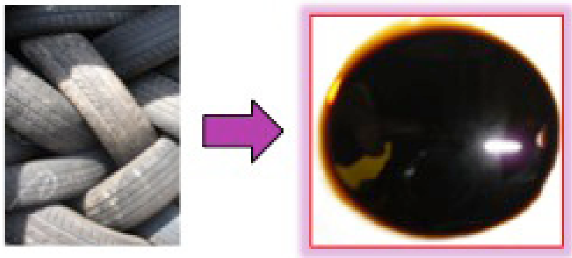
Bio-oil from Oil Palm fruit

Bi/tri Metallic Catalysts to Produce Hydrogen from Tyre Pyrolysis

Dr Valerie Dupont's group at Leeds have developed novel materials (bi- and tri-metallic catalysts) that act as oxygen transfer materials as well as catalysts for the steam reforming reaction with recalcitrant feedstock (e.g. waste lubricant oils and waste tyre pyrolysis oils). The group have optimised the performance of these catalysts using chosen materials Ni-Co/Al_2O_3 and Ni-Co-Ce/Al_2O_3 for hydrogen production. The chemical looping process, when applied to catalytic steam reforming process, permits higher yields of hydrogen, economically and with lower environmental costs.

Innovative aspects:
Leeds University have developed bi/tri metallic catalysts which act as oxygen transfer materials as well as catalysts. Traditionally, such catalysts (Ni-Co) have been studied with methane, while Ni-Co-Ce hasn't been studied. The novel aspect is to get these catalysts to work with complex HC feed stocks.

Advantages:
The novel catalysts offer high performance and at the same time enable an autothermal reaction minimising the use of external heat. Waste oils from many sources, including the food industry and problematic waste such as used tyres, can be used as feedstock.



Notes

Current stage of development and outlook:
The Ni-Co and Ni-Co-Ce catalysts have been optimised for performance using methane as feedstock. The next step is to optimise the process using oils derived from waste lubricants and tyre pyrolysis oils as the primary feedstock.

Industrial collaboration sought:
Collaboration/sponsorship is sought from businesses involved in the production and/or disposal of problematic hydrocarbon-based waste materials and/or the development of novel chemical plant and energy systems.

Contact:

Dr Valerie Dupont
V.Dupont@leeds.ac.uk

Plasma-assisted Catalysis Technology for Hydrogen Production from Methane Conversion

Prof. Whitehead's group at Manchester University have long-standing expertise in the area of plasma-assisted catalysis, which offers an environmental-friendly option for the efficient conversion of biogas or landfill gas into hydrogen together with value-added chemicals (e.g. carbon nanofibres, oxygenates). The hybrid process under development, is based on the combination of atmospheric plasma and heterogeneous catalysis. The interactions between the plasma and catalyst can generate a synergistic effect, which provides a unique way to separate the activation steps from the selective reactions at low temperatures. Plasma-catalytic dry reforming of CH_4 with CO_2 provides a promising route to sustainable production of H_2 and CO.

Gliding arc discharge

Innovative aspects:
The process deals with two major green-house gases (CH4 and CO2), converting them into hydrogen and other value-added co-products (carbon nanofibres) at low temperatures.
The catalysts can also be regenerated and activated in-situ by non-thermal plasma at low temperatures.

Main advantages:

- The production of hydrogen and value-added co-products such as carbon nanofibres, methanol.
- An improved selectivity towards desired products can be achieved using optimal catalyst combined with plasma.
- Production can be carried out at low temperature (e.g. 200 °C) with extremely high reaction rates.
- Plasma-catalysis technology breaks the barrier of thermodynamic equilibrium of a chemical reaction.
- The catalyst can be reduced, activated and regenerated by non-thermal plasma at low temperatures (e.g. 200 °C)
- The integrated plasma-catalysis system is compact and flexible for installation.

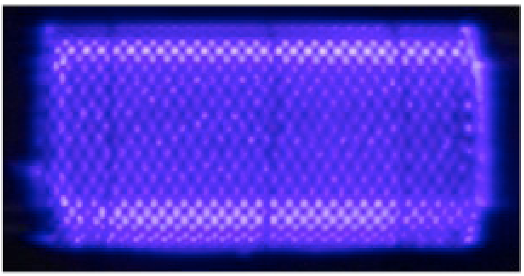
Notes

Current stage of development and outlook:
Process development has been carried out to optimise the lab-scale integrated plasma-catalysis system in terms of reaction performance and catalyst screening has been operating to obtain an optimal, low cost and stable catalyst for this reaction.

Industrial collaboration sought:
Collaboration or co-development is sought for the system scale-up of industrial applications and plasma technology, for environmental and renewable energy applications (not limited to methane conversion), such as CO_2 reduction or waste oil treatment.

Contact:

Professor Christopher Whitehead
j.c.whitehead@manchester.ac.uk



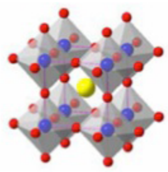
Non-thermal plasma

High-temperature Steam Electrolysis

Researchers at St. Andrews University have developed new ceramic- based (lanthanum-doped strontium titanate oxide perovskite) electrode materials for use in efficient steam electrolysis and simplified electrolyser design – without the inherent drawbacks of nickel-based cermets.

Quality waste heat from other processes can be used to reduce the electrical demand of electrolysis significantly below that of typical ambient electrolysis, thus increasing the efficiency of a combined system. Use of such a secondary energy input source can lead to an electrical efficiency of over 100%. However, likely operating parameters suggest that a typical electrical efficiency will be around 100%.

The electrolysis of steam also generates high purity O_2 as a secondary saleable commodity.



Perovskite structure, substitution of the yellow and blue atoms allows tuning of material properties.

Innovative aspects:
The ceramic oxides being developed can be fine-tuned via chemical doping to suit the highly reducing conditions experienced during steam electrolysis. In contrast, the chemistry of the current benchmark nickel cermet electrode is fixed and cannot be tailored specifically for steam electrolysis. The novelty of our approach lies in the strategies for the formulation and design of materials structure in order to achieve better performance, stability and facilitate processing.

Main advantages:
- Simplified electrolyser design and hydrogen savings under standby conditions.
- Unlike the nickel-cermet electrode, the redox and dimensional stability of the ceramic oxides being developed means that protecting hydrogen is not required for the electrode.
- Device lifetime is extended in comparison with the state-of-the-art. Ceramic oxides are not expected to suffer from the problem of coarsening often associated with the nickel-cermet electrode.

Notes

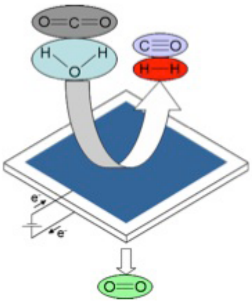
Current stage of development and outlook:
The research group have been undertaking laboratory research for about two and half years, with all ceramic oxide compositions synthesised and tested in-house.

Industrial collaboration sought:
Industrial partners (e.g. electrolyser and wind energy producers) are sought for scale-up from current 1 cm^2 electrodes to, for example, 16 cm^2 electrodes and then integrate these electrodes into an electrolyser stack. Prototype electrolyser stacks could then be coupled to a wind turbine to produce hydrogen at times of excess wind power.

Contact:

Dr George Tsekouras
gt19@st-andrews.ac.uk

Professor John Irvine
jtsi@st-andrews.ac.uk



Ceramic materials can operate in unprotected steam without performance degradation (CO_2 and H_2O electrolysis)

High-Temperature Carbon Dioxide Electrolysis

Researchers at St. Andrews have developed new ceramic based catalyst materials for the electrolysis of carbon dioxide. Electrolysis of carbon dioxide yields carbon monoxide (CO), an important feedstock in the industrial synthesis of a wide range of chemical products. This offers a way to turn waste CO_2 into a useful product, while simultaneously reducing carbon emissions. Electrolysis of CO_2 also generates high purity O_2, which has a significant market in its own right.

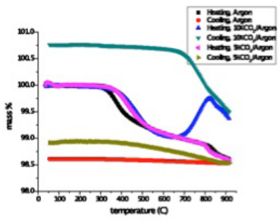
Research in this part of the project focuses on the utilisation of oxide materials including $(La,Sr)(Cr,Mn)O_3$, a perovskite-structured material and GdxCe1-xO_2 ceramic, which has previously demonstrated promise as a fuel electrode material for solid oxide fuel cells (SOFCs). These oxides are advantageous over the conventional Ni-based material in terms of superior carbon resistance and redox stability.

Carbon dioxide electrolysis provides a means to store CO_2 gas, as the CO produced can be used as raw material for synthetic fuel production (diesel, kerosene, etc.), an organic chemicals precursor or as a fuel in itself (town gas being a mixture of CO and hydrogen). Similar to steam electrolysis, CO_2 electrolysis could be cost-effective when electricity price is low during times of wind energy excess to store/convert the excess into alternative products/fuels.

Innovative aspects:
The materials studied exhibit lower cell resistance and higher faraday efficiency in various CO_2/CO mixtures for CO_2 electrolysis. Additional catalyst impregnation is also seen to improve catalytic activity towards CO_2 electrolysis.

Main advantages:

- The ceramic materials investigated are versatile in CO_2/CO atmospheres, unlike Ni-cermet materials which suffer from carbon deposition and redox instability under identical conditions.



$(Sm,Ba,Sr)_2Co_2O_5$ layered perovskites have been investigated as SOEC electrode materials showning stability to carbonation in carbon dioxide-containing atmospheres

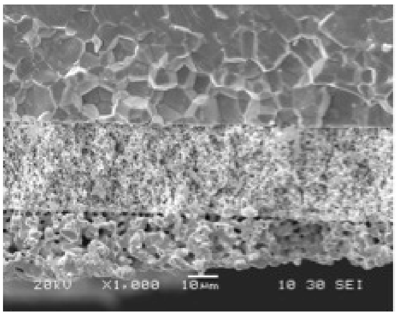
Notes

Current stage of development and outlook:
Laboratory research.

Industrial collaboration sought:
The research group seeks industrial partners, building electrolysers, wind energy producers and synthetic fuels producers to further test the materials and scale-up.

Contact:

Xiangling Yue
xy57@st-andrews.ac.uk



Engineering CO_2 electrolysis electrode materials

Production of Hydrogen using Organometallic Catalysts from Alcohols

Prof. Martin Wills' group at Warwick have developed organometallic catalysts capable of generating hydrogen directly from organic molecules such as; sugars, glycerol, alcohols and formic acid, at low temperatures and with the highest possible yield per unit time.

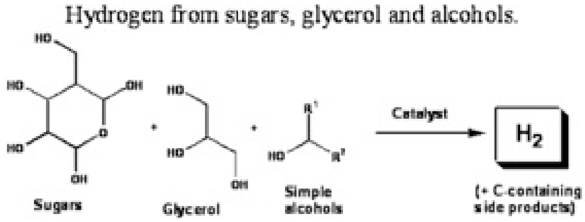
Expertise in the catalysis of organic reactions, particularly asymmetric transformations such as ketone and imine reductions, have been used in the application of organometallic catalysts to organic transformations and to dehydrogenate alcohols to form ketones and aldehydes together with hydrogen gas. Depending on the type of alcohol processed, in some cases the waste products (ketones and aldehydes) are likely to be useful in their own right as; potential fuels, useful solvents, antifreeze materials or chemical precursors.

Pre-project work involved scale-up of earlier lab-scale efforts and the production of enough hydrogen to run one of the University of Birmingham's hydrogen vehicles - proving that the idea works.

Innovative aspects:
The asymmetric transformations offer the potential to form high-value products. The hydrogen-generation catalysts offer a potential for the production of hydrogen under mild conditions.

Main advantages:
- Milder conditions for hydrogen generation and potential photocatalysis of the reactions.
- Production of other chemical feedstocks.
- Asymmetric synthesis may be of interest to relatively low volume, high value products such as pharmaceuticals.

Hydrogen from sugars, glycerol and alcohols.



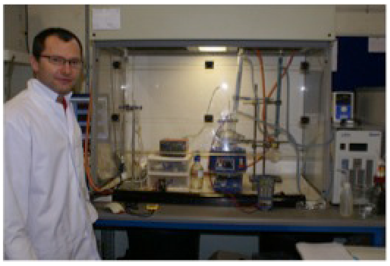
Notes

Current stage of development and outlook:
Extensive laboratory screening of catalysts has been carried, identifying many useful candidates. Process (hydrogen from formic acid) has also been converted to a low scale continuous process, as has early stage work incorporating otherwise liquid phase catalysts into solid phase polymers.

Industrial collaboration sought:
Industrial partners are needed to support the further development of catalysts and testing, including a prototype, to achieve close to market position.

Contact:

Professor Martin Wills
M.Wills@warwick.ac.uk



CO-free Hydrogen Production by Low Temperature Reforming of Methanol or Related Organic Molecules

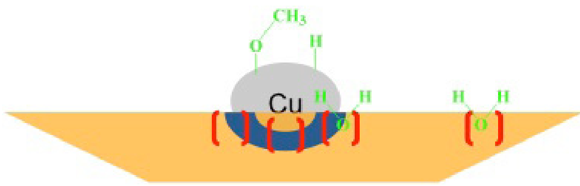
Prof. Edman Tsang's team at Oxford have developed an innovative process which involves Non-Syngas Direct Stream Reformation of methanol and other organic molecules at low temperature for the catalytic production of hydrogen. This system can supply high quality hydrogen gas, without CO contamination, for small mobile units such as PEM fuel cell devices. High energy density liquid methanol or related organic molecules can be stored in reservoir tank and be converted in-situ to hydrogen and carbon dioxide gas when required.

The Non-Syngas Direct Steam Reforming (NSGDSR) route over new proprietary catalysts for the conversion methanol or related organic molecules to hydrogen and carbon dioxide is carried out at 150-200°C. This new route is in sharp contrast with the conventional cumbersome route that involves high temperature steam reformation to syngas, followed by water gas shift and CO cleanup stages for the hydrogen production. A high quality of hydrogen, with CO content lower than 10ppm in the gas stream, can be produced in a single step reaction, which can thus be used to supply PEM fuel cells for mobile applications without invoking any CO shift and cleanup stages.

Innovative aspects:
A direct low temperature (operating temperatures below 200°C) catalytic steam reformation of methanol or related organic molecules to CO_2/H_2 can be executed to provide direct hydrogen supply - free from CO contaminant. This process can also couple directly to PEM fuel cells without CO cleanup. Proprietary solid catalysts are active and selective for this reaction.

Main advantages:

- In-situ catalytic hydrogen production from high energy and volume density liquid organic molecules to supply mobile PEM fuel cells devices without the need for hydrogen gas store.
- CO-free hydrogen is ideal fuel vector for clean energy utilization.



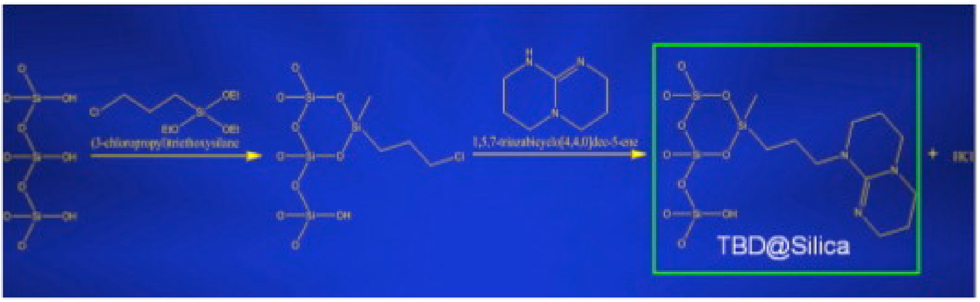
Notes

Current stage of development and outlook:
Hydrogen production rate of 393.6 mL/g-cat/hour at 150°C from methanol-water with CO content lower than 10ppm has been achieved.

Industrial collaboration sought:
Industrial partners and companies are sought for collaboration and co-development.

Contact:

Professor Edman Tsang
edman.tsang@chem.ox.ac.uk



Catalytic Hollow Fiber Membrane Micro-Reactors (CHFMMR) for High Purity Hydrogen Production

Imperial College London have developed a range of Catalytic Hollow Fiber Membrane Micro-Reactors (CHFMMR). A combination of these novel reactors, with appropriate catalysts, result in reaction-tunable micro-reforming devices. The devices can be manifolded and built up into arrays offering a highly scalable and compact solution, particularly for use in applications requiring small-scale efficient hydrogen/gas production. Larger scale production can also be obtained by adding additional tube-array blocks.

High purity COX free H_2 has been produced in the CHFMMR by different heterogeneously catalysed gas phase reactions such as: water gas shift (WGS), dry reforming of methane (DRM), ethanol steam reforming (ESR) and methanol steam reforming (MSR). Asymmetric ceramic hollow fibres, fabricated by a phase-inversion technique following by sintering at high temperature, have been employed as a single substrate for combining both Pd-based membrane and catalyst in the development of CHFMMR.

Although developed in the course of this research for hydrogen production, the micro-reactors can equally provide similar compact production of other gas species when combined with appropriate catalysts and separation membranes.

Innovative aspects:
The use of asymmetric ceramic hollow fibres as a support for both Pd-based membrane and catalyst in heterogeneous catalytic gas phase, enables faster and easier development of the membrane-micro-reactor technology.

Main advantages:
The CHFMMR can be proposed as an alternative reactor to produce high purity H_2, since it offers important advantages over conventional systems (CMR etc), such as:

- The possibility of working at significantly lower temperatures and/or using less catalyst.
- Combining the processes of generating and separation of H_2 in a single step.
- The high surface area/volume of the ceramic hollow fibres allows for more economical large-scale CO_x free H_2 production.
- The micro-channels structure of the ceramic hollow fibres results in a more efficient utilization of the catalyst deposited on their walls.
- The combination of high chemical, thermal and mechanical durability of the alumina ceramic makes it an attractive option for a number of reactions under very different operating conditions.
- The alumina micro-reactors show insignificant heat loss by conduction.

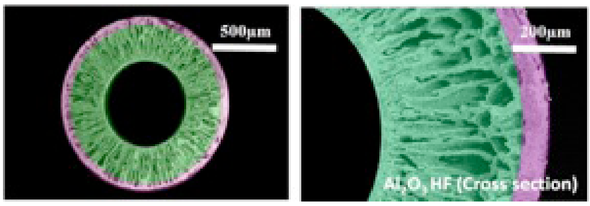
Notes

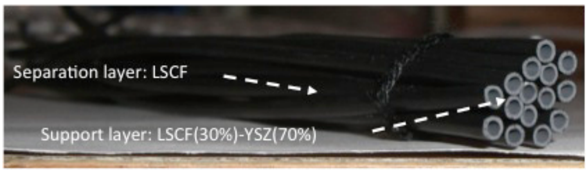
Current stage of development and outlook:
The micro-tube fabrication techniques have been developed to reliably produce a consistent product. Impregnation techniques are developed to offer a wide-range of in-situ catalyst options. Separation membrane deposition techniques have been successfully developed. High efficiency hydrogen (and other gas) production has been observed. Prototype bundles (arrays) of tubes have been successfully operated and tested in concert and micro-tubes have been successfully manufactured using alternative ceramics.

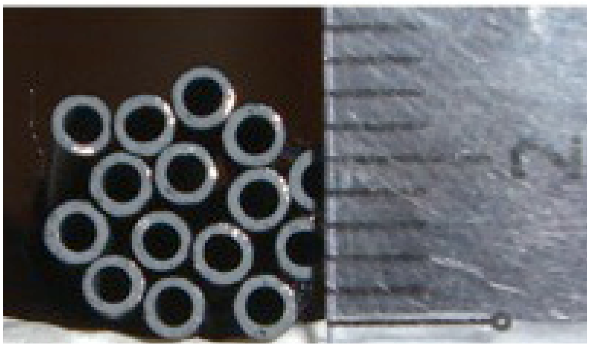
Industrial collaboration sought:
Industrial/Commercial partners are sought to develop prototype devices suitable for *in-situ* hydrogen production and other applications.

Contact:

Professor Kang Li
kang.li@imperial.ac.uk







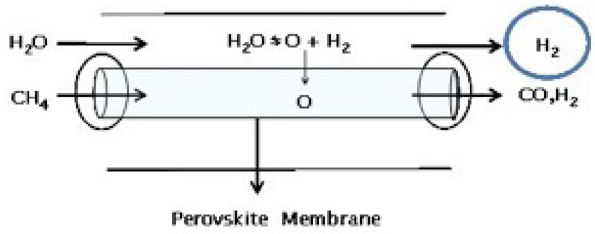
Production of Pure Hydrogen by Chemical Looping from Water, using Microtubular Perovskite Membranes

Researchers at Newcastle University, led by Prof. Ian Metcalfe, have developed a novel technology for the continuous production of hydrogen and syngas using mixed, conducting perovskite membrane. The process offers inherent separation of hydrogen from syngas streams.

The membrane system used in this project is operated to produce hydrogen and syngas, combining POM (partial oxidation of methane) with simultaneous water splitting, where the oxygen for the POM reaction is supplied from water. When exposed to oxygen at elevated temperatures perovskite membranes can transport oxide ions from the high partial pressure side to the low partial pressure side. This results in overall steam reforming of methane.

Innovative aspects:
This process produces pure hydrogen and syngas at different streams as water and methane are never mixed during the process.

Main advantages:
Pure hydrogen is produced as only oxygen ions can be transported through the membrane and a thus hydrogen separation step is not required, consequently lowering process costs.



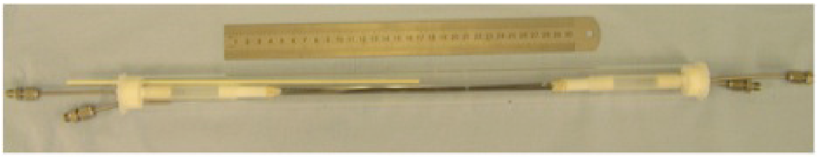
Notes

Current stage of development:
Membrane stability and the lifetime of the perovskite membranes, due to degradation, is a key challenge. Currently, the stability of the membrane is being carefully studied, and the membrane system has been operated for over 400 hours producing hydrogen and syngas. In addition, an autothermal membrane process using only air, water and methane to produce pure hydrogen and syngas is under investigation.

Contact:

Professor Ian Metcalfe
ian.metcalfe@newcastle.ac.uk

Industrial collaboration sought:
Industrial partners interested in scale up following further R&D and establishing membrane stability are requested.



Microtube Test set-up

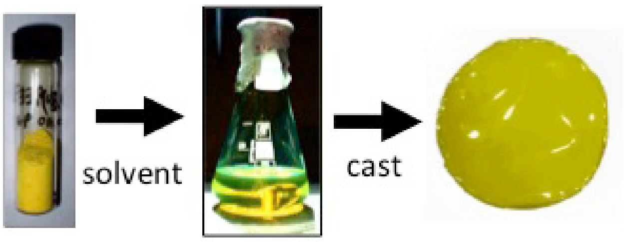
Hydrogen Separation using Micro-Porous Polymers

A unique patent-pending technology for hydrogen separation, developed by Prof. Neil McKeown's group at Cardiff, is based on polymers with micro-porosity (Polymers of Intrinsic Microporosity- PIMS) and is capable of gas separation including hydrogen. PIMS contain holes or pores of a molecular scale specifically designed to allow hydrogen to pass easily through them, whilst blocking larger molecules.

Innovative aspects:
A new class of micro-porous polymer has been developed that contains amine functionality to selectively bind to CO_2. Deliberate structuring of the polymers offers the ability to tune the materials to separate different gas mixtures.

Main advantages:

- Greater selectivity for CO_2 over H_2 and CH_4 is anticipated.
- Cost effective when scaled-up in comparison with conventional palladium-based alloys.
- These polymers can be made in large continuous rolls.
- Provides a high purity gas output.



Powder to Membrane

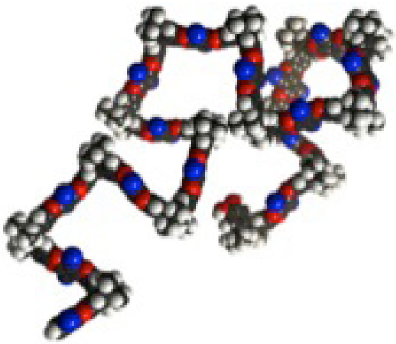
Notes

Current stage of development and outlook:
The synthesis of large numbers of polymers using the new methodology and the production of high mass polymer has been demonstrated. Gas separation testing is providing encouraging performance results and patents have been applied for.

Industrial collaboration sought:
Industrial partners working on gas separation, carbon capture and water purification using solid substrates or membranes are needed.

Contact:

Professor Neil Mckeown
MckeownNB@cardiff.ac.uk



Molecular Engineering

Hydrogen Separation using Improved Metallic Membranes

Dr David Book's group at Birmingham University, have developed an improved metallic membrane based on palladium alloys for separating hydrogen from other gases, in a cheaper and more efficient manner.

Hydrogen produced via reformation can contain large quantities of impure gases such as CO and CO_2, which must be removed before the hydrogen can be used, particularly in PEM type fuel cells, which can be badly damaged by some of these impurities. Hydrogen selectively diffuses through the crystal lattice of palladium and certain palladium alloys, leaving the impurity gas species behind. The reformation process can be combined with membrane separation in a 'membrane reactor'.

Thin-metal membranes are; compact, have a low capital cost and offer a one-stage high-purity hydrogen output. However, current alloys used (e.g. Pd-Ag) are relatively thick at 25 microns and need to be operated at high temperatures, leading to high material and operating costs.

Innovative aspects:
Birmingham University's Hydrogen Materials Group has developed novel, thin-film composite membranes – consisting of Pd-Rare-Earth alloys sputtered onto surface-treated porous substrates with an interdiffusion barrier layer. These offer significant improvement over conventional metallic membranes in terms of high-temperature stability and durability. These alloys have been shown to be three times more permeable to hydrogen and to also have superior mechanical properties.

Main advantages:
- High purity hydrogen following separation.
- Reasonable tolerance to impurities such as sulphur.
- Target operating temperatures of 250 ^{o}C.
- Can be deposited as thin films on a range of porous substrates.
- Markedly reduced precious metals cost.

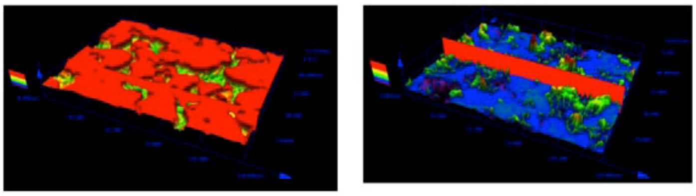
Notes

Current stage of development and outlook:
Current work focuses on cost reduction and improving the resilience of the membrane. Magnetron sputtering is being used to deposit novel Pd alloy thin films (3 micron) onto porous metal or ceramic substrates. The use of interdiffusion barrier layers is also being investigated. The membranes are being assessed on a membrane test rig, which measures gas-flow, pressure and gas composition.

Industrial collaboration sought:
Birmingham is looking for industrial partners with an interest in gas separation and/or hydrogen production, to further develop these technologies.

Contact:

Dr David Book
d.book@bham.ac.uk



Laser Microscopy of porous stainless steel support (left) and c/w 3 layers of sub 1 micron tungsten (right)

Wide Scale Distributed Electrolysis and the Grid

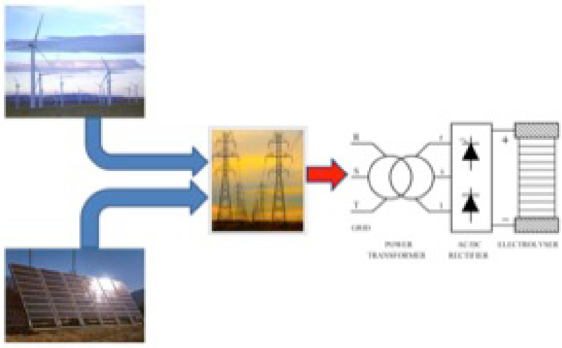
Research involves an investigation of the impact of large scale alkaline electrolysis plants on the performance of electrical grid and finding innovative control strategies to run the electrolysers in a way to improve the performance of the electrical power system. In particular, it addresses the demand side management potential of highly distributed electrolyser loads connected to the UK electricity system. The potential aggregated electrical load of such future electrolyser plants could be considerable and modelling/predicting its effect is important.

The work analyses the use of such a 'controllable load' for frequency reserve, load levelling and reduction of power station emissions via reduction of 'spinning reserve', improved energy trading and similar items/issues.

In our electrical power system models, electrolysers are used as dynamic demand to improve the frequency stability of the electrical grid while there is a high penetration of wind power in the system. In another work, the size and the location of the electrolysers in the electrical power system is optimised to achieve a 2.9% reduction in the aggregate electrical transmission losses of a power system in presence of wind farms.

Innovative aspects:
New strategies to run electrolysers and select their size and locations in the grid to improve the performance of the electrical grid have been developed. As have new control strategies used to run the electrolysers to reduce the frequency fluctuations in the electrical power system in the presence of high penetration of wind power.

Main advantages:
- Frequency stability improvement of the electrical grid using alkaline electrolysers
- Transmission loss reduction in the electrical power system using Alkaline Electrolysers



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Current stage of development and outlook:
Electrolysers are modelled in a UKGDS (United Kingdom Generic Distribution system) network - it is shown that electrolysers are able to reduce system transmission losses if they are sized and located properly and an appropriate control strategy is adopted.

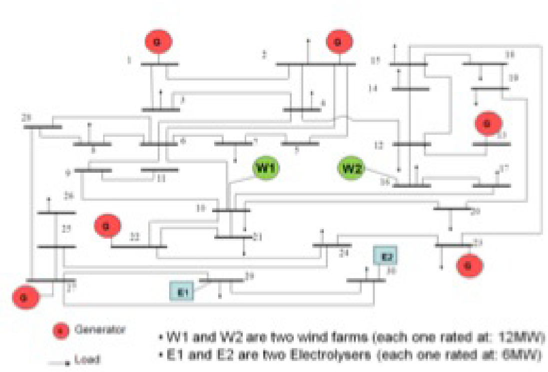
A model of the steam turbine generator is used to find out the impact of the electrolysers as dynamic loads on the frequency stability of the system, and it is observed that these electrolysers can help in stability of the frequency of the system in two cases:

1. There is a sudden generation loss in the power system
2. There is a high penetration of intermittent wind power in the system

Industrial collaboration sought:
Companies/organisations operating alkaline electrolysers from renewable primary sources could assist our modelling by supplying data. Furthermore, engagement with companies wishing to invest in hydrogen filling station networks on how to operate the electrolysers to improve the performance of electrical grid, especially in relation to the usage of intermittent renewable primary sources, are also sought.

Contact:

Dr Andrew Cruden
a.cruden@eee.strath.ac.uk



Scalable Hydrogen Liquefaction

The transportation of large quantities of hydrogen is one of the main obstacles in the emergence of hydrogen-fuelled infrastructure. Aside from pipeline supply, for which infrastructure is still nascent, liquid hydrogen offers a relatively efficient method of moving significant volumes. A liquid form of hydrogen certainly represents the most volume effective means of transport and storage. However, converting hydrogen gas to hydrogen liquid is far from straightforward.

Cambridge has extensive experience in cryogenics and superconducting materials. Within SUPERGEN DoSH$_2$ they are using this expertise to design and construct hydrogen liquefiers, which are of a suitable size to liquefy the hydrogen output that might be expected from electrolysis or other hydrogen production technology, in local community. The liquefaction devices they are targeting are little larger than a large domestic fridge -freezer unit. A key part of their strategy in increasing the efficiency of the process is utilising the oxygen also produced in electrolysis as one of the key refrigerants.

Hydrogen liquefaction process assisted by high pressure water electrolysis was considered. A cycle capable of producing variable amounts of liquid hydrogen per day has been modelled. The gain in efficiency is pursued by minimization of feed compressor losses due to the fact that the work of compression of liquid water is less than that for gaseous hydrogen product.

A design based on hydrogen–refrigerated hydrogen liquefaction system with three pre-cooling stages was developed, [Two liquid nitrogen baths (one liquid and one vapour) and hydrogen recycle refrigeration system in combination with J-T expansion valve]. The high pressure oxygen by-product can be used to provide cooling of the buffer refrigerant (nitrogen). Hydrogen output stream from high pressure electrolysis needs is to be subjected to cryo-purification in order to ensure required purity of the feed H_2 stream. An appropriate purification unit is also under development.

Innovative aspects:
Use of high-pressure oxygen by-product to perform pre-cooling work and cold nitrogen vapour to reduce hydrogen compression temperature.

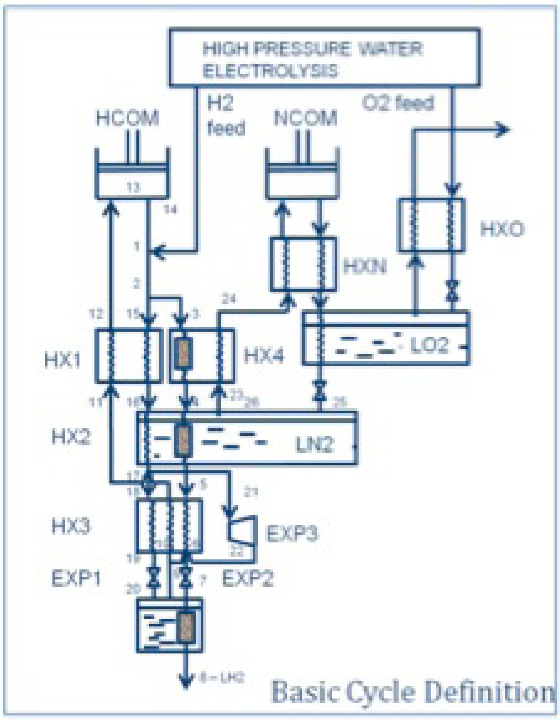
Main advantages:

- The proposed design reduces the amount of compression work per unit liquefied hydrogen gas leading to improved energy efficiency.
- The proposed design reduces the size of the compression units and thus system cost.
- Added value of compressed oxygen by-product is utilized.
- The warm oxygen gas can be re-directed for specific users (e.g. hospitals).
- Increased efficiency through optimisation of hydrogen recycling system.
- Offers compact means of developing decentralised liquid hydrogen supply.

Notes

Current stage of development and outlook:
Prototype design of the system for the hydrogen Lab in Cambridge.

Industrial collaboration sought:
Industrial players involved in hydrogen purification, liquefaction and delivery are required.

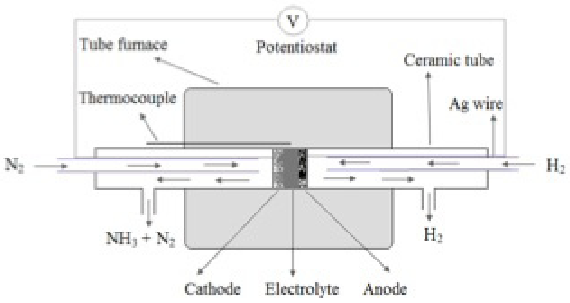


Contact:

Professor Bartek Glowacki
bag10@cam.ac.uk

Storage as Ammonia

Prof. Tao's research group at Strathclyde has developed a technology for the electrochemical synthesis of ammonia. This technology can be used to directly convert renewable electricity from wind, solar, wave and marine sources to ammonia. The energy stored in ammonia can be retrieved via an ammonia fuel cell or by simple decomposition of ammonia to produce hydrogen (and nitrogen). Ammonia can be compressed in liquid at 8 atm which is much easier to store than hydrogen. Therefore, ammonia is a good indirect hydrogen storage material for on-board hydrogen storage for transport applications.



Double-chamber reactor

Innovative aspects:
Traditional ammonia synthesis by Haber-Bosch Process has to be carried out on a large scale, at high temperature and pressure. The electrochemical synthesis can be carried out on any small scale and at atmospheric pressure. High temperature is not required either. The electrochemical cells for ammonia synthesis can be operated in a 'start-stop' mode.

Main advantages:
- To provide an alternative solution to the management of intermittence of renewable energy.
- Extra electricity generated by renewable energy can be used to produce valuable chemicals such as ammonia.
- This offers potential benefits in terms of security of fuel supply and decentralisation, while the energy density of liquid ammonia allows much more energy to be cheaply and easily stored than is the case with hydrogen gas.

Notes

Current stage of development and outlook:
The technology is at early stage, ammonia has been thus produced but only in small quantities to date.

Industrial collaboration sought:
Enquiries are sought from potential partners in developing small scale ammonia generation plant with interests in; renewables, using the ammonia as a form of hydrogen storage and for other purposes.

Contact:

Professor Shanwen Tao
shanwen.tao@strath.ac.uk

Socio-Technical Analysis

At the Low Carbon Research Institute (LCRI) in the Welsh School of Architecture (WSA), Cardiff University, work is being undertaken on the social, economic, environmental and technical processes that will help or hinder the potential uptake of sustainable hydrogen – called the socio-technical analysis.

The objective of this work is to see how the SUPERGEN DoSH$_2$ Consortium (and the UK as a whole) can more effectively promote the sustainable innovation, knowledge transfer, commercialisation and rapid uptake of hydrogen as part of the transition to a low carbon economy. This is being done via 'participatory technology assessment'. Here, individual interviews and deliberative workshops with hydrogen practitioners and researchers as well as industry data are revealing a rich mixture of qualitative and quantitative information.

The team is currently using an online version of the 'Delphi' survey process, an in-depth questionnaire that is repeated as opinions become more focussed, to characterise and describe the expectations individuals have about future hydrogen production technologies and post-production conversion processes. Questions cover inputs and outputs, indicative conversion efficiencies and operating ranges, energy and environmental impacts, projected costs, scale of operation, potential safety and systems integrations issues. In the team's final analysis, particular attention will be paid to how individuals assess uncertainties, technological risks and the potential for learning effects.

Team members are also comparing two national case studies, the UK and Germany, and the hydrogen from biomass sector in the UK, in terms of evidence for working models from the 'innovation systems' literature. This suggests that the presence or absence of certain key entrepreneurial functions in any economic system, in this case the global manufacture of sustainable hydrogen, will help to expose, in policy terms, which processes a national government needs to support in order to boost hydrogen's contribution to the national energy mix and even, ultimately, make a 'technological transition' to an energy system dominated by renewable and hydrogen. The team's resulting analysis will therefore be a series of specific policy recommendations for government and industry for research, policy and industrial development.

Notes

Current stage of development and outlook:
Currently the Delphi survey is in its second round stage. It has had over 100 completed responses and analysis is due in the coming months. Similarly, data is still being gathered the case studies from Germany and the UK – the target for 50 completed interviews is more than half way complete - and the interviews and analysis into the hydrogen from biomass sector continue. The team anticipates running a workshop and conference with industrial and commercial partners, amongst others, in 2012. After this, the team will begin synthesising key messages from all the data and identifying recommendations for future research, policy and industrial development in its final reports.

Industrial collaboration sought:
Industrial/commercial partners are welcome, at any stage, to participate in our development of best practice and policy guidance for managing a transition pathway towards greater hydrogen uptake in the economy.

Contact:

Professor Malcolm Eames
eamesm@cardiff.ac.uk

Nick Hacking
hackingn@cardiff.ac.uk

Techno-economic Assessment of Novel Hydrogen Production Technologies

ICEPT (Imperial College Centre for Energy Policy and Technology) is assessing the economic and environmental sustainability potential of advanced H_2 production and delivery technologies, with emphasis on those being developed by the SUPERGEN DoSH_2 consortium. The analysis is supported by techno-economic scenario modelling of H_2 demand and supply (see below for a schematic representation of the modelling methodology) and uses a case study approach. Case studies selected so far are London and South Wales; in the case studies the emphasis is on on-site and decentralised H_2 production and delivery infrastructures.

In parallel, optimisation modelling techniques are also being used for UK-wide analysis, particularly with regard to the economics and logistics of large-scale gasification of carbonaceous feedstock and also the potential role of H_2 for large-scale energy storage in the UK.

Innovative aspects:
Although similar studies have been carried out before, they have mainly focussed on conventional H_2 production pathways and not on novel ones. Another distinctive feature of our analysis is the emphasis on novel H_2 production and delivery technologies as potential enablers of the transition to a large scale use of sustainable H_2. Moreover, we address specific UK case studies of particular interest which had not been analysed before in a similar way. Finally, we devote particular efforts to the analysis of waste-to-hydrogen pathways, which have so far received comparatively little attention and are potentially very promising.

Key outputs expected:
The analysis conducted aims to achieve a number of important objectives:

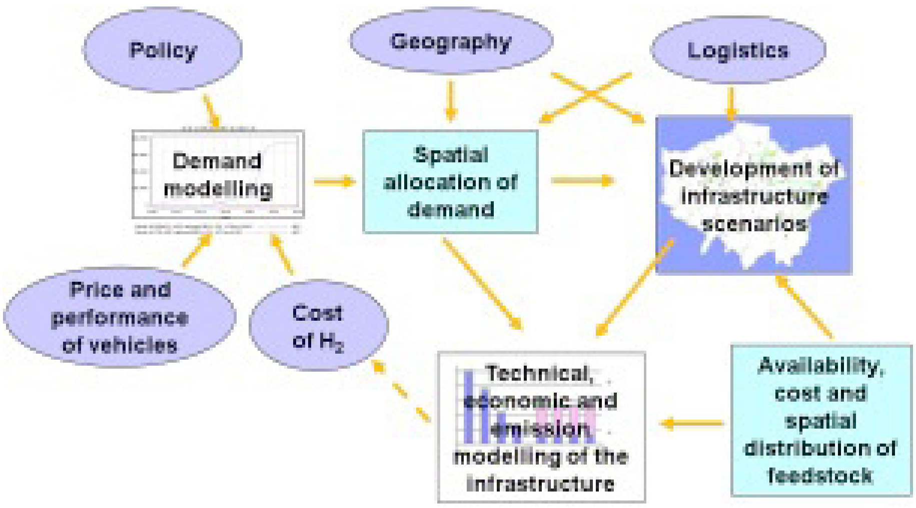
- To assess the potential role of a range of novel H_2 production technologies, particularly during the early phases of the transition to large-scale use of H_2
- To identify key areas for further development of these technologies, thus contributing to inform future R&D activity plans
- To identify key challenges to the development of economically and environmentally sustainable H_2 infrastructures, thus contributing to the development of national strategies on H_2
- By conducting key case study, to also inform local plans for the development of H_2 infrastructures

Notes

Industrial collaboration sought:
Industrial/Commercial partners are sought with a view to extend the analysis to more prospective H_2 production and delivery technologies as well as other regions.

Contact:

Marcello Contestabile
marcello.contestabile@imperial.ac.uk



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Delivery of Sustainable Hydrogen

SUPERGEN DoSH$_2$
Delivery of Sustainable Hydrogen

For more infomation please contact:

Dr Martin Smith
MJS6@st-and.ac.uk

Professor John T.S. Irvine
jtsi@st-andrews.ac.uk

www.supergen14.org

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Print Layout and Printing:

Andy Mackie,
Printing & Design Dept.,
University of St. Andrews,
St Katherine's West,
16 The Scores, St Andrews,
Fife, KY16 9AX.

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Research Councils UK
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For a Low Carbon Future

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