HYDROGEN CANADA STRATEGIC RESEARCH NETWORK

RÉSEAU DE RECHERCHE STARTÉGIQUE HYDROGÈNE CANADA

(H_2CAN)

SCIENTIFIC PROGRAM OVERVIEW

&

RESEARCH PROJECTS DESCRIPTION

NSERC H2CAN Network Specifics

Network Title: **Hydrogen Canada Network –Réseau Hydrogène Canada (H_2Can)**

Target Area: Sustainable Energy Systems (Production, Distribution and Utilization)

Keywords: Hydrogen, Systems, Storage, Production, Safety, Renewable energy, Energy storage, biomass conversion and co-product optimization, GHG reduction

Research Subject Codes: 2300 (Energy, 2303 **(**Fuel and energy technology: Other sources of energy**),** 2000 (Materials science and technology), 2200 (Fluid mechanics), 2203 (Fluid mechanics: modeling and simulations), 1800 (chemical engineering), 1803 (thermodynamics), 2500 (Electrical engineering), 2501 (power systems), 1806 (Separation processes), 2516 (Energy conversion and distribution), 3150 (theoretical physics), 3151 (Kinetic and transport theory of fluids, physical properties of gases), 3400 (Physical chemistry), 3402 (Surface and interfacial chemistry).

Scientific Director

CHAHINE Richard, Hydrogen Research Institute (HRI), Université du Québec à Trois-Rivières (UQTR) and NSERC Chair on Hydrogen Storage; (development of nanostructured physisorbents, characterization of porous materials, network scientific coordinator, group leader of B.2 *Development of materials for hydrogen storage*).

Managing Director

TCHOUVELEV Andrei, A.V. Tchouvelev & Associates Inc.

Network researchers, their expertise and role within the network

AGBOSSOU Kodjo, Hydrogen Research Institute, UQTR; (Theme A: hydrogen production from renewable sources, control of integrated energy systems based on hydrogen, group leader for A.1 *Production from wind power*);
BAKER, R. Tom, Director of Centre for Catalysis Research and Innovation and Canada Research Chair (Tier I) in Catalysis Science for Energy Applications, University of Ottawa; (Theme B: Novel chemical hydrogen storage concepts);
BAUWENS Luc, University of Calgary; (Hydrogen safety: detonation of hydrogen-air mixtures, group leader for C.2 *Safety*);
BÉNARD Pierre, Hydrogen Research Institute, UQTR; (Theme A: calculation of transport properties using quantum chemistry calculations, Theme B: statistical physics and thermodynamics of adsorption processes, Themes B and C: fluid dynamics simulations of hydrogen releases);
BOTTON Gianluigi, McMaster University, Canadian Centre for Electron Microscopy and Canada Research Chair (Tier II) in Microscopy of Nanostructured Materials (Themes A and B: microscopic characterization of nanostructured materials, group leader for B.4 *Characterization*);
DAVIS Boyd, Queens University, Queen's-RMC Fuel Cell Research Centre (Theme B: Chemical storage of hydrogen, Theme B coordinator, group leader for B.3 *Storage system design and optimization*);
DJILALI Ned, Inst. for Integrated Energy System (IESVic) and Canada Research Chair (Tier I) in Energy Systems Design and Computational Modeling, University of Victoria; (Themes C and B: System studies, computer fluid dynamics (CFD) simulations of hydrogen flows, turbulence);
DOMINGUE, Frederic, Hydrogen Research Institute, UQTR; (Theme B: Hydride storage systems metering; hydrogen and oxygen sensors; microelectronics);
FRITZSCHE, Helmut, NRC Canadian Neutron Beam Centre (All themes, Neutron diffraction analysis);

GOYETTE Jacques, Hydrogen Research Institute, UQTR; (Themes B and C: Heat transfer in solid state hydrogen storage systems);
GUAY Daniel, Institut National de la Recherche Scientifique, Énergie, Matériaux et Télécommunications (INRS-EMT), Canada Research Chair (Tier I) on Energy Nanomaterials; (Theme A: Development of new materials for hydrogen purification, group leader for A.3 *Purification and and separation technologies*);
HAMELIN Jean, HRI, UQTR; (Theme A: Hydrogen production from biomass);
HUOT Jacques, HRI, UQTR; (Theme B: High volumetric density storage metal hydrides for portable applications);
IDEM Raphael, Engineering HTC Industrial Research Chair in Clean Energy, University of Regina; (Theme A: Reaction Kinetics, Reaction Mechanisms and Heterogeneous Catalysis, Reformer Technology/Fuel Processing for Fuel Cell Application);
LEVIN David, University of Manitoba (Biosystems engineering, biological production of hydrogen, production by reforming of organic molecules, Theme A coordinator, group leader for *A.2 Production from biomass and renewable hydrocarbon*);
MEDRAJ, Mamoun, Concordia University (Theme B: High volumetric density storage metal hydrides);
MITLIN David, University of Alberta and National Research Council (NRC) National Institute for Nanotechnology (Theme B: destabilized hydrides for hydrogen storage, combinatorial co-sputtering);
McGRADY Sean, University of New Brunswick (Theme B: quantum chemical modeling of solid state systems to predict their hydrogen storage properties, group leader: *B.1: Theory and simulations of hydrogen storage materials*);
OSHKAI Peter, IESVIC, University of Victoria (Theme C: experimental determination of flow velocity field of hydrogen jets);
PARASCHIVOIU Marius, Concordia University (Themes C and B: CFD simulations of outflows from solid state storage);
PEPPLEY Brant, Fuel Cell Research Centre, Queens University, NSERC Industrial Research Chair on Fuel Processing for Fuel Cell Systems (Theme A: Fuel preprocessing, conversion of landfill gases to commercial grade hydrogen);
RADULESCU Matei, University of Ottawa (Theme C: Safety, self-ignition of hydrogen releases);
RIPMEESTER John, NRC Steacie Institute for Molecular Sciences (SIMS); member, Expert Group on Unconventional Gas Supply, Climate Change Technology and Innovation Initiative (Theme B: NMR characterization of hydrogen sorption processes);
ROUÉ Lionel, INRS-EMT (Theme A: preparation of nanostructured materials by mechanosynthesis, electrochemistry);
ROWE Andrew, IESVic, University of Victoria (Theme C: Systems design and magnetic refrigeration, Theme C coordinator, group leader of C.1 *Infrastructure*);
VARIN Robert, University of Waterloo (Theme B: Catalyzed lithium alanate complex hydride and its composites);
WILKINSON, David, Director of Clean Energy Research Centre and Canada Research Chair (Tier I) in Clean Energy and Fuel Cells, University of British Columbia; (Theme B: High volumetric density storage metal hydrides);
WRONSKI Zbig, CANMET Energy Technology Centre-Ottawa (Theme B: preparation and testing of hydride storage and non-metallic support phases with nano-metric phase partitioning.

Partners

Agence de l'efficacité énergétique Québec, Air Liquide, Atlantic Hydrogen, Angstrom Power, BC Transit, BC Hydro, BC Ministry of Energy, Mines and Petroleum Resources, Canadian Hydrogen and

Fuel Cell Association, Defence Research and Development Canada, Hydro Québec, Hydrogen Centre for Expertise Inc., HSM Systems, Greenleaf Integrated Energy Systems, Lignol Innovations, Ministère des Ressources naturelles et de la faune du Québec, National Research Council of Canada, NRC IFCI, Natural Resources Canada, Palcan Energy Corp., Powertech Labs, Sacré-Davey Engineering, SiM Composites, SOFC Network, Vale Corp., Xebec Adsorption.

Canadian University Partners

Université du Québec à Trois-Rivières, University of Alberta, University of British Columbia, University of Calgary, Concordia University, University of Manitoba, University of New Brunswick, University of Ottawa, Queen's University, University of Regina, University of Victoria, University of Waterloo, Institut national de la recherche scientifique, Énergie, Matériaux et Télécommunications, McMaster University.

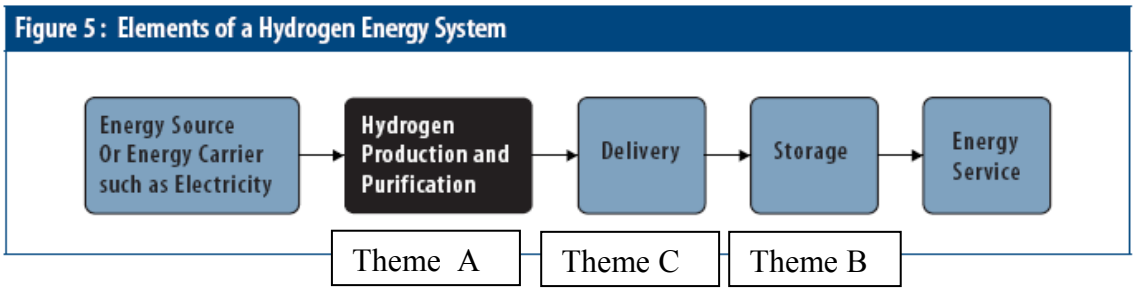
Network objectives

The network will strive to address both the short term goals of the industry (lowering costs by improving the current technology) and its long term goals (technology innovation: development of new processes and new materials). It proposes a system's approach to hydrogen energy technologies centered on the three strategic research poles of hydrogen production and purification, storage, infrastructure and safety.

The objectives of this network is to overcome the technical barriers to the introduction of hydrogen energy technologies by (1) improving and developing cleaner renewable methods to produce pure, high quality hydrogen at lower cost either from waste or renewable resources; (2) increasing the energy density of hydrogen applications by improving and developing storage strategies that are practical and economical as a function of application in the short and long term and (3) devising efficient, safe infrastructure strategies to facilitate the deployment of hydrogen energy technologies.

Overview of the scientific programme

Schematically, hydrogen energy systems can be described in terms of components as follows (from the Sustainable Development Business Case Report on Hydrogen by Sustainable Development Technology Canada (SDTC), page 16):



The research activities of the network will address the technical barriers of each component of a hydrogen energy system to improve commercial viability of the systems by lowering their cost and improving their efficiency, performance and durability. These components cannot be treated individually, production and delivery depends on storage, and the storage technology relies very much on the purity of hydrogen. The research activities will span the areas of production and purification, storage and infrastructure (including safety). The R&D programme will thus be articulated around three themes: *Production, purification and infrastructure (Theme A)*, *Storage (Theme B)* and *Infrastructure Safety (Theme C)*, which corresponds to the three objectives of the network. The research programme will require cross-cutting research between engineering, physics, chemistry and biology. The research

activities performed in the three themes will cross-correlate strongly and cannot be treated independently, as one theme will affect the other. The nanoporous materials developed for Theme B can be applied to the purification technologies studied in Theme A. Purification technologies of Theme A dictates the degree of purity of hydrogen, which influences the performance of the storage systems of Theme B. Similarly, the fluid mechanics studies of hydrogen and the safety studies of Theme C have implications for system modeling in both themes A and B. The infrastructure studies of Theme C will rely strongly on input from Themes A and B to determine production costs and storage system properties.

The large scale production of hydrogen as chemical feedstock is well developed in Canada. The work plan of theme A will aim to develop cost effective, renewable, low volume hydrogen production pathways from low cost "waste" biomass feedstock that will be cost competitive with SMR and could be used to satisfy the relatively low volume hydrogen demand in the energy sector of the near future (5-7 years). Cost-effective low volume production from biomass as well as improved purification pathways have been identified as potential disruptive technologies and near term priorities by the Sustainable Development Business Case Report on Hydrogen by Sustainable Development Technology Canada. New biomass production technologies would complement the capture of waste or by-product hydrogen. Waste, by-product, and hydrogen obtained from biomass all require advanced purification technologies to be used in hydrogen energy technologies such as PEM fuel cells or to be stored in materials such as metal hydrides. An important, longer term priority is the production of hydrogen by electrolysis from renewable energy sources. With this in mind, the researchers of Theme A will investigate the most promising hydrogen production and purification technologies ranging from wind power to biological and thermocatalytic conversion of biomass to the capture and conversion of landfill gases. The theme will be divided into three working groups: *A.1 Hydrogen production from wind power*, *A.2 Hydrogen Production from Biomass and Renewable Hydrocarbons*, *A.3 Purification and Separation Technologies.*

Designing storage systems for automotive applications or portable electronics that could operate close to ambient conditions and meet commercial performance objectives requires more than what current conventional storage technologies such as compression and liquefaction can offer. Exploiting chemical and physical interactions of molecular and atomic hydrogen with other atoms could bind important quantities of hydrogen in small volumes. The scientific programme of Theme B aims to develop materials-based storage strategy that could meet market expectations. The work plan of Theme B is structured as follows. Preliminary screening of materials for both metal hydrides and porous nanostructured adsorbents will be performed using ab initio quantum chemical simulations to estimate the enthalpy of formations, the binding energies and to understand the nature and strength of the hydrogen bond. Molecular dynamics and Monte Carlo simulations will be performed to estimate the hydrogen uptake and determine the sorption isotherms for nanostructured adsorbents. Synthesis and preparation of optimal materials as determined from the network objectives will be performed. The materials will be synthesized as a function of their structural, transport and thermodynamic properties. The volumetric and gravimetric storage densities as well as the cycling properties will be measured using the facilities of the participating institutions. Combinatorial analysis will be performed to examine the storage properties of mixtures for metal hydrides. The thermodynamic analysis and heat transfer properties of both metal hydrides and physisorption storage systems using the materials developed will be performed. The study of the behavior of such materials in sorption-based storage systems will be performed to optimize system design and determine operating parameters. As part of the activities of Theme C, the results will be used to study a niche application for distribution of hydrogen by cryosorption on nanomaterials and perform a comparative analysis with liquid hydrogen distribution schemes. For reactive chemical hydrides, cost reduction using alternative production methods for

compounds like sodium borohydride ($NaBH_4$), as well as investigations into hydrogenated compounds will be pursued. In addition, work will focus on the potential to provide mobile fuelling stations as a means of supplying the automotive industry without requirements for high pressure delivery and infrastructure costs. The tasks associated with this work plan correspond to the projects of the individual researchers. The project researchers are grouped thematically within the theme to increase interactions. The four groups are: *B.1 Theory and simulations, Group B.2 Development and characterization of materials, B.3 Storage systems design and optimization* and *B.4 Characterization*. We have set specific objectives based on partner input: achieving a *system* gravimetric storage density of 2% (which would amount to a materials storage density of about 3.5%), a volumetric storage density of 6 g/cc and a cost of the materials better than $30/kg over the five-year span of the network. The secondary objective is to determine pathways to achieve ambitious storage objectives of the DOE, discussed in the full Theme B description.

Theme C is composed of two research groups addressing hydrogen energy technologies issues from an energy system's point of view. The deployment of hydrogen systems at scales exceeding typical technology demonstrations requires more rigorous planning for both safety and cost. This is now happening with BC Transit bringing a significant hydrogen load on-stream with a fleet of fuel cell buses. The possible addition of hydrogen shuttle buses will result in the single-largest hydrogen based transportation system in the world. Production, distribution, and refueling technologies are required for the operation of the fleet while safety will be critical in all aspects. Safety is often seen as one of the main issues delaying the introduction of hydrogen energy systems and public concerns must be addressed. Research activities range from fundamental studies of hydrogen releases to high-level techno-economic modeling of infrastructure development. The work of Theme C is closely tied to projects in all of the other themes. Group C.1 "Infrastructure" examines cost, logistics, and technical requirements for infrastructure development. The group objective is to determine the preferred pathways for the hydrogen distribution chain considering specific Canadian conditions. Models of hydrogen energy system processes are developed using the performance characteristics of conventional and advanced hydrogen technologies. How technologies are best integrated to make a system, and how such a sub-system then performs in a regional setting will be examined. Advanced distribution technologies and liquefaction devices will be studied from a fundamental and systemic perspective. Outcomes of infrastructure studies will inform planning, policy, system and technology development activities. The objectives of Group C.2 "Safety" are to develop a scientific and engineering basis for determining safety standards and safe industry practices specific to hydrogen. Studies will focus on refueling infrastructure and safety of portable, stationary and transportation hydrogen energy applications. The safety of hydrogen technologies and systems should be as good, or better, than current energy systems. Safety concerns of the public, industry and government must all be addressed. Failure modes, probability of occurrence, and impacts of system failures must be quantified. Outcomes of this group will assist in determining safety standards and safe industry practices. Solid, compressed, and low-temperature storage modes will be studied. Research outcomes will help to reconcile perceived dangers with actual dangers and will guide the best practices of system developers and users. The research activities in Theme C complement each other by providing information for system studies, and by ensuring common approaches are leveraged wherever possible. For instance, the impact of new distribution and transportation technologies will be used in techno-economic studies of fleet fuelling and for examining distribution infrastructure. Another example is the Safety group, through clearance distance determinations, helping to establish the footprint of hydrogen distribution and storage points and to address acceptance issues.

The network participants will have access to the best material preparation and characterization equipment available in Canada. Preparation and characterization of metal hydrides and porous nanostructures and the measurement of the sorption properties of hydrogen in such materials over a wide range of pressure and temperature will be available through the Université du Québec à Trois-Rivières (UQTR). The UQTR facilities also include fully equipped test benches to study storage systems (hydrides and sorption) under real operating conditions. Extensive electron microscopy characterization of the materials developed by network participants will be carried out at McMaster, site of the Canadian Centre for Electron Microscopy (CCEM). The Steacie Institute's Materials Structure and Function group has extensive capabilities to carry out solid state NMR experiments, including a new 900 MHz instrument; offering unique, world-class materials characterization. Of special interest is the custom-built NMR probe able to operate at variable H_2 pressures up to 120 bar and temperatures down to -20^{o}C. Atomic and molecular scale information on material structure, interatomic interactions and transport properties are often required to characterize the processes involved in hydrogen production, storage, and use. Neutron scattering provides unique capabilities for such a purpose. The Canadian Neutron Beam Centre (CNBC) has developed a new cryostat that can operate at 10 bar H_2 (50 bars is planned) and down to 80 K to characterized H_2 sorption materials. Global quantitative images of hydrogen flow fields for the safety, storage and production themes can be obtained using the time-resolved digital particle image velocimetry (TR DPIV) system at the University of Victoria. In addition, network participants will have access to the facilities and the systems of the project partners to verify the performance of the materials and systems developed. For example, BC Transit will provide data for safety and infrastructure studies, the materials developed for portable systems would be tested in industry partners applications, Powertech labs will provide valuable data for safety studies and access to their testing facilities, etc. The research network will also provide access to ab initio quantum chemical modeling of complex solid state systems using the built-in code of well-established computational softwares through the University of New Brunswick (UNB) and UQTR (CRYSTAL, VASP, DMOL 3-Solid State for instance). The electronic structure and the thermodynamic properties of solids can thus be calculated at high accuracy and low computational costs. This will allow the efficient screening a wide range of composite materials and alloys. Simulation tools can thus be used to screen candidate materials so that only the most promising materials could then be studied experimentally, increasing the likelihood of success and reducing the number of costly experiments. Other simulation tools available include computer fluid dynamics tools such as Fluent, FLACS/Hydrogen, as well as Grand Canonical Monte Carlo and Molecular Dynamics simulation packages. The simulations will be carried out on the high performance computing facilities at UNB, UQTR, UVic and CLUMEQ.

Network relationships

Within Canada, we will closely collaborate with the hydrogen programmes of Natural Resources Canada, who will be a major co-sponsor of activities within this network (particularly in storage and distribution and infrastructure). We will also closely participate to the NRC hydrogen initiative. The network's scientific director, Richard Chahine, is a member of the steering committee of this initiative. We also hope to collaborate closely with the PEM Fuel Cell network proposed as part of the Strategic Network Grant programme and the SOCF Strategic Network, who would be the end users of some of the work performed by the Hydrogen network. Dr. Greg Naterer of the University of Ontario Institute of Technology (UOIT) leads a multi institutional, national and international research team to design a copper-chlorine cycle for producing hydrogen from nuclear energy. While hydrogen production using nuclear energy is beyond the scope of H2Can Net, UOIT expertise in thermochemical hydrogen production will be of benefit to H2Can Net researchers, and discussions between scientists and engineers in both groups will be encouraged. Where appropriate, non-disclosure or confidentiality

agreements will be developed to permit exchanges of ideas and/or information. The network will strive to closely coordinate its activities with the network of Centres of Excellence Auto 21 and avoid duplication of projects.

International collaborations be a priority of this network. Network researchers are actively involved in major international hydrogen initiatives such as tasks 19 (safety) and 22 (storage) of the Hydrogen Implementation Agreement of the International Energy Agency, the International Partnership for a Hydrogen Economy (IPHE), the European community's HySafe network on hydrogen safety, and the US DOE hydrogen programme and the Japanese NEDO hydrogen programme. Projects on hydrogen safety will be contributed to Task 19 on hydrogen safety of the IEA. The existence of a Canadian Hydrogen Network will intensify these interactions with the national hydrogen programmes of the United States, Japan and Europe, and foster international collaborations whenever they are possible or advisable. As a specific example, researchers at the National Renewable Energy Laboratory in Golden, Colorado, USA will work with Dr. Levin's group at the University of Manitoba to improve the molar yield of H_2 produced during dark fermentation of cellulose. The team will seek to gain a more in-depth understanding of the metabolic pathway profiles and gene regulation during cellulose conversion to H_2, and to develop a system for genetic transformation of C. thermocellum. Lignol Energy Inc. of Vancouver, BC, will provide delignified wood fibers that will be used as feedstock for both thermocatalytic and biological hydrogen production.

Training of highly qualified people (HQP)

The training of highly qualified people is one of the most important activities of the network. The participating institutions, through their educational programmes, and the experts involved in the network will foster the development of HQP, ensure that their educational experience is relevant and current and link them with the industries and the government agencies that need their skills. The participating institutions of the network offer advanced degrees in Physics, Chemistry, Engineering (Chemical, Electrical, Mechanical and Industrial) as well as Material Science and Energy. We intend to use 55% of the network grant funding to support HQPs. This estimate includes stipends for all students and post-doctoral fellows (PDF's) and salaries for research associates. Travel assistance for graduate students is not included in this percentage.

These investments will result in the training of at least 32 additional graduate students and PDF's, 2 research associates and 15 undergraduate students (including the internship programme of the network). The network will budget 12 internships of $4,500 for undergraduate students. One internship supervised by a network researcher at a given institution will be attributed to an undergraduate student registered at a different participating institution. The network will also budget an amount of $10,000/year to assist in travel expenses of eligible network researchers (graduate students are eligible) visiting network institutions (including industry partners) in the course of their collaboration (maximum of $2000 per researcher). Leveraged money (student scholarships, bursaries, etc.) will help to add to this number of HQP. It is worth mentioning that the students of the network will have access to advanced equipment and powerful computing resources. They will also get their training in an important, exciting, and expanding field with promising and challenging employment opportunities. The projected number of HQPs as a function of time is given in the table below.

HQP Themes A-C (cumulative)	Year 1	Year 2	Year 3	Year 4	Year 5
M.Sc. Students	25	25	1	1	1
Ph. D. Students	2	2	26	26	26

Post-doctoral fellows	5	5	5	6	6
Undergraduate students	3	3	3	3	3
Research associates	2	2	2	2	2
Total	37	37	37	38	38

Networking and Communications

The primary networking and communication activity of the network is its annual conference and general meeting of all network researchers, students, and participating industries and institutions. The Network also organizes annual HQP workshops that serve as the main avenue for networking of students accros the Network. There is also a communications committee composed of the scientific coordinator of the network and the three theme leaders to overview communications issues. Each theme coordinator will insure public diffusion of results when in the public interest. They will provide regular, high level summaries of theme activities which will be made publically available on the web site of the network. Each network researcher, as part of their annual report, will be required to submit high level summaries of their activities to assist the theme coordinators in that respect. A biannual newsletter will also be published to announce network activities, relevant conferences and showcase network successes. The website will be used to inform participants and researchers of network activities (conferences, publications, relevant events) and the public of its activities. We plan to have a preprint depository of network publications that would be accessible to network researchers and participating industry. The network has also budgeted a specific travel assistance programme to allow researchers (both professors and students) to visit participating institutions (industry partners, universities, participating NRC institutes) to enhance communications. The network will also institute a network-wide student internship programme to encourage undergraduate students from participating institutions to visit network researchers located at other facilities. Finally, the network will produce white papers on the status and prospects of hydrogen energy technologies.

The detailed scientific programme of each theme is described below.

Theme A – Hydrogen Production and Purification

Theme objectives

The objectives of the theme are to i) develop clean, renewable H_2 production and purification technologies to efficiently produce price-competitive, high-grade H_2 with minimal environmental impact for energy and other applications, and ii) determine which renewable H_2 production and purification technologies can meet the cost delivery targets set by the DOE.

The US DOE has established a target of reducing the cost of distributed production of H_2 from biomass-derived renewable liquids to $3.80/gge (delivered at the pump), or from biomass gasification to < $3.30/gge (delivered at the pump) by 2012, and < $3.00/gge or $2.10/gge, respectively (delivered at the pump) by 2017 (US DOE, 2006). The emergence of a significant price differential between natural gas and biomass as feedstocks for H_2 production creates a huge potential for production of H_2 as a high value-added product from low cost biomass.

Programme description

The Theme is divided into three groups: A.1 "H_2 Production from non-fossil sources", which will focus on H_2 production from wind power; A.2) "H_2 Production from biomass and renewable hydrocarbons", which addresses biological H_2 production, and hydrogen production via thermocatalytic conversion of biomass; and Group A.3) "H_2 Purification and Separation". A detailed breakdown of these research groups and the research projects to be conducted is presented below. The specific projects (or tasks) that will be funded and performed by individual network researchers within a research group are given in Table 15.1. Budget details contributed by the network to the projects are given in Tables 15.2 and 15.3.

Table 1 Theme A project list

Project ID	Title	Researcher
Group A.1 H_2 production from wind power (group leader: Kodjo Agbossou)		
Project A.1.1	Optimized electrolyzer hydrogen production from renewable energy system for fuel cells and hydrogen powered generators	PI: Kodjo Agbossou (with A. Rowe and N. Djilali)
Group A.2 Production from biomass and renewable hydrocarbons (group leader: D. B. Levin)		
Project A.2.1	H_2 production via cellulose fermentation	David B. Levin
Project A.2.2	H_2 production via aqueous reforming of organic molecules	David B. Levin
Project A.2.3	H_2 production by biomass gasification	Jean Hamelin
Project A.2.4	H_2 production by water gas shift reaction	Raphael Idem
Group A.3 Purification and Separation Technologies (group leader: Daniel Guay)		
Project A.3.1	Metallic membranes for H_2 gas separation	Daniel Guay with Lionel Roué
Project A.3.2	Purification and analysis of hydrogen derived from biomass	Brant Peppley

Project B.2.4 (*Hydrogen storage in novel hybrid nanoporous materials*) will also impact the purification R&D activities of the network. The overall goal of Theme A is to develop renewable cost-effective H_2

production pathways from low cost "waste" biomass feedstocks that will be cost competitive with SMR. The research programme of the Production and Purification theme is in agreement with the research priorities of the SDTC business case of hydrogen quoted above, namely improving purification technologies for valorization of hydrogen byproducts (A.3.1, A.3.2 and project B.2.4), and developing advanced reforming processes that use new feedstock.

We will investigate diverse H_2 production and purification technologies ranging from Wind power to biological and thermocatalytic conversion of biomass to the capture and conversion of landfill gases. Despite the varying nature of these technologies, there will be considerable networking and collaboration within the theme. For example, there will be extensive collaboration and networking between David Levin at the University of Manitoba, Jean Hamelin at the Université du Québec à Trois-Rivières, and Raphael Idem at the University of Regina with respect to thermocatalytic conversion of biomass to H_2. Moreover, the primary scientific and engineering challenge common to all the conversion technologies will be how to capture, purify, and store the H_2 produced. We anticipate that there will be an extensive exchange of ideas, information, data, and technologies between the H_2 production groups (A1 and A2) and the H_2 purification and separation technology group (A3).

Collaborations with the other themes

There will also be extensive exchange of ideas, information, data, and technologies between Theme A and Theme B. Once H_2 has been produced and purified, it must be stored by means that permit it to me transported safely, and recovered efficiently when required for application. Each of the different H_2 production technologies investigated in Theme A will present unique problems and challenges with respect to integrating H_2 purification and storage components. Thus, we anticipate a great deal of collaboration, and information flow between Theme A and Theme B.

Knowledge, data, and technologies generated by Theme A will also flow directly to Theme C, which will provide input to the infrastructure studies through the identification of site-specific hydrogen production pathways and production cost estimates. Theme C will find niche applications for H_2 energy systems, study their limitations and propose optimal pathways to their integration into the energy market within a 5 to 10 year time-frame. The R&D activities of Themes A and B will directly feed into the activities of this theme, integrating the activities of the other two themes into systems that meet consumer demands. The theme can be viewed as interfacing the end-users of energy technologies and R&D activities on hydrogen production, storage and energy conversion devices.

Project B.2.4 (H2 Storage in novel hybrid nanoporous materials) as well as the R&D activities of Project B.3.2 (Heat and Mass Transfer in Sorption-based storage systems) are of direct relevance to the research interests of the purification and separation group. Both of these projects can be viewed as cross-theme projects between A and B, as the nanoporous materials developed for storage are of direct relevance to purification and separation.

Theme A Project descriptions

Projects are network funded contributions from individual network researchers (principal investigator). The principal investigator may have collaborators in his project who are not funded through the network.

Group A.1 H_2 production from wind power

Project A.1.1 Optimized hydrogen production using electrolyzers from renewable energy for fuel cells and hydrogen powered generators

Kodjo Agbossou, Institut de recherche sur l'hydrogène (IRH), Department of Electrical Engineering, Université du Quebec à Trois-Rivières

Summary: The objective of this collaborative project with Hydro Québec is to study the impact of the storage units and the production methods of hydrogen on the durability and reliability of fuel cells. Specifcally, this project will (1) analyze the quality of H_2 produced with an electrolyzer using wind power and photovoltaic renewable energy systems as it exists a storage system (either compressed gas or materials-based) prior to its use to feed a fuel cell system; and (2) to address durability and reliability issues of fuel cells as a function of the storage system. Accurate diagnosis is a key step in the maintenance process of the fuel cell system in order to increase its performance and durability. This project will mainly use the stand-alone renewable energy (RE) system based on hydrogen production from wind and solar energy at the IRH of the UQTR. The diagnosis analysis will be based on chemical detection and atomic adsorption to detect the presence and concentration of harmful compounds in the stored hydrogen. Diagnosis techniques using statistical tools and artificial intelligent tools will be applied for compounds thresholds detection. The diagnosis study will be validated on our fuel cell test bench at the Institut de recherche sur l'hydrogène.

Collaborators: Andrew Rowe and Ned Djilali, Institute for Integrated Energy Systems, Department of Mechanical Engineering, University of Victoria.

Group A.2 H_2 Production from biomass and renewable hydrocarbons

Project A.2.1 H_2 production via cellulose fermentation

David B. Levin, Department of Biosystems Engineering, University of Manitoba

Summary: Fermentation of cellulose by the thermophilic, anaerobic celluloltyic bacterium, *Clostridium thermocellum*, generates H_2 and CO_2 (at a molar ratio of approximately 1:1). We have established a continuous culture system for biological H_2 production via direct fermentation of cellulosic biomass. Rates and/or yields of H_2 synthesis can be increased by maintaining low H_2 partial pressures within the bioreactor. The objectives of this project are to: 1) determine if H_2 synthesis can be enhanced using a membrane bioreactor to facilitate rapid removal of gases (H_2 and CO_2) from the culture medium; 2) develop a method to purify H_2 from the gas mix; and 3) develop a method to accumulate and store the purified H_2.

Collaborators: Richard Sparling (Microbiology, University of Manitoba) and Nazim Cicek (Biosystems Engineering, University of Manitoba) will collaborate with respect to microbial metabolism and cellulose fermentation. Daniel Guay (Institut National de la Recherche Scientifique, Énergie, Matériaux et Télécommunications) and Andrew Rowe (Mechanical Engineering, University of Victoria) to develop the purification and/or storage methods.

Project A.2.2 H_2 production via aqueous reforming of organic molecules

David B. Levin, Department of Biosystems Engineering, University of Manitoba

Summary: Alkaline Enhanced Reforming (AER) can convert aqueous hydrogenated organic molecules to gaseous H_2 at low temperatures and pressures. The AER process used an alkaline pH, which creates conditions that are thermodynamically more favorable than conventional steam reforming. As a result, the reforming occurs at significantly lower temperatures than the corresponding conventional steam

reforming. A solid salt (Na_2CO_3) by-product is formed, rather than the carbon monoxide (CO) and carbon dioxide (CO_2) gases formed during conventional steam reforming, making the AER reactor simpler, and offering the potential to generate renewable H_2 without the concomitant production of greenhouse gases. Various fuels can be processed using the alkaline enhanced reforming process, but the process needs to be optimized for feedstocks with different consistencies and densities. We will investigate H_2 production via AER using a variety of renewable "waste" feedstocks that are abundantly available in the Prairie provinces of Canada: glycerol derived from biodiesel synthesis, stillage and dried distillers grains derived from bioethanol production, and liquid hog manure. Each of these residues has a different chemical content and density, and will require a unique set of operating conditions to maximize conversion to H_2. Each feedstock may also affect the conditions required for effective H_2 storage. The specific objectives of this proposal are to optimize the AER for each feedstock process by varying 1) catalyst type (Ni-based) and amount, 2) operation temperature (140 ˚C to 300 ˚C) and pressure (70 psi to 250 psi), and 3) reactant composition (ratio of the different components: alkaline/fuel/water) and alkaline type (examples: NaOH, $Ca(OH)_2$, LiOH).

Collaborators: Benny Reichman, Energy Storage Devices, Rochester Hills, Michigan; Jean Hamelin, Institut de recherche sur l'hydrogène, Physics department, Université du Québec à Trois-Rivières

Project A.2.3 H_2 production by biomass gasification

Jean Hamelin, Institut de recherche sur l'hydrogène (IRH), Physics department, UQTR

Summary: We propose a modified application of a novel method developed by Ishida *et al*. (2006. *Energy & Fuels* 20, 749), for the synthesis of hydrogen without CO or CO_2 for fuel cells through the reactions of biomasses, alkali metal hydroxides and water vapor at relatively low temperatures (200 to 350 °C) under atmospheric pressure. In our method, biomass mass consisting of numerous and cheap sources, such as wood chips, saw dust… widely distributed in pulp & paper mills can be utilized as raw materials for the production of clean hydrogen. Roughly, 80% of the pulp mills run kraft chemical recovery process to recover the kraft pulp digestion chemicals from the effluent black liquor. This reduces the amount of chemicals required for pulp digestion and reducing the effluent load that must be treated prior to discharge. Sodium hydroxide (NaOH) required for pulp digestion can be recovered by treating the green liquor (treated black liquor) in a causticizer, which converts the molten inorganic salt - sodium carbonate (Na_2CO_3) into sodium hydroxide. This sequence of chemical processes can also be used to convert the byproduct sodium carbonate from hydrogen production into sodium hydroxide. The clean hydrogen produced can be stored or directly fed to polymer electrolyte membrane fuel cells to produce electrical energy, which can be used for several applications.

Collaborations: David B. Levin, Department of Biosystems Engineering, University of Manitoba; Benny Reichman, Energy Storage Devices, Rochester Hills, Michigan

Project A.2.3.4 H_2 production by Water Gas Shift Reaction

Raphael Idem, Faculty of Engineering, University of Regina

Summary: Methane derived from anaerobic digestion of organic material, from land-fill, or generated by gasification of biomass can be converted to H_2 by the water gas shift reaction (WGSR). Carbon monoxide (CO) generated by gasification can also be converted to H_2 plus CO_2 by the WGSR. The CO_2 may be captured by conducting the WGSR in a membrane reactor. The challenge lies in (1) developing a cheap nickel based catalyst for dry reforming without catalyst deactivation, (2) conducting the dry reforming reaction at lower temperatures without catalyst deactivation by coke deposition, (3) developing a suitable catalyst for the WGSR at higher temperatures in order to minimize the temperature mismatch between the endothermic dry reforming temperature and the exothermic WGSR temperature.

Dry reforming is a very effective way to use low quality natural gas and biogas (both containing large fractions of CO_2 with CH_4). This group will work on catalyst and process development to solve these issues.

Collaborators: David B. Levin, Department of Biosystems Engineering, University of Manitoba; Jean Hamelin, Institut de recherche sur l'hydrogène, Physics department, UQTR

Group A.3 Purification and Separation Technologies

Project A.3.1 Metallic membranes for H_2 gas separation

Daniel Guay and Lionel Roué, Institut National de la Recherche Scientifique, Énergie, Matériaux et Télécommunications, Université du Québec à Trois-Rivières

Summary: Advances in gas separation technologies, such as improved separation membranes, resulting from the need to recover pure hydrogen from a mixed gas stream, have the potential to improve efficiency and recovery while decreasing the costs of hydrogen production. Palladium-based membranes are viable candidates for membrane reactors because of their high hydrogen permeability and catalytic activity with respect to hydrogen dissociation. However, Pd membranes are very rapidly deactivated by trace concentration of sulfur (among other contaminants). Binary Pd-M alloys have been proposed to improve the membrane resistance to deactivation. The choice of M will vary with the composition of the gas stream and we will concentrate of optimizing the nature of M to meet the particular requirement of the hydrogen source. Also, recent calculations have shown that the diffusivity of hydrogen in body-centered-cubic (bcc) Pd-Cu is several times larger than in face-centered-cubic (fcc) Pd-Cu. However, the bcc Pd-Cu phase is converted to a fcc phase above ~ 873 K. To be compatible with the temperature found in industrial H_2 separation process, it is crucial to increase the stability domain of the bcc phase. This can be achieved by the addition of a third element (ternary Pd-alloy), a domain that has very seldom been explored. Quantum mechanical calculations will be performed to help in the choice of M. Therefore, in this project, we propose to investigate bcc Pd-Cu-M alloys as novel H_2 separation membranes having high hydrogen permeability, high resistance to poisoning and high thermal stability.

Collaborators: Pierre Bénard, Institut de recherche sur l'hydrogène, Université du Québec à Trois-Rivières.

Project A.3.2 Purification and Analysis of Hydrogen Derived from Biomass

Brant Peppley, Canada Research Chair in Fuel Cells, Queen's University, Kingston

Summary: The objective of this research is to develop innovative and commercially practical processes H_2 production from landfill gases. Methods for capture and purification of landfill gases with subsequent conversion to commercial grade H_2 suitable for fuel cells and other energy conversion devices will be developed and evaluated. The research and development work will consist of the following set of tasks: i) Develop analytical methodologies for precisely determining the concentrations of various contaminants in landfill gas; ii) Develop methods for evaluating the capacity, efficiency and reliability of methods of contaminant removal. Contaminants to be examined include: sulphur compounds, organic acids, metal salts and organic compounds, and siloxanes; iii) Investigate the effect of various contaminants on the rate of deactivation of catalysts used in the process for converting landfill gas to hydrogen; and iv) Develop advanced process simulations for determining efficiencies, and energy and material balances in a landfill to hydrogen system leading to the development and design of new technologies for hydrogen production. Specifications and design requirements for the fuel conditioning system will be developed through discussions with personnel from the private sector. Existing patented fuel-conditioning system designs and components will be continuously monitored with the intention of

developing new intellectual property of commercial value. Areas in which intellectual property may be developed include but are not limited to components designs for gas conditioning equipment, adsorbent regeneration methods, contaminant measurement methods, and process design and control strategies.

Collaborators: Daniel Guay, Institut National de la Recherche Scientifique, Énergie, Matériaux et Télécommunications, Université du Québec à Trois-Rivières.

Theme B – Hydrogen Storage

Theme objectives

Both cryogenic and high pressure hydrogen storage are rapidly maturing, and the potential for breakthrough research is minimal. For this reason, Theme B is focused on materials storage. The proposed network in hydrogen storage (Theme B) has been structured around three promising strategies: *chemical hydrogen storage*, *reversible metal hydrides* and *reversible sorption on porous nanostructures*. The use of these materials in systems will be a prime concern of the theme. The scientific programme aims to develop and evaluate new materials-based hydrogen storage strategies for portable applications (short term) and transportation (long term) from the perspective of material science and system design and optimization. The theme objectives are:

(1) Application-targeted storage density improvement: In consultation with industry partners, we have set the main network objective for storage to achieving a *system* gravimetric storage density of 2% (which would amount to a materials storage density of about 3.5%), a volumetric storage density of 6 g/cc and a cost of the materials better than $30/kg over the five-year span of the network. This objective, which we feel is realistic, would provide a competitive advantage to micro fuel cell applications, which we see as the short term pathway to introduce hydrogen on the energy market. For transportation, we adopt the targets for automotive applications set by the U.S. Department of Energy as performance benchmarks for the storage materials (12 MJ/kg gravimetric and 10 MJ/L volumetric for a range of 560 km).

(2) Performance evaluation of materials and systems: The network will strive to provide to network partners with quantitative evaluation of properties of materials for hydrogen storage and of their performance when used in storage systems.

Programme description

Three hydrogen storage strategies will be investigated: absorption in destabilized and high volumetric density metal hydrides, adsorption in highly porous nanostructured materials and hydrogen storage using chemical hydride processes. These strategies will be studied and optimized from the point of view of material science and as systems and processes. Reversible metal hydrides provide an attractive on-board hydrogen storage technology particularly suited to smaller portable applications where the inherent weight of the hydride material is not a serious impediment. Through careful system design, metal hydride based hydrogen fuel cell systems have the potential to outperform all other technologies in these applications. Lower capacity reversible metal hydrides thus have a significant potential for early market penetration of hydrogen via portable applications. Indeed, commercially available AB5 or AB2 hydride alloys have 25% more energy density than lithium-ion batteries. BCC alloys can double that capacity but they are too costly for early market penetration. Our objective will be to cut the cost by using different alloying strategies. Other alloys that may be suitable for transportation applications will also be investigated. In particular, destabilized alloys which may operate close to ambient conditions will be studied. Finally, the structural optimization of metal-doped or scaffolded nanoporous materials (MOF, carbon nanostructures) for hydrogen storage by physisorption will be investigated. These materials can also be used for purification, and this topic will cross-correlate with the activities of the production theme. A low-pressure route to the synthesis of hydrogen clathrate hydrate will also be pursued, as well as the use of tuning approaches to the synthesis of mixed clathrate hydrates with a high hydrogen storage capacity. An area that requires further investigation is the design and performance of storage systems subjected to arbitrary dynamic loads. Likewise, when integrated with a fuel cell system, the ability to effectively capture and utilize waste exhaust heat can be a challenge. At small storage scales (cubic centimeters), issues relative to prismatic packaging and determining the state of charge must be

addressed for practical implementation in commercial products to occur. This research will examine these system-level issues for small-scale portable metal hydride storage systems, as well as stationary systems, under dynamic loads. Finally, a thermodynamic analysis of systems based on hydrides and nanoporous materials will be performed to optimize flow and thermal management. In addition to reversible storage on materials, new storage strategies involving reactive chemical hydrides, cost reduction using alternative production methods for compounds like sodium borohydride ($NaBH_4$), as well as investigations into hydrogenated compounds will be pursued. We will seek to improve the storage density of $NaBH_4$ and other non-reversible hydrides through the use of non-reactive solvents and develop a more efficient recycling process of the product material through the use of molten hydride melts. As well, the value of reactive chemical hydrides will be investigated in terms of their abilities to generate very high hydrogen gas pressures, well above those economically possible with conventional methods.

The theme will be organized in 4 research groups: Theory and simulations of hydrogen storage materials, Development of materials for hydrogen storage, Storage systems design and optimization and Characterization. The theme targets metal hydrides for portable and vehicular applications, sorption on porous nanostructures for hydrogen distribution and vehicular applications, and chemical hydrides for vehicular applications. The group activities are related to each other in the following way:

(1) Preliminary screening of materials for both metal hydrides and porous nanostructured adsorbents of will be performed using ab initio quantum chemical simulations to estimate the enthalpy of formations, the binding energies and to understand the nature and strength of the hydrogen bond.

(2) Molecular dynamics and Monte Carlo simulations will be performed to estimate the hydrogen uptake and determine the sorption isotherms for nanostructured adsorbents.

(3) Synthesis and preparation of optimal materials as determined from the network objectives will be performed.

(4) The materials will be synthesized as a function of their structural, transport and thermodynamic properties.

(5) The volumetric and gravimetric storage densities as well as the cycling properties will be measured using the facilities of the participating institutions.

(6) Combinatorial analysis will be performed to examine the storage properties of mixtures for metal hydrides.

(7) The thermodynamic analysis and heat transfer properties of both metal hydrides and physisorption storage systems using the materials developed will be performed. The study of the behavior of such materials in sorption-based storage systems will be performed to optimize system design and determine operating parameters. As part of the activities of Theme C, the results will be used to study a niche application for distribution of hydrogen by cryosorption on nanomaterials and perform a comparative analysis with liquid hydrogen distribution schemes.

(8) For reactive chemical hydrides, cost reduction using alternative production methods for compounds like sodium borohydride ($NaBH_4$), as well as investigations into hydrogenated compounds will be pursued.

The specific projects (or tasks) that will be funded and performed by individual network researchers within a research group are given in Table 16.1 below. Budget details contributed by the network to the projects are given in Tables 16.2 and 16.3.

The theme will have access to the best characterization tools available to probe the properties of metal hydrides and nanostructured microporous adsorbents. The characterization activities of the network researchers in support of the materials and system development are in group 4.

The activities of B.4.2 and B.4.3 are not included in the budget of the proposed network. Characterization of the nanoscale structure of the produced materials synthesized in the network will be necessary at all stages throughout this project. Group B.4 have a fundamental networking role to play within H2Can: they will be to support the research activities of the network, particularly of groups 1 to 3 of Theme B and of Theme A by providing a materials characterization infrastructure.

Table 2 Theme B project list

Project ID	Title	Researcher
Group B.1 Theory and simulations of hydrogen storage materials (group leader: Sean McGrady)		
Project B.1.1	DFT modeling of hydrogen storage materials	Sean McGrady
Project B.1.2	Simulations of hydrogen adsorption isotherms for nanoporous materials	Pierre Bénard
Group B.2 Development of materials for hydrogen storage (group leader: Richard Chahine)		
Project B.2.1	High volumetric density storage metal hydrides	Jacques Huot
Project B.2.2	Mg-Ti films for hydrogen storage	David Mitlin, Jacques Hout
Project B.2.3	Catalyzed lithium complex hydrides and its composites	Robert A. Varin, Z. Wronski
Project B.2.4	Hydrogen storage in novel hybrid nanoporous materials	Richard Chahine
Group B.3 Storage systems design and optimization (group leader: Boyd Davis)		
Project B.3.1	Hydride Storage Systems	Andrew Rowe
Project B.3.2	Heat and mass transfer in sorption-based storage systems	Jacques Goyette
Project B.3.3	Novel chemical hydrogen storage concepts	Tom Baker and Boyd Davis
Group B.4 Characterization (group leader: Gianluigi Botton)		
Project B.4.1	Microscopy of nanostructured hydrogen storage materials	Gianluigi Botton
Project B.4.2	Neutron diffraction analysis	Helmut Fritzsche
Project B.4.3	NMR characterization	John Ripmeester / Chris Ratcliff

Porous structure characterization and hydrogen uptake measurements will be performed by the team of Richard Chahine at the Hydrogen Research Institute (UQTR). The facilities include a test bench for hydrogen as a function of pressure (0-20 MPa, 77-300 K, maximum volume of 3 liters), a granulometry measurement system (63-850 microns), a mercury porosimeter (diameter 4-400 microns, max pressure

415 MPa), a BET surface analysis (diameter 0.35-500 microns), a X-Ray diffractometer, a Differential scanning calorimeter, and volumetric and gravimetric hydrogen sorption measurement systems from 77-300 K and 0-10 MPa. The facilities also include a computer aided cycling system for hydrogen absorption measurement.

Theme B Project descriptions

Projects are network funded contributions from individual network researchers (principal investigator). The principal investigator may have collaborators in his project who are not funded through the network.

Group B.1 Theory and simulations of hydrogen storage materials

Project B.1.1 DFT Modeling of Hydrogen Storage Materials

Sean McGrady, University of New Brunswick

Summary: Perhaps the most demanding requirement for a viable hydrogen storage material is the facile release of hydrogen, typically between 80 and 150 °C. In addition, the system must be easily reversible so that rehydrogenation can be effected under reasonably straightforward conditions. These requirements place strict limitations on the thermodynamics of the system: the enthalpy of H_2 release, ΔH_{dec}, must lie close to –20 kJ per mole of H_2. In practice, only a small number of systems meet this requirement, and undirected research efforts can be very inefficient and time-consuming. We will employ accurate quantum chemical modeling of solid state systems to avoid such problems. Using Hartree-Fock and (hybrid) density functional theory approximations for periodic systems incorporated in well-established computational softwares such as *CRYSTAL*, or the more precise augmented plane-wave methods in *WIEN2k* or *VASP*, the electronic structure and associated ground-state and thermodynamic properties of solids can be obtained with high accuracy and low computational costs. Such an approach has only just begun to find application in the quest for an understanding of the energetics of hydrogen storage system. This will allow us to study a wide range of composite materials and alloys *in silico*, and to predict accurate ΔH_{dec} values. We can then make judicious choices about which systems to concentrate on synthetically, rather than having to prepare each one laboriously in the laboratory and characterize its thermodynamics experimentally. Additionally, theoretical investigations will also be helpful for a deeper understanding of the fundamental properties of the material. Electronic densities of states (DOS), the charge distribution, overlap populations, and the electron localization function (ELF) all allow for a detailed insight into the bonding within the structural framework, and may therefore assist in tuning material properties.

Collaborators: Professors David Mitlin, Robert Varin and Jacques Huot on calculations of their mixed-metal hydride systems for hydrogen storage, HSM Systems Inc.

Project B.1.2 Modeling of hydrogen adsorption processes in nanoporous materials

Pierre Bénard, Université du Québec à Trois-Rivières

Summary: We will use Grand Canonical Monte Carlo and Molecular dynamics simulations to calculate the physisorption isotherms of the MOF and carbon nanostructures studied by the theme using a Morse pair potential fitted from Møller-Plesset ab initio calculations. Quantum corrected potentials will be used for low temperatures (below 100K). Additionally, in support of the activities of D. Guay, we will use DFT calculations to estimate the diffusivity of hydrogen in binary Pd-M alloys and ternary Pd alloys studied by his team. Finally, based on the modeled isotherms, we will study the thermodynamics of hydrogen physisorbents to predict the properties of physisorption based storage systems using the Myers formalism.

Collaborators: Professors Richard Chahine (uptake predictions), S. McGrady (determination of force fields), A. Rowe (systems studies), Daniel Guay (Theme A, purification, calculation of the diffusivity), NRCAN, Air Liquide.

1. Months 0-3: Literature review and selection of initial materials in concert with network partners
2. Months 3-18: Ab-initio calculation of the binding energy of and configuration of physisorbed molecular hydrogen on selected MOF and doped nanocarbons and feedback to project B.2.4
3. Months 3-12: Ab-initio (DFT) calculation of the diffusion constant of hydrogen in Binary Pd-M alloys (in collaboration with project A.3.1)
4. Months 6-18: Determination of the profile of the pair potential of the initial materials selected
5. Months 12-15: Feedback from project A.3.1.
6. Months 15-30: Calculation of the diffusion constant of hydrogen in Ternary Pd alloys for project A.3.1 and optimization of the ternary alloy
7. Months 18-21: Fit of the binding energy as a function of distance on Morse and Lennard-Jones pair potentials
8. Months 18-24: Modification of HRI GCMC code and Quantum GCMC code to include Morse potential and selected adsorbents
9. Months 21-30: Calculation of adsorption isotherms using GCMC simulations of hydrogen sorption using the fitted potentials
10. Month 24-30: Feedback & results collected from projects B.2.4 and B.3.1 and calculation of volumetric and storage densities of systems based on studied materials
11. Month 30-48: Calculation of adsorption isotherms for new materials using feedback from project B.2.4 and other network researchers and studies of the effect of contaminants (purification and storage implications).
12. Month 48-60: Estimation of system volumetric and storage densities of the new materials, comparison to network storage objectives and identification of potential niche applications.

B.2 Development and characterization of materials for hydrogen storage

Project B. 2.1 Storage materials with high volumetric capacities

Jacques Huot, Université du Québec à Trois-Rivières

Summary: Metal hydrides with high volumetric capacity and low cost are needed for small portable fuel cell applications such as cell phone, laptop, flashlight, etc. Recently, Ti-based alloys with a body centered cubic (BCC) crystal structure have been shown to have interesting characteristics for practical applications (high hydrogen capacity, room temperature operation). However, more development is needed to reduce cost and increase volumetric and gravimetric capacities. One part of this project will be the investigation of Ti-V-Mn and Ti-V-Cr alloys. One aspect is to study the synthesis and preparation of these alloys by different techniques such as arc-melting, cold rolling, ball milling or a combination of these. Simultaneously, different composition will be investigated in order to find the optimum composition. Particularly, crystal structure modifications and the modification of this structure by cold rolling and ball milling will be studied. Also, relationship of hydrogen capacity and hydrogenation kinetics with crystal structure will be investigated. For cost reduction we will examine the replacement of vanadium by ferro-vanadium. Once the optimum alloy composition and synthesis technique is found

we will study the effect of cycling and a prototype tank will be build in collaboration with other IRH group (J. Goyette). Another aspect of the project will be to study the synergy between BCC alloys and nanoporous materials (IRH-Chahine). Nanoporous materials (carbon nanotubes, metal-organic framework, etc) could be used as a support for BCC alloys. This could enhance the hydrogen sorption kinetics and improve cycle life. Composites with high capacity hydrides such as magnesium, complex hydrides and alanes will also be investigated.

In addition to BCC alloys we will study the Mg-Ni-Ca system. Recently, the PI has published a paper on the crystal structure of $(Mg_xCa_{1-x})Ni_{2.6}$ (S. Miraglia et al. *Journal of Alloys and Compounds* **478**, L33 (2009)) showing that this class of material could have interesting hydrogen storage properties. This part of the project will be in close collaboration with the group of Prof. M. Medraj of Concordia University. Dr. Medraj's group will use combination of thermodynamic modeling and experimental characterization to find the optimum compositions in the Mg-Ni-Ca-H system which is suitable for hydrogen storage applications. Constituent ternary systems will be developed by the means of computational thermodynamics combined with ICP, DSC, XRD and SEM/EDX experiments at Concordia University. A self-consistent database will be constructed to predict the phase relations and various thermodynamic properties of any composition in the system and to identify the most promising alloys for hydrogen storage application. The effect of high energy ball milling on these alloys will then be investigated at IRH.

UBC and NRC-IFCI researchers have developed and assembled very good metal hydride research capabilities, which include ball milling, an inert glovebox, PCT equipment, and a wide range of physical/chemical characterization tools (XRD, SEM-EDS, TGA/DSC, Raman etc.) at NRC-IFCI and UBC's Advanced Materials and Process Engineering Laboratory and are essentially ready to tackle any hydrogen storage materials research now. The work at UBC, which has already started, will initially focus on bimetallic catalysts for MgH_2. Transition metals that has not been studied and reported will be examined for their catalytic behavior on the desorption and absorption of hydrogen from MgH_2. This work will then expand into complex metal hydride composites. Recently, Liu and Vajo have reported some of the best desorption measurements of $LiBH_4$ from ball milled composites of $LiBH_4/Mg_2NiH_4$ (P. Liu and J. J. Vajo, IV.A.1i *Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage*, US DOE Annual Progress Report – 2009). Novel magnesium alloys (e.g. Mg_2-M-H_4, M = Co, Fe, Pd, etc.) will be synthesized and examined for their hydrogen storage properties. This work will be conducted in collaboration with the research group of Dr. Jacques Huot of Université du Québec à Trois-Rivières. The work will then continue with further complex metal hydride systems which possess high gravimetric capacities. Synthesis and PCT measurements will be performed by Dr. Wilkinson's research group at UBC's Clean Energy Research Center. Other material properties (structure, composition, morphology, etc) will be studied at NRC-IFCI.

Collaborations: R. Chahine (IRH-UQTR) Nanoporous materials, J. Goyette (IRH-UQTR): Storage tanks with BCC alloys, R. Varin (Waterloo): Mg-BCC composites made by ball milling, A. Yonkeu (Chalk river): Study of crystal structure of BCC alloys by neutron diffraction, S. McGrady (UNB): Calculation of stability and hydrogen storage in BCC alloys, D. Mitlin (U. Alberta): Thin films BCC alloys, NRCAN, Angstrom Power, M. Medraj (Department of Mech. and Ind. Engineering, Concordia University): Mg-Ni-Ca system, D. Wilkinson (UBC, NRC-IFCI) and R. Hui (NRC-IFCI): synthesis and characterization of Mg and bimetallic catalysts (MgH_2-M-M') and $LiBH_4$/magnesium alloy hydrides.

Project B.2.2 Mg-Ti films for hydrogen storage

David Mitlin, University of Alberta and NRC National Institute for Nanotechnology and Jacques Huot, Hydrogen Research Institute.

Summary: Cold rolling is a new method for the industrial fabrication of promising metal hydride alloys for hydrogen storage applications. Recent studies of magnesium-based alloys showed that it is possible to synthesize intermetallics by a judicious choice of rolling parameters and heat treatment. In order to assess the full capability of this technique, fundamental understanding of the rolling mechanism should be acquired. For example, in cold rolling, foils of raw elements are stacked and then repeatedly rolled to achieve a good dispersion of one element into the other. With thin films, the thickness of each element could be precisely controlled and, thus, provide useful knowledge on cold rolling technique.

We will study Mg-Ti alloys produced by combinatorial co-sputtering to create a variety of microstructures as thin film model systems. We will consequently test the alloys' sorption properties and determine which composition and types of microstructures are most effective for achieving destabilization of magnesium. While the obvious drawback of thin films is that they cannot be produced in quantities necessary for commercial-scale hydrogen storage, their clear advantage is that they are well-controlled, impurity-free, generally microstructurally uniform systems, that are significantly more conducive to detailed structure analysis and modeling than powders. Additionally, films allow us to de-convolute the effect of microstructure from that of variations in sample surface area on the sorption characteristics. A fully-dense thin film has a constant surface area, whereas the surface area of a powder will evolve simultaneously during processing (e.g. high-energy milling) and sorption cycling.

This project is complementary to the project B.2.1 High volumetric density storage metal hydrides and, thus, strong collaboration between these two projects is anticipated. First, we will investigate the effect of high strain in thin films on hydrogen storage properties. Thin films with a controlled thickness of Mg and Ti layers will be prepared and send to IRH where cold rolling will be performed. In this way, the effect of interdiffusion of the elements could be investigated. University of Alberta's TEM facilities will be used to study both thin films and cold rolled alloys.

Collaborators: Planned collaboration with project B.2.1.

Project B.2.3 Catalyzed lithium complex hydrides and its composites

Robert A. Varin, University of Waterloo and Zbig Wronski, CANMET Energy Technology Centre-Ottawa

Summary: In our on-going research program we attempt to improve hydrogen sorption properties of complex hydrides such as alanates, amides and borohydrides. In the present project research efforts will be focused on the development of catalyzed $LiNH_2$-based hydrides and their composites. The hydride systems based on light metals provide the highest available theoretical hydrogen capacities.

The most recent assessment of the suitability of various hydride systems for the automotive hydrogen storage by the U.S. Department of Energy (D.O.E.) [*Materials Go/No-Go Decisions made within the Department of Energy Metal Hydride Center of Excellence (MHCoE), Sandia National Laboratories, September/October 2007*] identifies three promising candidate systems for hydrogen storage based on $LiNH_2$. The first one is based on the formation of the intermediate LiMgN compound as a result of the following reaction: $LiNH_2+MgH_2 \rightarrow LiMgN+2H_2 \leftrightarrow LiH+0.5MgH_2+0.5Mg(NH_2)_2$ **(System 1).** It is to be noted that the second part of this reaction is predicted theoretically to be reversible with the standard enthalpy change of 32 and 51 kJ/mol H_2 for the first and second stage, respectively. Theoretical modeling predicts 8.2wt.%H_2 capacity for the system. No experimental studies of this system have been attempted yet. In order to further optimize the desorption/absorption temperature range of the $LiNH_2/MgH_2$ system, we propose to investigate the effect of catalyzing agents such as the proprietary batches of nano-Ni produced by Vale Inco, Mississauga, Ontario, as well as a number of transition metal chlorides MCl_n (where M=Ti, V, Mn, Ni, Fe) either as separate species or composited together. Mixture

of hydrides will be processed by controlled mechanical milling which induces formation of nanostructure. It is anticipated that a nano-scale partitioning enforced by high-energy ball milling will yield nanocomposites with improved sorption/desorption properties. Two other systems will also be investigated. The second system consists of complex lithium alanate and amide in the 3:1 $3LiNH_2+Li_3AlH_6 \leftrightarrow 3Li_3NH+Al+4.5H_2$ **(System 2)**. The predicted H_2 capacity is 7.3wt.% at the temperature range 200-300°C. The intermediate Li_3AlH_6 will be produced by ball milling from $LiAlH_4$ according to the well-known reaction: $LiAlH_4 \rightarrow 1/3Li_3AlH_6+2/3Al+H_2$. $LiAlH_4$ doped with catalytic additives (e.g. nano-Ni) easily decomposes during high energy ball milling. The studies of the ($3LiNH_2+Li_3AlH_6$) system are continued in the US laboratories (JPL, HRL, NUS, Utah). The third composite involves carbon, and the appropriate reaction is as follows: $LiNH_2+C \rightarrow Li_2CN_2+2H_2$ **(System 3).** Theoretical modeling indicates that the standard enthalpy change is ~31 kJ/mol H_2 and the theoretical hydrogen capacity is 7wt.%. No experimental studies of this system have been attempted yet. A novel approach in this system can involve the application of carbon nanotubes in addition to a regular activated carbon. This task can be carried out in collaboration with Dr. John Wen from the Department of Mechanical and Mechatronics Engineering, University of Waterloo who is an expert on the fabrication of carbon nanotubes. Microstructure and sorption properties will be studied by XRD, DSC/TGA, neutron diffraction and volumetric Sieverts-type apparatus. Predictive modeling efforts in collaboration with other group researchers will also be attempted.

Collaborators: Dr. S. McGrady-modeling of catalyst-hydride systems, Dr. D. Met-modeling of thin film-based hydride systems, Dr. J. Huot-volumetric hydrogen storage measurements, Vale Inco Technical Services, Mississauga, Ont.; Dr. Z.S. Wronski, NRCan-CanmetEnergy-HyFATE; Dr. A. Yonkeu, NRC-Canadian Neutron Beam Centre, Chalk River.

Project B.2.4 Hydrogen Storage in novel hybrid nanoporous materials

Richard Chahine, Université du Québec à Trois-Rivières

Summary: Recent breakthrough in the design and processing of hybrid nanoporous materials open the way for significant advances in hydrogen storage, purification, and production. Commonly known as MOFs (for metal-organic frameworks), these materials are extended porous structures composed of transition metal ions that are linked by organic bridges. Given the number of metals and organic reagents that can be used, the number of possible combination of these moieties is immense. The increasingly rational approach for their synthesis give us the ability to tune their porous properties (skeleton, surface, cages and/or tunnels) for dedicated applications. Most of them are inspired by previous orientations (catalysis, gas separation/storage), but with highly improved performances. Some of them are unprecedented. For example, MOF-177 has 50% more surface area (and hence 50% more storage capacity) than the best known activated carbon. Our projects is based on interdisciplinary partnerships combining high level modeling, synthesis, activation and characterization of the proposed materials for hydrogen storage, transport, and purification applications. The improvement of the performances adsorption storage will go through a better understanding of mechanism and thermodynamics of adsorption, and of a better knowledge of the adsorption sites. Because the materials studied are of direct relevance to hydrogen purification issues, this project will also address Theme A (purification and separation) objectives. The materials study of this work will serve as inputs to Theme C projects: C.1.2 – Distribution by cryosorption storage technologies and Project C.2.1 – Outflow modeling.

Collaborators: The theory group at HRI (modeling and throughput screening), McGrady Group (new Brunswick), NRC group Chalk River neutron diffraction, Air Liquide.

Group B.3 Storage systems design and optimization

Project B.3.1 Hydride Storage Systems

Frederic Domingue and Jacques Huot, Université du Québec à Trois-Rivières

Summary: Chemical and metal hydrides provide an attractive hydrogen storage technology particularly suited to smaller portable applications where the inherent weight of the hydride material is not a serious impediment, or to stationary systems. Through careful systems design, hydride based hydrogen fuel cell systems have the potential to outperform other technologies in these applications. An area that requires further research is the development of new methods for determining state of charge of these solid hydrogen storage technologies. The commercial systems need low cost and compact sensors embedded into the storage devices with a proper measuring technique for the hydrogen metering. The objective of the project is to develop and test different sensing technologies for selected hydride storage materials. In addition to the metering applications, the developed technologies will be considered for improved hydrogen safety sensors.

Collaborators: The industrial collaborator for this project is Palcan Energy Corporation (Vancouver, Canada). Palcan commits itself to develop and commercialize renewable energy products based on hydrogen energy.

Project B.3.2 Heat and mass transfer in sorption-based storage systems

Jacques Goyette, Université du Québec à Trois-Rivières

Summary: The development of efficient hydrogen reservoirs based on solid-gas interactions (in metal hydrides, activated carbons, metal oxide frameworks, etc.)-will require a thorough understanding of the heat and mass transfer processes in those storing materials. Moreover, the cost of construction of a reservoir of almost any size and capacity precludes building many reservoirs in order to find the optimal configuration of the storing beds and heat exchanging elements. Therefore, the only practical way of studying these kinds of hydrogen storing systems is through computer simulation. The proposed project would develop tools that would permit to estimate the performances of hydrogen storing systems. These tools should be easy to adapt to different kinds of reservoir geometry and versatile enough to take into account different reaction mechanisms between hydrogen and the solid storing materials. The goal of the project would to optimize the configurations of the different elements of the reservoir and to answer these questions: (1) what the optimal filling speed of the reservoir? (2) What is the maximal hydrogen flow rate that can be outputted from the reservoir? (3) As a safety concern, if a leak opens in the side wall of the reservoir, what is the hydrogen flow rate?

Collaborators: Our tools could help in integrating a production process to a well adapted hydrogen storing system. This applies to Theme A – Production. For Theme C in Safety, the tools developed to evaluate reservoirs can be easily adapted to study the rate at which hydrogen escapes from a punctured reservoir (leak rate)

Project B.3.3 Novel chemical hydrogen storage concepts

R. Tom Baker, University of Ottawa

Summary: Collaborator Davis proposed previously to investigate the use of a solid chemical hydride feed dissolved in methanol with water injected as the reactant in order to increase the system's volumetric storage density (recycling the methanol as the hydride carrier). Our work will focus initially on catalyzed sodium borohydride solvolysis using aqueous methanol. The borate 'spent fuel' would then be a mixture of sodium borate and methoxyboron compounds (reactions 1-2). However, work by Davis

has indicated that the reaction is substantially hydrolysis (reaction 1) if the temperature is above 0oC. Note also that the water in this scheme could be supplied from the fuel cell exhaust.

$$NaBH_4 + 2\ H_2O = NaBO_2 + 4\ H_2 \quad 1)$$
$$NaBH_4 + 4\ MeOH = NaB(OMe)_4 + 4\ H_2 \quad 2)$$

Key targets in the catalysis development are:

1. Supported inexpensive metals (Fe, Co), alloys or metal borides including nanostructured variants;

2. Catalyst/support combinations optimized to withstand long term evolution of hydrogen;

3. Catalyst/support combinations engineered to resist accumulation of insoluble 'spent fuel' on the catalyst surface.

Catalyst synthesis and characterization (solution and solid state NMR and IR spectroscopy) will be initiated by an existing postdoctoral fellow at the University of Ottawa and then transferred to a new graduate student in January. Catalyst activity, selectivity and lifetime will be assessed using an automated hydrogen burette and solution 11B NMR spectroscopy. Promising catalysts will then be tested at Queen's with collaborator Davis.

For the proposed work plan, previously reported supported iron and cobalt catalysts (Xu, 2008) will be prepared and evaluated for the methanolysis of NaBH4 containing substoichiometric water (first two quarters). Refinement of catalyst/support combinations will then be tested against the above desired attributes (third and fourth quarters). The best combinations will then be tested at Queen's (fifth and sixth quarters) with collaborator Davis.

Reference: D. Xu, P. Dai, X. Liu, C. Cao, and Q.Guo, *J. Power Sources* **2008**, *33,* 1845-52.

Collaborators: Boyd Davis, Queen's University

Group B.4 Storage systems design and optimization

B.4.1 Microscopy of nanostructured hydrogen storage materials

Gianluigi Botton, McMaster University

Summary: Microscopic characterization of nanostructured materials will be performed by the group of network researcher Gianluigi Botton, Canada Research Chair in *"Microscopy of Nanostructured Materials"* to provide information on their structure, composition and chemical state. State-of-the-art advanced microscopy characterization with ultrahigh resolution electron microscopy and electron energy loss spectroscopy will be provided by McMaster University through the instrumentation available at the Canadian Centre for Electron Microscopy-CCEM. This center is equipped with a VG HB 601 dedicated scanning transmission electron microscope (TEM), a JEOL 2010F TEM and two aberration corrected Titan TEM to study the nanoscale structure of the composite materials. This facility is ideally suited for the analysis of materials at the high spatial resolution required to probe the chemistry of complex nanoscale materials, MOFs, carbon nanostructures coated with metals, and a range of metallic alloys. With the instrumentation available at the CCEM, it will be possible to observe the samples in cryogenic conditions and load the samples at cryogenic temperature (liquid nitrogen temperature) in a H_2

environment so that the sample can be observed in the microscope in the conditions of exposure to hydrogen. Samples can then subsequently be heated in-situ in a controlled fashion to release the hydrogen and follow phase transformations. It will be possible for samples to be transferred from a glove box environment to the microscope without exposure to air (making it possible to send samples from the various partner laboratories in the network to McMaster for observations). The instrumentation and expertise in imaging and analysis of nanomaterials are unique in the world. Professor Botton will closely interact with the all of team members and provide the necessary feedback required to understand the storage properties of the materials. The McMaster group will use electron energy loss spectroscopy to detect the presence of hydrogen in the samples (using plasmon peak shifts) and well as electron diffraction to detect phase changes. It will be possible to map the composition of the samples with a spatial resolution in the order of 1nm.

B.4.2 Neutron diffraction analysis

Helmut Fritzsche, Steacie Institute for Molecular Sciences (SIMS)-Canadian Neutron Beam Centre (CNBC).

Summary: Powder neutron diffraction analysis will be performed by the Steacie Institute for Molecular Sciences (SIMS)-Canadian Neutron Beam Centre (CNBC). Powder Neutron diffraction is a powerful analytical method in understanding the crystalline properties of materials under ambient and non-ambient conditions. Neutrons are sensitive to light elements such as oxygen and including hydrogen / deuterium. Structural changes that show little effect with X-ray diffraction methods can show major changes with neutron diffraction. Complicated sample environments can be handled due to the penetrating power of neutrons. Samples can be probed at low temperatures (down to 1.8 K) and high temperatures (up to 1900°C). Gas pressurization and mixing is also possible.

B.4.3 NMR characterization

John Ripmeester and Chris Ratcliff, NRC Steacie Institute for Molecular Sciences (SIMS)-Materials Structure and Function (MSF) group

Summary: The NRC Steacie Institute for Molecular Sciences (SIMS)-Materials Structure and Function (MSF) group has extensive capabilities to carry out solid state NMR experiments. They have access to NMR spectrometers working at a number of different magnetic fields (200 – 500 MHz), including the new 900 MHz instrument, which is a unique, world class facility for materials characterization. Of special interest is the home-built NMR probe able to operate in the NMR magnet at variable H_2 pressures up to 120 bar and down to -20^{o}C, which has already been applied in some studies of hydrogen clathrate hydrates. They also have NMR probes capable of variable temperature work down to 77K or even to 10K for certain nuclei. Other new equipment recently commissioned include a powder diffractometer with linear detector, a new 2nd generation single crystal X-ray diffractometer, a high pressure calorimeter (-40C). Additional equipment which should be especially useful for the characterization of hydrogen storage materials is a recently commissioned confocal Raman microscope (with pressure cell) on which they have just obtained their first spectra of H_2 trapped in hydrate cages. Increased high pressure capabilities will be installed on a number of instruments. Other equipment available on site includes a pore size analyzer, DSC/TGA, and a quartz crystal microbalance.

Theme C – Infrastructure and Safety

Theme objectives

The diversity of subjects grouped into Theme C makes for a range of goals for each project. The broad objective of the theme is to determine optimal infrastructure configurations that create safe, efficient and clean hydrogen systems in a Canadian context. Canada has been at the forefront of the development of hydrogen energy technologies for the last 20 years. A diverse industry has developed with companies bringing many hydrogen technologies to market. Industrial timelines for deployment of technologies are short and viable options for developing infrastructure must include short, medium, and long-term outlooks. The theme will strive to find niche applications for hydrogen energy systems, study their limitations and propose optimal pathways for their integration into the energy market within a 5 to 10 year time-frame and beyond. This theme integrates the work of the other two themes into systems that meet consumer demands. The theme can be viewed as interfacing the end-users of energy technologies with research and development activities. The R&D activities of Themes A and B will directly feed into the activities of this theme.

Programme description

Theme C is composed of two research groups addressing unresolved issues with hydrogen energy systems in Canada. Research activities range from fundamental studies of hydrogen releases to high-level techno-economic modeling of infrastructure development. The work of Theme C is closely tied to projects in all of the other themes.

Group C.1 “Infrastructure” examines cost, logistics, and technical requirements for infrastructure development. The group objective is to determine the preferred pathways for the hydrogen distribution chain considering specific Canadian conditions. Models of hydrogen energy system processes are developed using the performance characteristics of conventional and advanced hydrogen technologies. How technologies are best integrated to make a system, and how such a sub-system then performs in a regional setting will be examined. Advanced distribution technologies and liquefaction devices will be studied from a fundamental and systemic perspective. Outcomes of infrastructure studies will inform planning, policy, system and technology development activities.

The objectives of Group C.2 “Safety” are to develop a scientific and engineering basis for determining safety standards and safe industry practices specific to hydrogen. Studies will focus on refueling infrastructure and safety of portable, stationary and transportation hydrogen energy applications. The safety of hydrogen technologies and systems should be as good, or better, than current energy systems. Safety concerns of the public, industry and government must all be addressed. Failure modes, probability of occurrence, and impacts of system failures must be quantified. Outcomes of this group will assist in determining safety standards and safe industry practices. Solid, compressed, and low-temperature storage modes will be studied. Research outcomes will help to reconcile perceived dangers with actual dangers and will guide the best practices of system developers and users.

The research activities in Theme C complement each other by providing information for system studies, and by ensuring common approaches are leveraged wherever possible. For instance, the impact of new distribution and transportation technologies will be used in techno-economic studies of fleet fuelling and for examining distribution infrastructure. Another example is the Safety group, through clearance distance determinations, helping to establish the footprint of hydrogen distribution and storage points and to address acceptance issues.

The deployment of hydrogen systems at scales exceeding typical technology demonstrations requires more rigorous planning for both safety and cost. This is now happening with BC Transit bringing a

significant hydrogen load on-stream with a fleet of fuel cell buses. The possible addition of hydrogen shuttle buses easily creates the single-largest hydrogen based transportation system in the world. Production, distribution, and refueling technologies are required for the operation of the fleet while safety will be critical in all aspects. Safety is often seen as one of the main issues delaying the introduction of hydrogen energy systems and public concerns must be addressed. Research activities in Group C.2 will inform revisions to the Hydrogen Installation Code, a national standard for Canada, and thus improve the safety of hydrogen energy systems.

The development of novel technologies addressing hydrogen distribution will enable more cost-competitive fleet deployments to occur. The value of hydrogen as an energy currency can be realized using internal combustion engines, but an overall benefit of the system must still be evident. Techno-economic studies of infrastructure evolution will help identify systems with maximum value for Canadians. The benefits of hydrogen will be quantified thereby facilitating the development of hydrogen energy systems now and in the future. New distribution technologies with high density and reduced cost will alter the pathways and scales for hydrogen deployment.

Interactions between groups and regular meetings of networks researchers will ensure students are fully aware of the latest advancements. Partnerships with companies at all stages of technology deployment will enhance their opportunities for further contributions after their academic programme is complete. Students who wish to continue their studies at a higher level will be well aware of the many institutions in Canada with expertise in hydrogen systems. A longer-term benefit of the Network will be to attract international students to Canada to pursue advanced studies in hydrogen energy systems. Unique laboratory capabilities such as those for the magnetic liquefaction project, cryosorption, and the experimental study of dispersion will be a draw for high caliber researchers.

The specific projects (or tasks) that will be funded and performed by individual network researchers within a research group are given in Table 17.1 below. Budget details contributed by the network to the projects are given in Tables 17.2 and 17.3.

Table 3 Theme C project list

Project ID	Title	Researcher
Group C.1 – Infrastructure (Group Leader A. Rowe)		
Project C.1.1	Techno-economics for fleets	Ned Djilali (with A. Rowe and C. Crawford)
Project C.1.2	Distribution by cryosorption storage technologies	R. Chahine (with P. Bénard)
Project C.1.3	Magnetic Liquefaction	A. Rowe
Group C.2 – Safety (Group leader: Luc Bauwens)		
Project C.2.1	Hydrogen release and dispersion simulations for codes and standards	Pierre Benard
Project C.2.2	Experimental and numerical investigation of hydrogen outflow from pressurized vessels	Peter Oshkai, Ned Djilali and Pierre Benard
Project C.2.3	Large Eddy Simulation of hydrogen dispersion	Marius Paraschivoiu
Project C.2.4	Jet ignition in hydrogen energy systems	Luc Bauwens
Project C.2.5	Self ignition of hydrogen releases	Matei Radulescu

Safety of sorbent materials used in solid-state storage strategies of hydrogen is critical to its certification, particularly as it pertains to portable applications. This topic, although not formally part of the network, is the object of a research project by Richard Chahine and Pierre Bénard within the context of the International Partnership for a Hydrogen Economy (IPHE). In this project, the safety of solid-state storage units will be considered, from the perspective of toxicity, flammability of the storage sorbents, and properties of sorbent/hydrogen mixed phase jets resulting from a sudden failure from containment. To put the safety analysis in perspective, comparative analysis with lithium-ion batteries will be performed. This project will strongly rely on input from Theme B, and as such, closely linked to network activities.

Theme C Project descriptions

Projects are network funded contributions from individual network researchers (principal investigator). The principal investigator may have collaborators in his project who are not funded through the network.

Group C.1 - Infrastructure

Project C.1.1 – Techno-economics for Fleets

Ned Djilali, University of Victoria

Summary: This project examines the optimal pathways for hydrogen use in vehicle fleets. A techno-economic analysis of hydrogen fueling pathways in the context of British Columbia will be carried out with a focus on the deployment of fuel cell buses by BC Transit. Future avenues for hydrogen fueling infrastructure development that make use of the unique features of British Columbia will be developed and analyzed. Social costs such as emissions will be included. Recommendations will be made regarding preferred operating modes, vehicle characteristics, fueling generation and distribution, and filling station characteristics needed to maximize benefit and enable larger scale implementation. Recommendations will be made based upon specific characteristics of British Columbia, including electricity generation costs and emissions characteristics, industrial and commercial hydrogen production or consumption needs, and any integration opportunities that reduce costs or leverage other activities in BC. An example of a research questions for this group could be: “What technologies can have the greatest impact on increasing system feasibility?” “What changes to cost structures or operating characteristics of existing systems may enhance the feasibility of hydrogen energy systems?” “What are the preferred pathways for developing hydrogen fueling infrastructure for given load in a specific region?” The answers to these questions will rely on computational tools and models developed at UVic. Other third-party software tools such as RETScreen, HOMER (Hybrid Power Systems Analysis), and Advisor may also be used. One MSc student and one PhD student will be responsible for model development and for performing case studies on the growth of hydrogen fuelled bus fleets in British Columbia. The tools created for these studies will be generic and easily allow for studies of other regions in Canada.

Collaborators: Andrew Rowe, Curran Crawford, BC Transit

Project C.1.2 – Distribution by cryosorption storage technologies

Richard Chahine and Pierre Bénard, Université du Québec à Trois-Rivières

Summary: Based on the work performed in projects B.2.4 and B.1.2, a cryosorption storage unit designed for shipping hydrogen from production sites to distribution points will be modeled, partly based on the systems studies performed during the course of Project B.2.2. The system considered will be optimized for a set charge/discharge rate corresponding to the fill/unload rate required by industry (this differs from a storage application connected to an energy conversion device where the system must be designed to accommodate variable discharge flow rates determined by the power requirements of the

application). Boil-off rates will be estimated, and overall energy efficiency issues will be addressed. These approaches will be validated by test-bench. A distribution system based on cryosorption will be analyzed and compared with current liquid hydrogen distribution systems and a distribution infrastructure based on local liquefiers using magnetic refrigerators.

Collaborators: A. Rowe, N. Djilali, P. Bénard

1. Months 0-3: Literature review
2. Months 3-18: Development of a three dimensional CFD model of the storage system
3. Months 12-18: Fit of available experimental and simulation isotherms of physisorbents to Dubinin model (activated carbon).
4. Months 18-24: Parametric study of the system using a zero-dimensional (thermodynamic) model (rough determination of system parameters optimized for a specific charge and discharge rate)
5. Months 24-30: 3D simulations using these parameters, calculation of boil-off rates and energy costs.
6. Months 24-48: Validation at HRI/UQTR using cryosorption storage test-bench.
7. Months 30-42 System optimization using fitted isotherms obtained from projects B.2.4 (experimental) and B.1.2 (simulations).
8. Months 42-48: Performance study boil-off rate calculation, energy efficiency analysis. Feedback from partners
9. Months 48-54: Simulations using new input from projects B.1.2 and B.2.4
10. Months 42-60: Comparative techno-economic analysis of a distribution system based on cryosorption with a standard liquid hydrogen distribution and a liquid hydrogen distribution system relying on a distributed liquefactors system (project C.1.3). Feedback into project C.1.1.

Project C.1.3 – Magnetic Liquefaction

Andrew Rowe, University of Victoria

Summary: This project expands upon other work by the PI in the area of magnetic refrigeration. The optimum configurations of magnetic liquefaction devices for hydrogen will be investigated. Models of parallel and series staging of magnetic cycles will be created and their impacts on process efficiency examined. As part of this work, optimized regenerator compositions will be determined based upon preferred device configurations and operating regimes. In addition, how the costs of liquid hydrogen scale with device capacity will be modeled. The potential for distributed liquefaction devices will be investigated and results will be incorporated in to projects C.1.1 and C.1.2 to determine the impact on distribution infrastructure. Models of optimized regenerator compositions for staged liquefaction devices will be validated using experimental data from an Active Magnetic Regenerator Test Apparatus (AMRTA). Both single material and multi-material testing will be carried out to determine the most cost-effective staging arrangement. Various magnetocaloric alloys will be needed to create regenerator compositions specific to the temperature range identified for a proposed stage. Researchers at UQTR will assist in material selection and characterization as well as provide co-supervision for students working on modeling of devices.

Collaborators: Richard Chahine, Pierre Benard (UQTR)

Group C.2 – Safety

Project C.2.1 – Hydrogen release and dispersion simulations for codes and standards

Pierre Bénard, Université du Québec à Trois-Rivières

Summary: Outflow from storage units constitutes the basic input for dispersion studies of hydrogen and depends on the storage technology used (storage on solid, by compression or as a liquid). For instance, sorption dynamics must be taken into account when simulating a leak form a metal hydride or a physisorption-based storage unit. Unlike compressed gas, multiphase flow must be considered for liquid hydrogen releases. In this project, outflow models will be devised for each storage system being considered, providing density, temperature and pressure data required as input for dispersion simulations. In addition, effective diameter models will be examined for sonic releases and studied in relation to the shock wave structure generated close to the leak point.

Links: Relies on the thermodynamic models developed in the course of Theme C and project C.1.2 for the solid state storage systems.

Collaborators: J. Goyette, R. Chahine, A. Rowe

1. Months 0-3: Literature review
2. Months 3-12: Development of a generic, thermodynamic, time-dependent discharge model for sonic and subsonic releases of hydrogen using the real gas equation of state (NIST) based on the UQTR and Concordia compressed hydrogen discharge model.
3. Months 8-12: Comparison with a full 3d release CFD simulation using a real gas equation of state.
4. Months 12-24: Development of a zero dimensional thermodynamic discharge model from physisorbed hydrogen and for absorbed hydrogen in a metal hydride bed and integration of the generic discharge model.
5. Months 24-42: Comparison with a full 3d release CFD simulation from physisorption and metal hydrige storage systems using the modeling approaches developed in C.1.2 and B.3.1.
6. Months 24-48: Calculation of flammable extent of hydrogen releases from physisorption-based, metal-hydride based storage units as a function of storage conditions with and without surfaces
7. Months 48-54: Comparison with compressed hydrogen storage
8. Months 54-60: Feedback from partners and Codes and standards implication

Project C.2.2 – Experimental and numerical investigation of hydrogen outflow from pressurized vessels

Peter Oshkai and Ned Djilali, University of Victoria

The development of safety standards and formulation of safe practices requires and understanding of the behavior of hydrogen when it is suddenly released into the environment from a compressed vessel and a characterization of its dynamics and concentration levels. Such releases can be due to the failure of the vessel, or due to a controlled venting. In either case, the structure of the resulting hydrogen jet will impact directly on the spreading characteristics of the hydrogen. This, in turn, affects the concentration levels around the vessel, which determines safety issues such as minimum safety distances and infrastructure requirements. In the course of the Auto 21 project, particle velocimetry experiments of helium jets were carried out to characterize the velocity field of low buoyancy jets. Comparison with

high resolution simulations is being performed to validate direct numerical simulations of the jets. The experimental data will yield the velocity fluctuations and the Reynolds stresses for helium jets, which will be compared with current, widely used turbulence models such as the k-epsilon approach. In addition to providing a detailed validation of these approaches, these results will be used to calibrate the adjustable parameters of these models to provide more reliable turbulence modeling. In the next phase, we will combine particle velocimetry measurements with Rayleigh scattering measurements of the concentration field of helium and hydrogen. This will provide a detailed data set for validation of CFD approaches for hydrogen safety and allow for the determination or validation of adjustable parameters in common turbulence models. These experiments and simulations will be carried out for free horizontal and vertical jets, and for surface jets. The scaling behavior of the jets will be compared to the scaling functions predicted by turbulent jet models, which are used in the most recent engineering correlations that have been proposed to determine the extent of flammable jets and thus establish clearance/separation distances. The validated CFD models will also be applied to a series of limiting case scenarios including combinations of: jet orientation, presence of contiguous surfaces (structures, walls etc.), cross winds.

Collaborations: Pierre Bénard (UQTR)

Project C.2.3 – Large Eddy Simulation of Hydrogen Dispersion

Marius Paraschivoiu, Concordia University

During the Auto 21 safety project, a code to simulate the dispersion of a sonic jet from compressed gas storage units was developed based on a compressible LES approach. In this project, compressible effects are negligible, so an incompressible code also based on LES will be adapted for solid state storage outflow modeling. The advantage of this in-house code is that it is orders of magnitude faster to compute LES solutions than commercial codes like Fluent. Once this code is validated it will permit the investigation of many different scenarios with LES accuracy at a cost comparable to RANS models. To adapt this code for hydrogen dispersion a transport equation must be discretized with finite elements as they are used in the main code. A low velocity hydrogen jet will first be simulated to validate this in-house code.

Project C.2.4 – Jet ignition in hydrogen energy systems

Luc Bauwens, University of Calgary

The problem of self ignition of hydrogen jets will be studied analytically, experimentally and through CFD simulations. The conditions for flame acceleration from hydrogen deflagrations and the propagation of shock waves, potentially resulting in detonation, will be analyzed and the consequence on hydrogen systems will be determined. The role of specific features of hydrogen-air chemistry on these processes will be studied. The sub-scale model derived as part of project C.2.4 will be coupled to simplified models of the expanding reactive-diffusive system (Bauwens) to clarify physical mechanisms. Experimental research performed by HySafe partners (Warsaw University and HSL, Buxton, UK) will be used for validation. Fundamental mechanisms leading to jet ignition will be explored and defined. One key unresolved issue affecting the safety of high pressure hydrogen storage is jet ignition ("spontaneous" ignition). Experimental evidence shows that at the early stage of a sudden release, ignition may occur in the jet. The actual mechanism leading to ignition remains uncertain, but shock heating likely plays a role. From a safety standpoint, jet ignition is a mixed blessing; in some scenarios, it will lead to ignition and fire which would otherwise be avoided. In closed environments, however, combustion of hydrogen as it is released means that there will be no detonable mixture. Better predictive tools for jet ignition are needed; to that effect, a better fundamental understanding of the process and

mechanisms is needed. This project will participate in experimental research performed by HySafe partners (Warsaw University and HSL, Buxton, UK) and experiments performed by Powertech and at DRDC Valcartier. Based upon results from experiments, numerical and analytical models will be developed, to better predict jet ignition, in collaboration with Matei Radulescu and Marius Paraschioviu. Risk of flame acceleration and detonation will be analyzed.

Project C.2.5 – Self ignition of hydrogen releases

Matei Radulescu, University of Ottawa

The storage pressure of gaseous hydrogen appears to be limited by the risk of auto-ignition during accidental releases in air. This transient spontaneous ignition, which is due to shock wave heating and localized mixing of the released gases, is not currently amenable to numerical prediction, even with dedicated supercomputers. This is due to the inherent multi-scale character of the phenomenon involving small scale diffusive and reactive phenomena occurring in a flow field evolving at scales approximately 10^6 larger. The present study will hence address this problem by developing a sub-scale predictive model for the ignition phenomenon, and permit to couple the formulation to the three-dimensional gas-dynamic evolution of the flow field, which can be accurately determined on coarser grids. The sub-scale model will address the ignition of a one-dimensional diffusion layer separating cold fuel and hot oxidizer undergoing volumetric cooling via expansions. The link to the original jet problem and the methodology, detailed in (Radulescu & Law, Journal of Fluid Mechanics 578:331–369(2007) is through the appropriate initial conditions and the rate of global expansion obtained analytically or from inviscid calculations. The one-dimensional reaction-diffusion model will be solved both with accurate chemical and transport properties and simple models permitting analytical solutions to be obtained. It is expected that the model will be able to predict the critical storage pressures above which spontaneous ignition will occur in terms of the release dimension and time scales.