Fuel Cell Freeze Startup and Landscape of FC Freeze Patents

DOE Workshop on Fuel Cell Operations at Sub-Freezing Temperatures

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Ahmad Pesaran
Tony Markel
Gi-Heon Kim
Keith Wipke

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NREL's FY05 FC Freeze Project

As part of a Task in the FY05 AOP to DOE's HFCIT.

Objective

- Investigate and evaluate strategies for rapid startup of PEM fuel cells from sub-freezing temperatures.

Approach

- Collect data/information through literature search and collaborations
  - Patent search
- Perform energy analysis to bracket energy/power requirements for startup.
- Use component/system models to evaluate merits of various solutions from fuel efficiency and other factors within a vehicle.

Freeze & Rapid Startup of PEM Fuel Cells
A systems-based Issue

A fuel "cell" can startup at sub-freezing temperatures, but product water can form ice if local sub-freezing still exist.

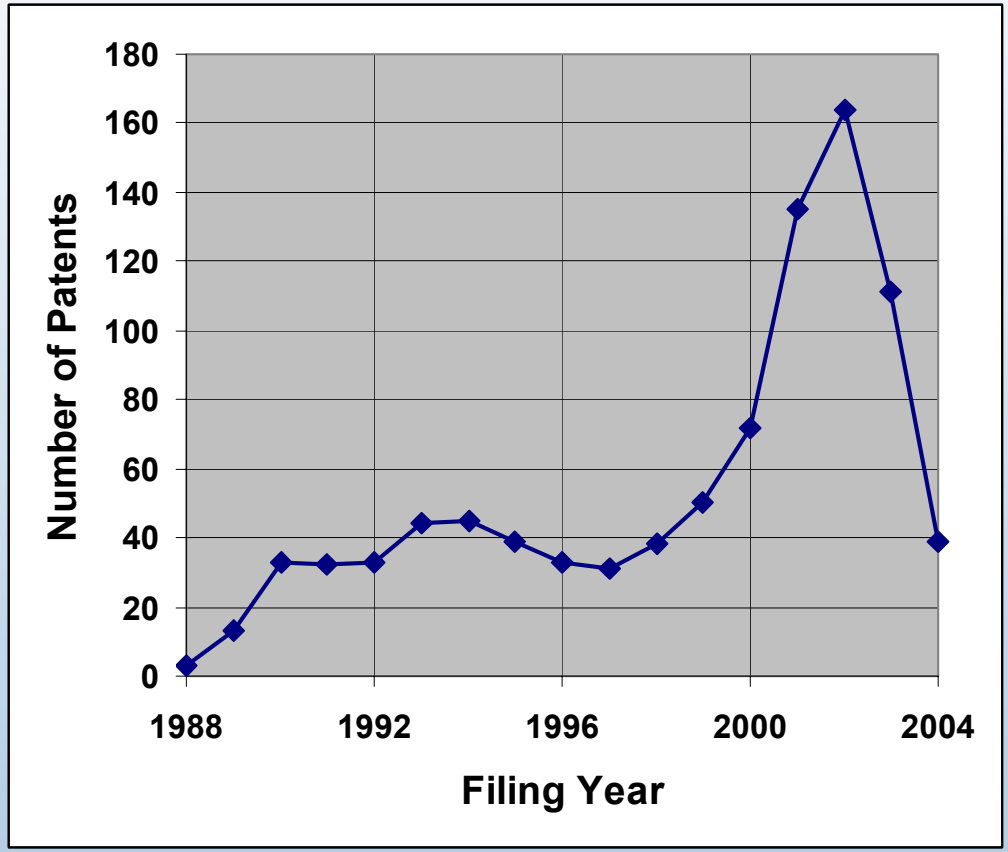
- Maintaining membrane integrity
- (Systems related) Fuel starvation (Elimination of water droplets from flow fields)
- (Systems related) Cathode ice formation
  - Product water forms ice on electrode and blocks air flow
  - Ice formation in cathode flow fields
- (Systems related) Rapid heat up of cell/cell manifolds to prevent ice formation
  - System heating issue:
    - Where is heat coming from and how much and how fast?
    - What is impact on energy consumption and overall efficiency?
  - Rapid heat up of humidifier to prevent membrane dry out
- (Systems related) Balance-of-plant: Heating of fluid/gas delivery systems
  - Prevent ice blockage
  - Thermal shock to mechanical components
  - Rapid startup and protection of components

Initial Patent Search

- Search included US, Japan, and world patents
- Period of January 1988 to January 2005
- In the initial round, we used “Fuel Cell” and “Freeze” and/or “Thaw”
  - We found 1324 patents
  - Some related to reformer startup and none-PEM
- Further restricting the research to PEM and non-reformer and rapid startup
  - Reduced the number of patents to 177 (with some duplication in US, Japan, and world)
- Number of articles in “academic” literature less than 15, indicating that industry recognized early the importance of freeze and rapid startup.

A Closer Look at the First 1324 Patents

- Top categories
  - Fuel cell stack (212)
  - Piping (104)
  - Solid electrolyte fuel cell (119)
  - Polymer electrolyte (109)
  - Manifold (102)
  - Catalyst (71)
  - Cold-Starting (26)
  - Tank,Pure water (23)
  - Fuel cell power plant (24)
  - Antifreeze (10)
  - Other



Industry recognized early the importance of freeze issue.

Assignee	Doc Count	Percentage
NONE (Patent Applications for Individual Inventors)	174	12.3%
FUJI ELECTRIC CO LTD	72	5.1%
TOSHIBA CORP	59	4.2%
HONDA MOTOR CO LTD	43	3.0%
NISSAN MOTOR CO LTD	43	3.0%
BALLARD POWER SYSTEMS INC.	36	2.6%
SIEMENS AKTIENGESELLSCHAFT	35	2.5%
SANYO ELECTRIC CO LTD	33	2.3%
HONDA GIKEN KOGYO KABUSHIKI KAISHA	32	2.3%
MITSUBISHI HEAVY IND LTD	32	2.3%
TOYOTA MOTOR CORP	31	2.2%
UTC FUEL CELLS, LLC	31	2.2%
NISSAN MOTOR CO., LTD.	26	1.8%
MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.	23	1.6%
MITSUBISHI ELECTRIC CORP	20	1.4%
Number of assignments in Top 15 assignees	**690**	
Total number of assignments	**1414**	
Number of documents after filter	**1324**	
Total number of documents in group	**1324**	

Patent Analysis

Which patents have been cited frequently?

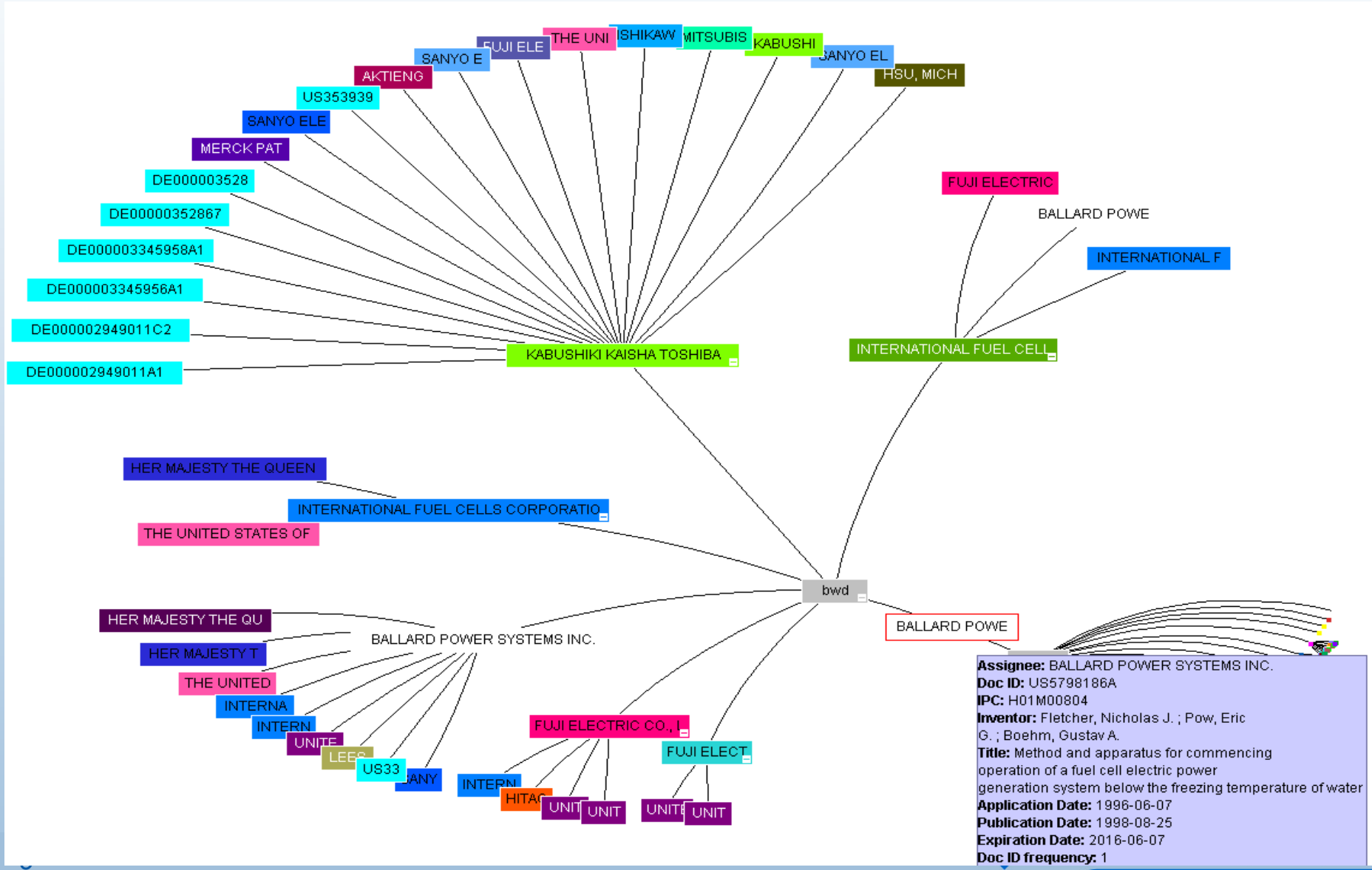
Basic Report: Average Number Of Forward Citations Per Year

source document list: **Fuel cell freeze thaw (1324) 1991 to 0105 (DeDup**

Document ID	Title	Year Issued	Cited by	Avg Cites by Year
US5798186	Method and apparatus for commencing operation of a fuel cell electric power generation system below the freezing temperature of water	1998	51	7.9
US6326097	Micro-fuel cell power devices	2001	22	7.0
US6057054	Membrane electrode assembly for an electrochemical fuel cell and a method of making an improved membrane electrode assembly	2000	31	6.5
US5514487	Edge manifold assembly for an electrochemical fuel cell stack	1996	43	4.9
EP0629015	Electrochemical cell provided with ion exchange membranes and bipolar plates	1994	47	4.6
US5976726	Electrochemical cell with fluid distribution layer having integral sealing capability	1999	22	4.2
US5372617	Hydrogen generation by hydrolysis of hydrides for undersea vehicle fuel cell energy systems	1994	39	3.8
US6068941	Start up of cold fuel cell	2000	18	3.8
US5472799	Solid polymer electrolyte fuel cell	1995	33	3.6
US6057051	Miniaturized fuel cell assembly	2000	16	3.4
US6316135	Direct antifreeze cooled fuel cell	2001	10	3.1
US6071635	Easily-formable fuel cell assembly fluid flow plate having conductivity and increased non-conductive material	2000	14	3.0
US5958616	Membrane and electrode structure for methanol fuel cell	1999	15	2.8
US5451249	Landfill gas treatment system	1995	26	2.8
US5945232	PEM-type fuel cell assembly having multiple parallel fuel cell sub- stacks employing shared fluid plate assemblies and shared membrane electrode assemblies	1999	15	2.7
Number of citations in Top 15 documents			**402**	
Number of documents after filter			**915**	
Total number of documents in group			**915**	

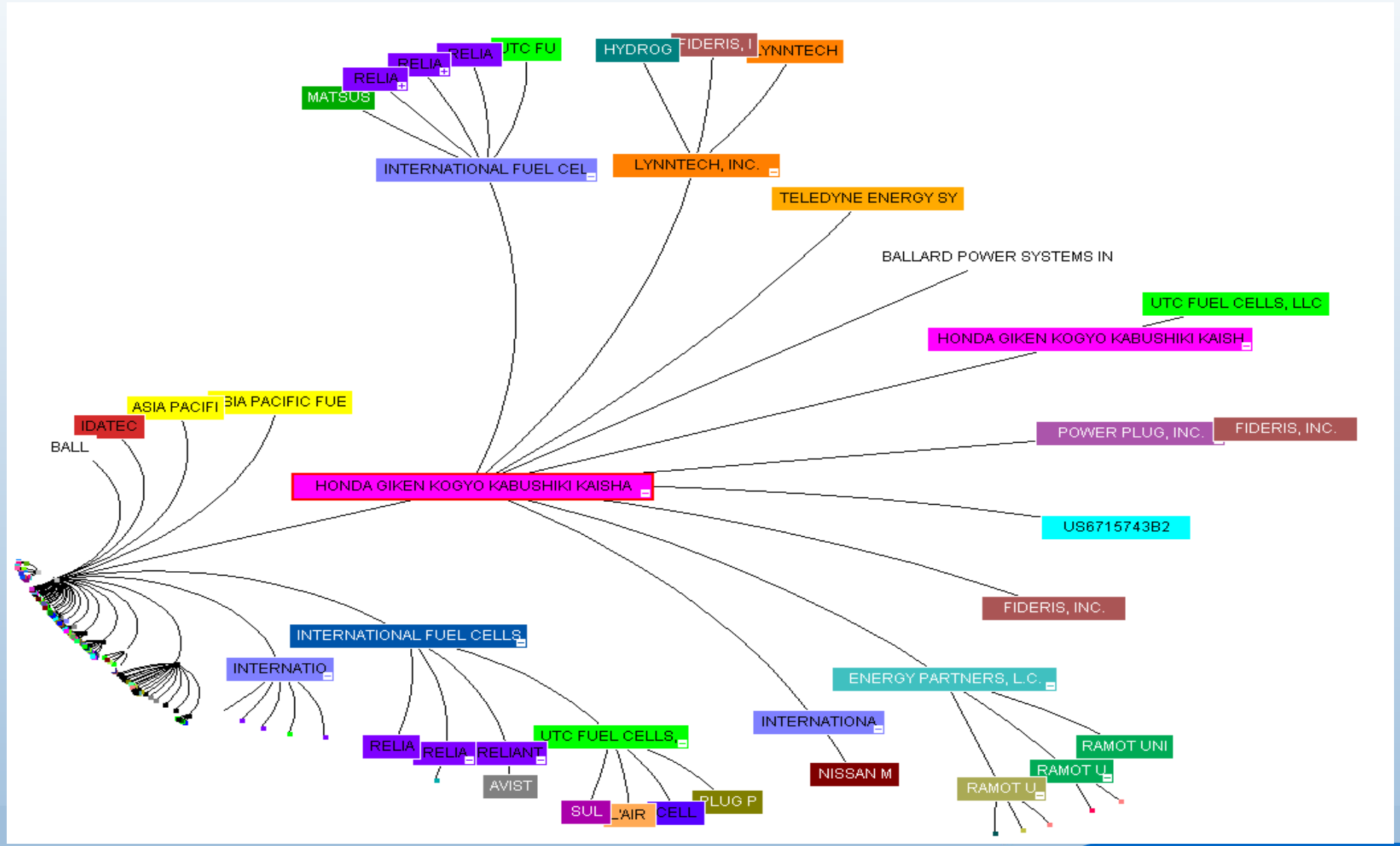
Citation Analysis

(Where patents are cited?)



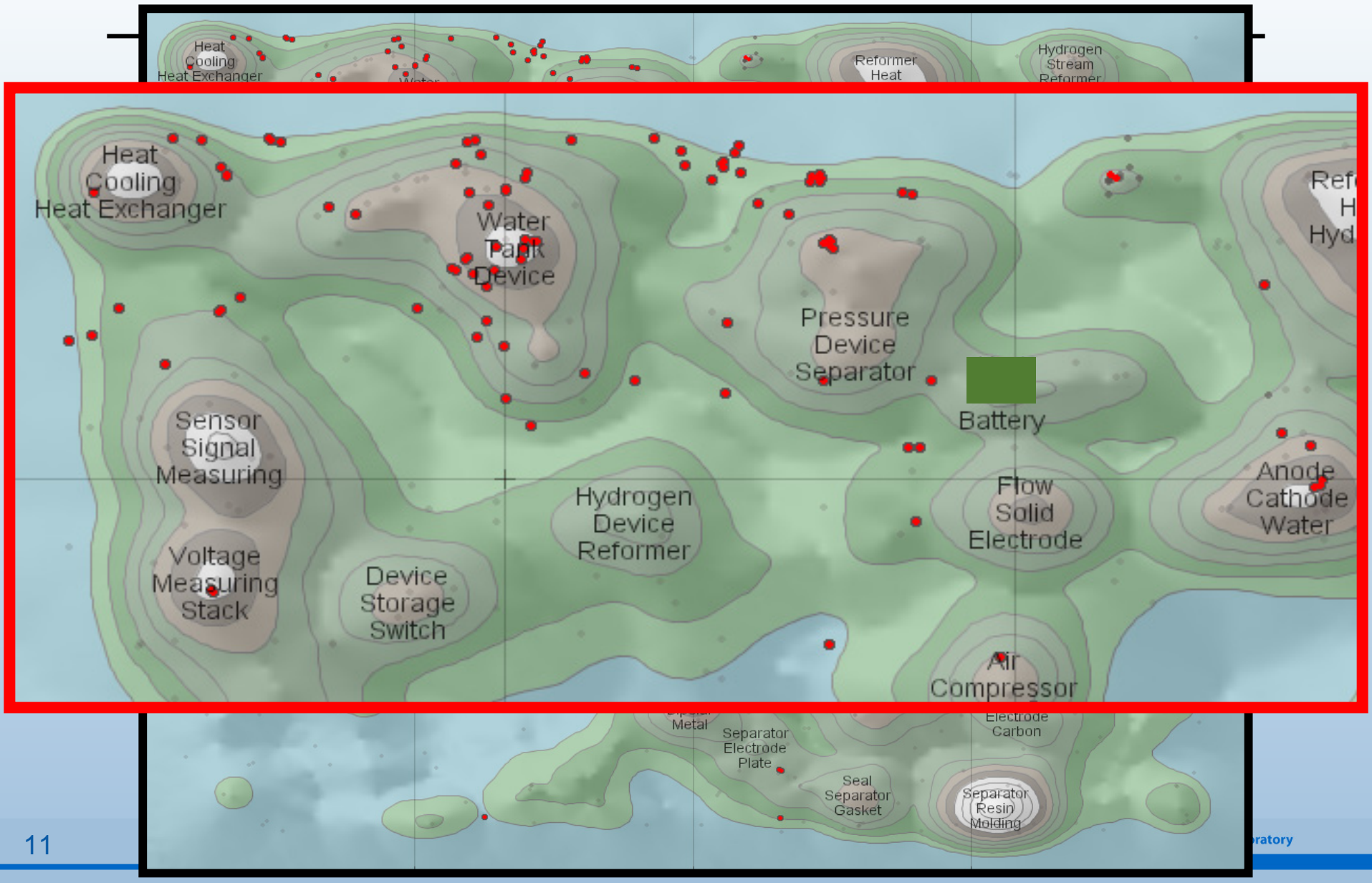
Citation Analysis

(Who is Citing who?)



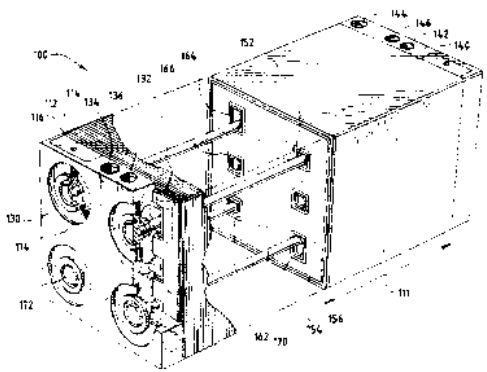
Fuel Cell January 2001 – March 2004

Freeze-Thaw Patents Highlighted in Red



Example of Results

US5709818



Method and apparatus for commencing operation of a fuel cell electric power generation system below the freezing temperature of water

A method and apparatus are provided for starting and operating an electric power generation system comprising an electrochemical fuel cell stack for supplying electric current to an external electrical circuit. The stack comprises at least one fuel cell comprising a membrane electrode assembly comprising an anode, a cathode, and a water permeable ion exchange membrane interposed between the anode and the cathode. A fuel stream and an oxidant stream are each flowable to the fuel cell. At least a portion of the membrane electrode assembly has a temperature below the freezing temperature of water. The supply of electric current to the external circuit from the fuel cell stack is commenced such that the temperature of the membrane electrode assembly exceeds the freezing temperature of water.

Ballard Power Systems Inc.

Fletcher, Nicholas J.
Pow, Eric G.
Boehm, Gustav A.

Initial Patent Search

Major categories of the patents

- Materials: 10%
- Controls: 19%
- Components: 24%
- Systems: 47%

} Systems Related Ideas: 90%

Planning to summarize the results of the search in a report.

System Perspective Evaluation

Examples of Fuel Cell Freeze Systems Level Questions NREL will Answer this Year.

- How much water is needed to operate during a warm-up from -30°C to 0°C, and then 80°C?
- How long does it take to get from –30°C to 0°C, and then to 80°C?
- How long does it take to get to 50% of rated power when starting at –30° C or 0°C? 90% of rated power?
- For minimal drive cycle performance degradation what kind of battery requirements and roles be needed?
- What is the fuel economy impact of the energy needed to warm-up the system?
- What components/parts are most critical to heat in a rapid-start strategy?
- What are the thermal response of each component?
- Impact of any non-consumed reactants in the stack at startup?
- What are source of energy for heating and cost/weight/FE impacts?

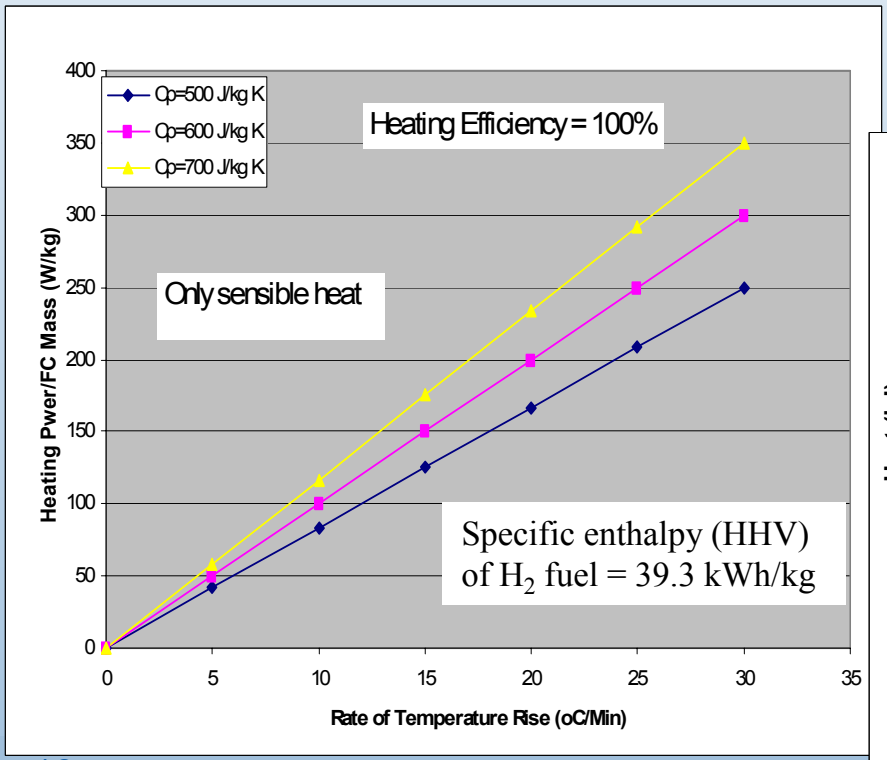
Energy Need for Heating a Frozen FC could be Reasonable, but How about Power?

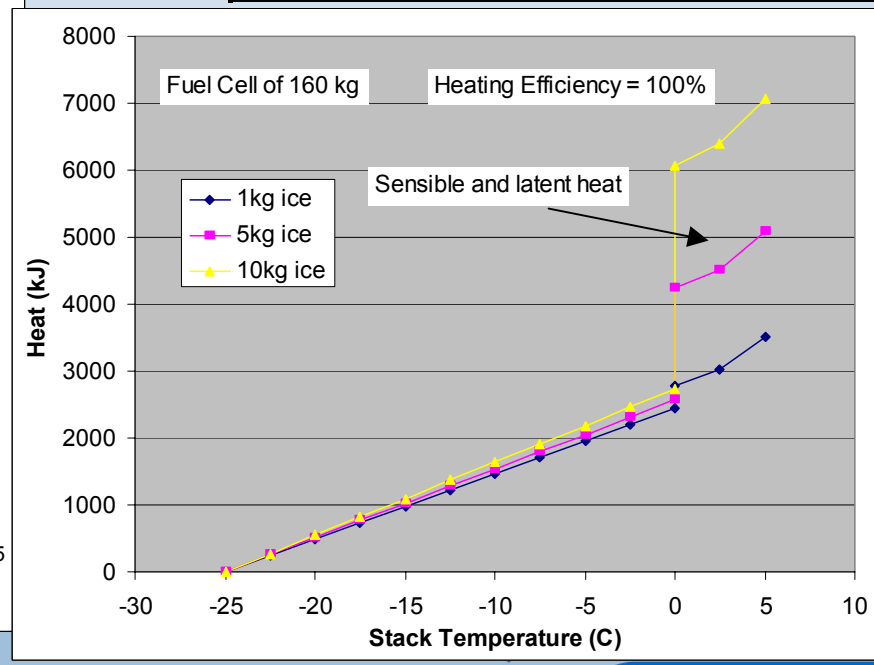
$E_{heating} = m\ C_p\ \Delta\ T$ $P_{heating} = m\ C_p\ \Delta\ T/\Delta t$

- Parametric assumptions
  - Heat capacity ranging from all stainless steel to all graphite
  - FC specific power ranging from 400 W/kg to 800 W/kg
  - Water content ranging from 0.5 lit to 10 lit

160kg FC with 5kg water contents

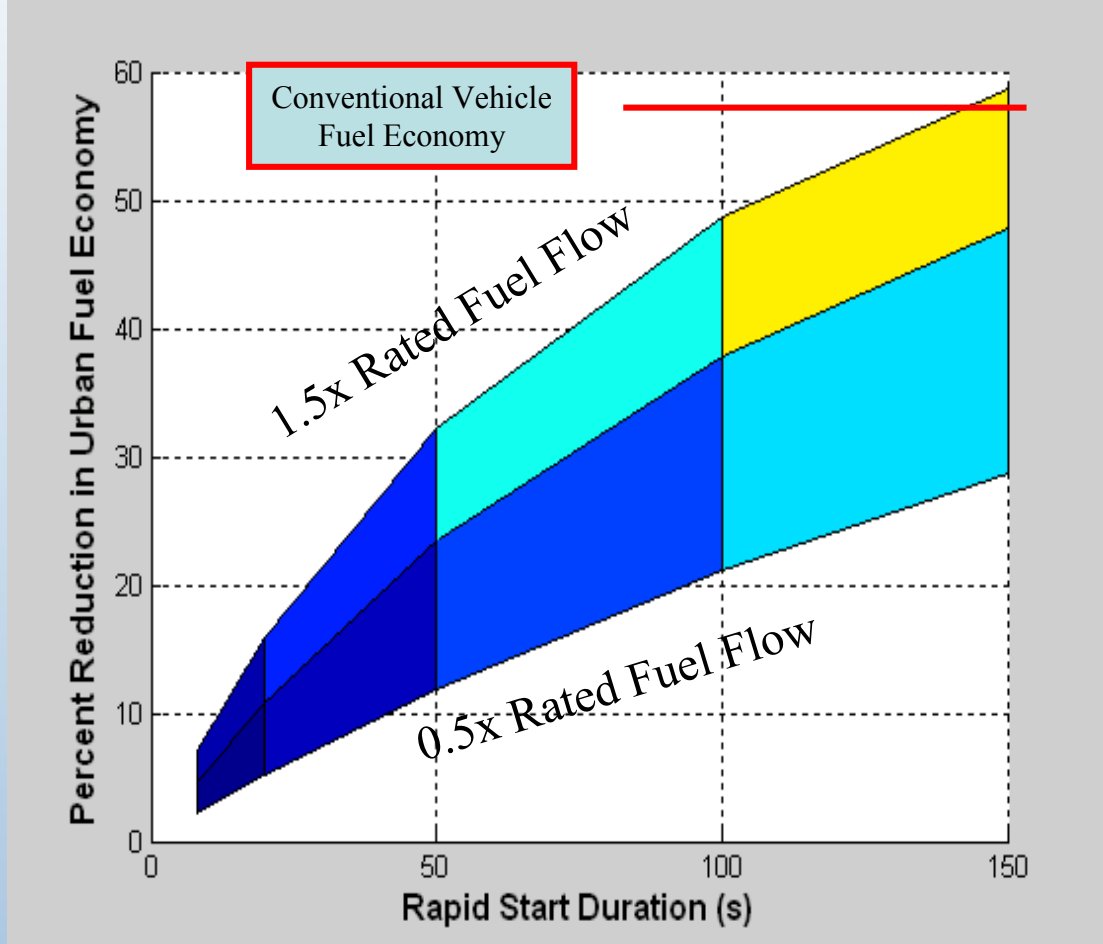
	-25C to 0C		-25C to 5C
	Sensible	Sens+Latent	Sens+Latent
Energy (kJ)	2567	4237	5091
Energy (Whr)	713	1177	1414
	Power (kW)		
for 1 sec	2567	4237	5091
for 10 sec	257	424	509
for 60 sec	42.8	70.6	84.9
for 120 sec	21.4	35.3	42.4
for 240 sec	10.7	17.7	21.2





Rapid-Start Process from a Cold-Soak Needs to be Optimized to Minimize Fuel Consumption Impacts

- Assumptions
  - System power output linearly ramps from 0 to 50% of rated power during the rapid start duration
  - Normal operation and fuel consumption assumed after reaching 50% of rated power
- Significance
  - To maintain reasonable vehicle fuel efficiency it is critical to minimize the duration and energy required for fuel cell rapid start



Summary

- There is high level of world wide activity in fuel cell freeze and startup issues.
- There are many more patents than published articles on the topic of fuel cell freeze and startup.
- The majority of proposed concepts/solutions is from system level perspective.
- Although many concepts are proposed, effectiveness and feasibility are not clear.
- There is a need to evaluate ideas with a systematic approach.
- NREL will use its system tools to evaluate these/other solutions.
- NREL will continue analyzing patent search results and disseminating them.

Appendix

(Supporting Slides)

Patent Search for "Fuel Cell"
Invention Assignees (until 03/04)

Basic Report: Documents By Top Assignees

source document list: **Fuel Cell 2001 to 0304 (DeDuped)**

Assignee	Doc Count	Percentage
NONE (Patent Applications for Individual Inventors)	1151	13.9%
NISSAN MOTOR CO LTD	318	3.9%
TOYOTA MOTOR CORP	274	3.3%
HONDA GIKEN KOGYO KABUSHIKI KAISHA	249	3.0%
HONDA MOTOR CO LTD	245	3.0%
MATSUSHITA ELECTRIC IND CO LTD	230	2.8%
MITSUBISHI HEAVY IND LTD	219	2.7%
SANYO ELECTRIC CO LTD	114	1.4%
FUJI ELECTRIC CO LTD	109	1.3%
NISSAN MOTOR CO., LTD.	107	1.3%
TOSHIBA CORP	103	1.3%
MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.	101	1.2%
SIEMENS AKTIENGESELLSCHAFT	100	1.2%
BALLARD POWER SYSTEMS INC.	89	1.1%
GENERAL MOTORS CORPORATION	87	1.1%
Number of assignments in Top 15 assignees	**3496**	
Total number of assignments	**8262**	
Number of documents after filter	**7773**	
Total number of documents in group	**7773**	

* None = Patent Applications or Individual Inventors

NREL's Systems Capabilities

- Modeling – components and systems
- Testing equipment
- Access to major freeze facilities for vehicles
- Vehicle and industry's perspective (relationships)
- Previous programs with freeze & rapid start-up
  - Batteries for hybrid electric vehicle
  - Solar water heaters
  - PV system durability
- Experience in addressing issues such freeze from system's perspective for vehicles

NREL's Modeling Capabilities
Modeling - Components and Systems

Tools/Software

- ADVISOR™ vehicle simulator
- Fuel cell model in Matlab/ADVISOR™
- Water and heat management in fuel cell systems
- Heat and mass transfer and fluid flow codes (e.g, ANSYS, FLUENT, StarCD, SINDA/FLUINT)
- Thermal and system analysis (FlowMaster, ASPEN+)

Recent Related Projects

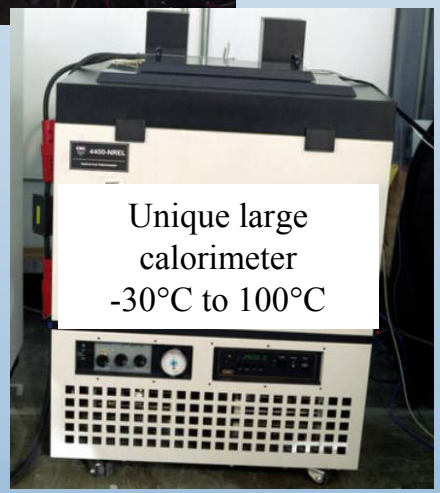
- Predicting the Fuel Economy Impact of "Cold-Start" for Reformed Gasoline Fuel Cell Vehicles (for OHFCIT)
- Effect of Material and Manufacturing Variations on Membrane Electrode Assembly Pressure Distribution (with Plug Power)
- Energy Storage System Requirements Analysis for Hybridized Fuel Cell Vehicles (for USABC and FreedomCAR Tech Teams)
- Dynamometer Testing of Insight and Prius Hybrid Vehicles, **Froze a Honda Insight** (for OFCVT)

NREL's Testing Capabilities

Battery and Power Testing Units

5- 440 V (1- 150 kW)
ABC-150 power conditioning units

0- 70 V (0-21 kW)
six Power conditioning units

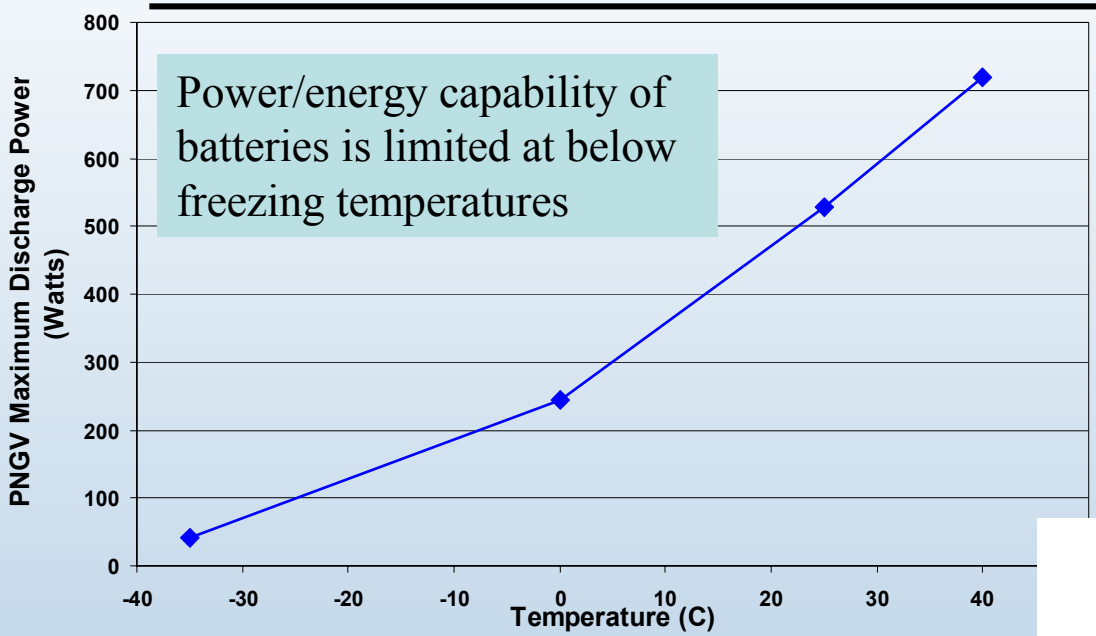


Unique large calorimeter
-30°C to 100°C

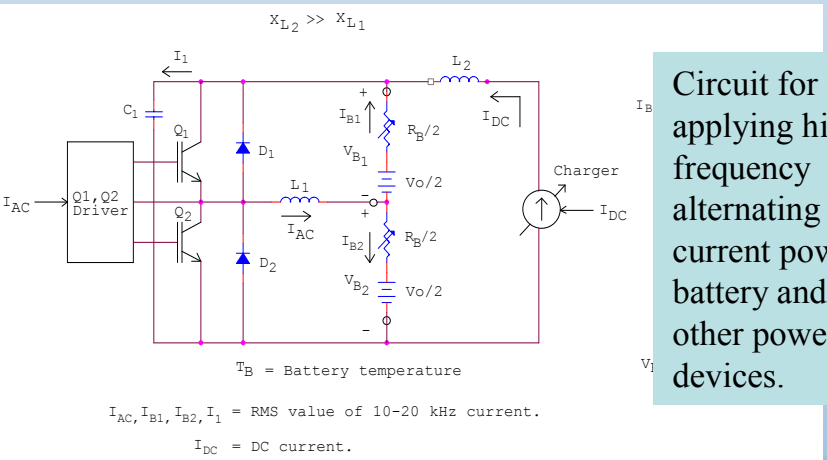
Energy Storage lab at TTF for power/energy evaluation of devices

NREL's Rapid Heating of Batteries in Cold Climates

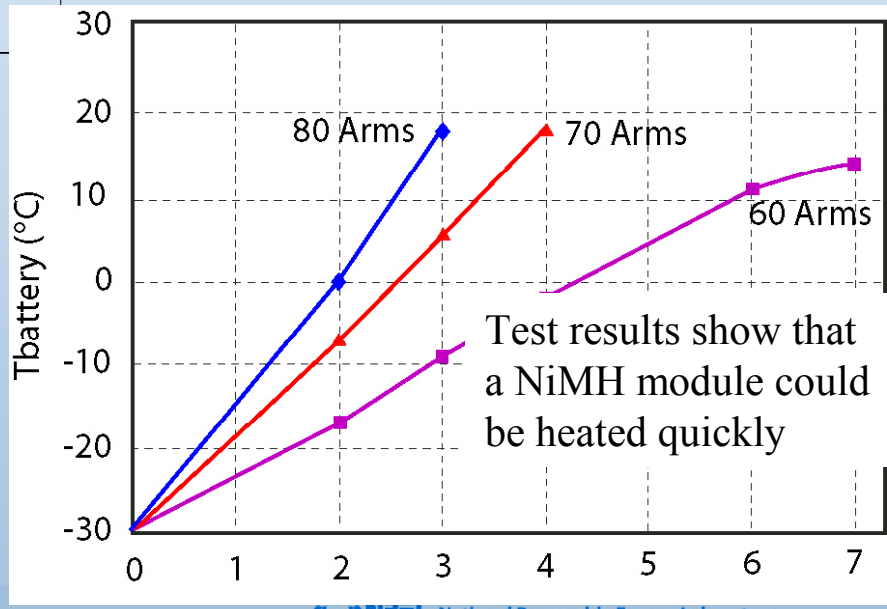
(OFCVT Energy Storage Program)



Power/energy capability of batteries is limited at below freezing temperatures



Circuit for applying high frequency alternating current power to battery and other power devices.



Test results show that a NiMH module could be heated quickly

NREL's Testing Capabilities

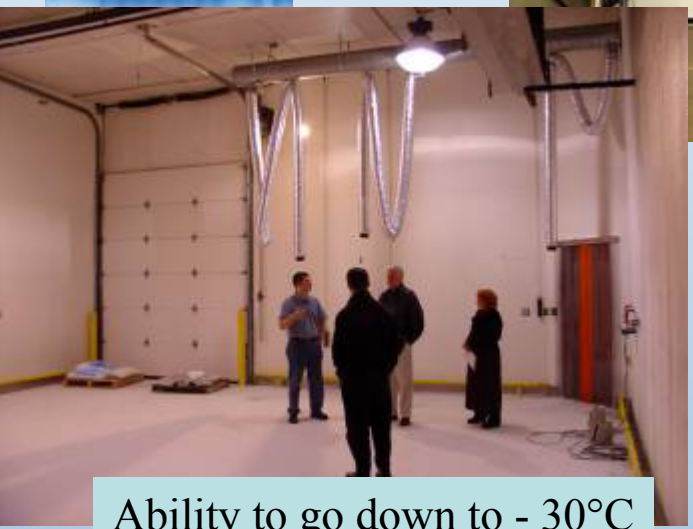
Environmental and freeze chambers (capability to go to – 40°C)

Environmental chamber for durability due to weather variations & freeze (at NREL's OTF)

Environmental chambers for battery cold and freeze studies (at NREL's TTF)

NREL's Complimentary Testing Capabilities

Freeze rooms along with dynamometer (at ETC, a private vehicle testing lab)



Ability to go down to - 30°C

Example of Assumptions for FC Rapid Cold Start Fuel Consumption Impacts

- Durations: 8s, 50s, 150s (from Ballard presentation)
- Fueling rate: 0.5x, 1.0x, 1.5x
- System rated power: 85kW
- Stack rated power: 105kW
- Hydrogen flow at rated power: ~1.7g/s
- Oxygen flow at rated power: ~13.4g/s