

MCFC and PAFC R&D Workshop Summary Report

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U.S. Department of Energy

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This workshop will address the continuing need for R&D on MCFC and PAFC stationary fuel cell technologies to improve performance and endurance and lower first costs. The goal of the workshop is to gain an understanding of the R&D issues that remain to be addressed in order to attain widespread use of these technologies in energy efficiency and renewable energy applications.

MCFC needs will be addressed by the workshop from 8:30 AM to 12:00 PM and PAFC needs will be addressed from 12:30 PM to 4:00 PM. The morning session will be chaired by [Dr. Prabhakar Singh \(Connecticut Global Fuel Cell Center\)](#) and the afternoon session chaired by [Doug Wheeler \(DJW Technology\)](#). All are welcome to attend although there is a room occupancy restriction of 75 people.

You are invited to attend the
MCFC/PAFC R&D Workshop
on

Monday, November 16, 2009
Palm Springs Convention Center
Mesquite Room G
8:30 AM to 4:00 PM

Presented in conjunction with the
[2009 Fuel Cell Seminar & Exposition](#)

January 13, 2010

Executive Summary

A two-session workshop on molten carbonate fuel cells (MCFC) and phosphoric acid fuel cells (PAFC) was held November 16 prior to the 2009 Fuel Cell Seminar in the Palm Springs Convention Center. The MCFC session was held in the morning and the PAFC session, which also included discussions of fuel cells using polybenzimidazole (PBI) electrolyte supports, was held in the afternoon at the same location. Both sessions brought together technical experts from industry, academia, and the national laboratories to address future development of advanced MCFC, PAFC, and PBI fuel cell technology.

The workshop was jointly sponsored by the Energy Efficiency and Renewable Energy and the Fossil Energy offices of the U.S. Department of Energy. Representatives from the respective DOE offices from industry and from academia contributed to identifying key barriers and gaps in fuel cell technology. Each workshop began with formal presentations from the industry representatives addressing the current state-of-the-art and technology gaps that are barriers to cost reduction. At the conclusion of the presentations, two breakout groups were formed in each session to discuss cell stack technology improvements and system cost and manufacturing improvements.

Industry experts from the leading MCFC fuel cell company, FuelCell Energy, Inc., presented in the morning workshop, and experts from the leading PAFC and PBI fuel cell companies, UTC Power, LLC and BASF Fuel Cells, GmbH, respectively, presented in the afternoon session. The industry speakers provided technology and manufacturing overviews identifying the critical issues for cost reductions, performance and durability enhancements, and pathways to commercialization. These industry experts declared that the major challenge to accelerated commercialization of MCFC systems is the short five-year stack life, while the major challenge for PAFC and PBI systems is the high cost of materials, in particular, the high platinum content, which represents 10% to 15% of the total PAFC system costs.

Both the industry presenters and the breakout session participants attending the MCFC session agreed that factors affecting stack life need to be the top priority. The MCFC breakout sessions recommended the following:

1. Further R&D is needed to understand the causes and limit the micro structural changes in the electrolyte support material that lead to early stack failure.
2. Research and development into the modification or reformulation of the electrolyte composition is needed to reduce loss of electrolyte from the cell stack.
3. Development of more robust cathode materials is needed to cut the rate of cathode dissolution by a factor of two or more.
4. Development of more cost-effective cleanup systems for fuel processing of biogas is needed to reduce both installed costs and maintenance costs.
5. Methods need to be developed to mitigate the loss of lithium from the electrolyte that results from chemical reactions between the electrolyte and the cell and stack hardware.
6. Automated methods for component manufacture and assembly, including real-time methods for QC/QA, need to be developed to reduce wastage, increase reliability, and lower labor costs.

7. The processes and methods used for initial system conditioning need to be reviewed and methods for shortening conditioning time developed.

Participants of the PAFC session agreed that first costs, consisting of capital equipment, manufacturing processes, installation, and warranty, need to be reduced. The breakout session attendees recommended the following technology and development pathways to reduce cost:

1. R&D is needed to eliminate anion adsorption either through electrolyte modification, development of an alternative electrolyte, or development of improved cathode catalyst.
2. Development of manufacturing processes for low-cost electrode and MEA manufacturing is needed that would include quality control procedures to reduce waste and rework.
3. New and faster methods of conditioning cell stacks and power plants should be developed.
4. Materials research and development programs to discover lower cost materials for the cell stack and the Balance-of-Plant components are needed. New polymers are required for fabrication of hardware that could replace Teflon in the cell stack.
5. Fuel processing research needed to develop steam-methane reforming catalysts that do not coproduce ammonia, from nitrogen impurities in the fuel, which can poison PAFC & PBI systems.
6. R&D is recommended to discover new electrode catalyst and catalyst support materials critical for stable performance over the extended life of the PAFC and PBI fuel cell systems.
7. Fundamental studies are recommended to define *in-situ* and *ex-situ* analytical tests for characterizing the properties of catalyst and electrode structures.

The recommendations developed at these two sessions create a foundation for solving the critical technology barriers and gaps that can help accelerate market penetration of MCFC, PAFC, and PBI fuel cell systems.

During breaks and after each session, the participants gathered informally to discuss what capabilities still existed at their various institutions to do MCFC and PAFC research and development. Argonne National Laboratory, for example, has capability to do fuel reforming catalysts development. Los Alamos National Laboratory has more than 30 lab-scale fuel cell test stands that can be adapted to PAFC studies. The National Renewable Energy Laboratory, teamed with the Colorado School of Mines, has capabilities for R&D on platinum and non-platinum electrode catalysts for PEM fuel cells that easily can be adapted for PAFC work. The Pacific Northwest National Laboratory and the Idaho National Laboratory have significant capabilities for high temperature fuel cell R&D. Virtually all of the DOE national laboratories have state-of-the-art capabilities for materials analysis.

Both FuelCell Energy and UTC Power are supporting R&D at the Connecticut Global Fuel Cell Center at the University of Connecticut and expressed interest in working with universities and national labs to address their critical R&D priorities.

While no formal agreements were struck, participants agreed to stay in contact with one another and work toward forming appropriate teaming arrangements if funding becomes available in the future.

Table of Contents

	<u>Page</u>
Executive Summary	ii
Molten Carbonate Fuel Cell Session	1
Introduction	1
Welcome and MCFC Session Overview	1
Presentations	3
DFC Technology Status	3
DFC Opportunities	4
MCFC in Europe and Elsewhere	4
Breakout Groups	7
Increased Durability/Lifetime	7
Electrolyte Loss	7
Cathode Dissolution	9
Cost Reduction	10
Balance-of-Plant Cost Reduction	11
Summary of MCFC R&D Priorities	13
Phosphoric Acid Fuel Cell Session	14
Introduction	14
Welcome and PAFC Overview	14
Presentations	15
PAFC History and Successes	15
PAFC Cost Challenges	17
PBI-Phosphoric Acid Based MEA: Status Update	19
Breakout Groups	22
Highlights of PAFC Cell Stack and Cell Components Breakout Group	22
Highlights of PAFC Cost Reduction and Balance-of-Plant Breakout Group	23
Summary of PAFC R&D Priorities	24
Acknowledgments	24
Appendix A: DFC Technology Status, Mr. Pinakin Patel, FuelCell Energy, Inc.	
Appendix B: DFC Opportunities, Dr. Mohammad Farooque, FuelCell Energy	
Appendix C: MCFC in Europe and Elsewhere, Dr. J. Robert Selman, Illinois Institute of Technology	
Appendix D: PAFC History and Successes, Mr. John Ferro, UTC Power, LLC	
Appendix E: PAFC Cost Challenges, Mr. Sridhar Kanuri, UTC Power, LLC	
Appendix F: PBI-Phosphoric Acid Based Membrane Electrode Assemblies: Status Update, Mr. Emory De Castro, BASF Fuel Cells	

Molten Carbonate Fuel Cell Session

Introduction

On November 16, 2009, a MCFC Workshop was held at the Convention Center in Palm Springs, California, in conjunction with the Fuel Cell Seminar. The workshop was a joint activity of the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy (EERE) and the Office of Fossil Energy (FE). Dr. Prabhakar Singh, University of Connecticut, served as workshop organizer and facilitator. Dimitrios Papageorgopoulos from the Fuel Cell Technologies Program Office of EERE welcomed the attendees and set the agenda. Representatives from the DOE national laboratories, industry, and academia participated in the workshop. The objectives of the MCFC workshop were:

1. To provide an overview of the state-of-the-art and most recent technical progress in the development and commercialization of MCFC
2. To identify critical areas and important barriers and gaps in the current MCFC technology restricting commercialization
3. To identify opportunities for R&D that will reduce or eliminate barriers and fill technology gaps with the goal of accelerating commercialization of MCFC systems
4. To promote research collaborations and create or strengthen partnerships.

Three formal presentations were made followed by breakout sessions addressing R&D needs. The first presentation by Mr. Pinakin Patel of FuelCell Energy (FCE) addressed the commercial status of the FCE products. The second presentation was given by Dr. Mohammad Farooque, also from FCE, who described the FCE view of long-term R&D needs. The third and final presentation was made by Professor J. Robert Selman, Illinois Institute of Technology (retired), who discussed the status of MCFC development in the European Union. Copies of all three presentations are available as appendices to this report.

Welcome and MCFC Session Overview

The purpose of this workshop session was to bring together technical experts from industry, academia, and the national laboratories to discuss the continuing need for advanced R&D to help accelerate commercialization of MCFC systems. Experts from the leading U.S. MCFC manufacturer, FuelCell Energy, were invited to provide technology updates and manufacturing overviews of the field and to identify issues slowing the progress of commercialization that might be addressed by a new round of R&D projects. Professor J.R. Selman, IIT, reviewed the status of MCFC work in the EU and summarized the results of a fuel cell workshop held in Ulm in 2008. The organizers acknowledge the contributions of FuelCell Energy and Professor Selman for their presentations.

The U.S. origins of the MCFC date back to a 10-year RD&D project conducted in the late 1960s and early 1970s called Team for Advanced Research on Gas Energy Transformations (TARGET). Pratt and Whitney, now United Technologies Corporation (UTC), was prime contractor on the project and much of the fundamental R&D is being performed at the Institute

of Gas Technology (IGT) on the IIT campus in Chicago. The foundations laid by the TARGET project eventually led to three major DOE/FE-funded MCFC development efforts in the U.S. in the late 1980s and 1990s. One was led by UTC, one by the Energy Research Corporation (now FuelCell Energy), and the third by M-C Power Corp., a subsidiary of IGT. Of these three, only FuelCell Energy has achieved commercialization of an MCFC power plant. However, several participants at the workshop were veterans of the UTC and M-C Power efforts and were able to provide broad insight into the technical issues.

MCFC systems have been successfully demonstrated at the 300 kilowatt size-class and are now being sold as commercial products in sizes up to 3.4 megawatts. The baseline FuelCell Energy 300 kW power plant, designated the Direct Fuel Cell (DFC) 300, has achieved lifetimes of 40,000 hours with availability as high as 95%. The net electrical efficiency of the DFC product line is about 47% (LHV) when operating on natural gas. The baseline DFC product operating on natural gas in non-combined-heat-and-power (CHP) applications produces 52% less carbon dioxide (CO₂) per megawatt-hour of power generated than a fossil-fueled steam-electric power plant, 35% less than a single-cycle natural gas turbine, and 30% less than the combined average CO₂ emissions of all U.S. generation. All DFC products can be configured to provide cogenerated heat in addition to electricity, which further lowers the carbon footprint of the DFC systems.

The major challenge to the cost competitiveness of MCFC systems is stack life. A ten-year maintenance agreement on a DFC system includes the cost of replacing the fuel cell stack module after year five. At present, the cost of the stack module makes up two-thirds of the cost of a DFC power plant. Therefore, doubling stack life to ten years would result in a substantial reduction in life-cycle costs. The approximate first cost for a 1.4 megawatt DFC 1500 power plant is about \$5.6 million or about \$4,000/kW. Although this is a high first cost, the current package of government incentives can make a DFC power plant cost competitive with other options for on-site generation, especially in California and Connecticut where substantial state incentives exist. However, the government-funded incentives are scheduled to end in the 2016 to 2018 timeframe.

The Department of Energy's Office of Fossil Energy has supported the development and demonstration of both PAFC and MCFC systems since the 1970s, with additional financial support from the natural gas and electric power industries. Operation of both fuel cell types has been demonstrated on a variety of fuels, including pipeline natural gas, propane, and bio-fuels (methane) derived from landfills and anaerobic digesters. While PAFC operation has been successfully demonstrated on pure hydrogen streams and steam-reformed naphtha, long-term operation of MCFCs has been demonstrated on a variety of fuels produced by coal gasification and by reforming of logistic fuels. Case studies and market penetration analysis, however, indicate that the largest extant market for PAFC and MCFC stationary systems is for use with natural gas and, more recently, with biogas and methane derived from renewable resources such as agriculture, dairy, industrial, and municipal wastewater. The primary interest of EERE in these stationary fuel cells is their efficient use with renewable fuels for which a good business case can be made, along with positive environmental impact and carbon foot print reduction. EERE-funded R&D projects addressing manufacturing and systems-related challenges for

transportation fuel cells may also address issues related to durability and first costs of stationary fuel cells.

Presentations

The following are summaries of the information provided in the presentations.

DFC Technology Status, Mr. Pinakin Patel, FuelCell Energy, Inc.

FuelCell Energy offers three DFC products; the DFC 300, DFC 1500, and DFC 3000, which are 350 kW, 1.4 MW, and 2.8 MW power plants, respectively. All of them use the same 350 kW baseline MCFC stack; the DFC 300 is a single stack; the DFC 1500 consists of four stacks in a module; and the DFC 3000 consists of two four-stack modules. The DFC 300, for example, is sized for the average grocery store or 300-bed hotel. The DFC 1500 matches up well with the needs of a 1000 bed-hotel, a wastewater treatment plant, or a food processing facility where methane produced by anaerobic digestion can be efficiently utilized to produce electricity. The DFC 3000 is a good match for a 300-bed hospital, a university, or a manufacturing facility. Multiple DFC 3000 units can be integrated together to provide 10 MW or more of grid support.

The single cycle net electrical efficiency of DFC systems ranges from 45% to 50%. The combined-cycle net electrical efficiency of DFC systems mated to a turbine downstream of the fuel cell stack can approach 65%. The NO_x, SO_x, and particulate emissions per megawatt-hour of power generated by DFC systems are four and five order of magnitudes below those of the average U.S. fossil-fuel steam-electric power plant. FCE currently has the largest fuel cell power plant operating anywhere in the world: a 4.8 MW facility operating on natural gas in Pohang, Korea.

The DFC technology offers higher net electrical efficiency and a cleaner exhaust stream when operating on biogas from an anaerobic digester than any competing conventional technology such as reciprocating engines or gas turbines. The DFC systems also have a good heat-to-power ratio for support of digester operations. FCE's first demonstration of a megawatt MCFC operating on digester gas was at a wastewater treatment facility in King County, Seattle, WA, in June 2004. A valuable lesson was learned: the gas output from a digester is variable in quantity and quality. FCE addressed these issues by appropriate cleanup and fuel switching from biogas to natural gas during those times when biogas production was insufficient. FCE has successfully implemented these lessons and integrated DFC systems with anaerobic digesters at several sites in the U.S. and Asia.

FCE is currently manufacturing 30 MW of DFC products per year in Torrington, CT, and has a strong supply chain. FCE has the capacity to manufacture up to 70 MW/year at its current location and has plans to expand to 150 MW/year. FCE also has several hybrid products under development. In addition to mating a DFC with a turbine to achieve very high electrical efficiency, FCE is developing a tri-generation product that integrates a DFC system with a hydrogen concentration system and can tri-generate electricity, heat, and hydrogen. FCE also is investigating mating a DFC system with a fossil fuel power plant to increase electrical efficiency

and facilitate carbon dioxide capture. In short, the future looks bright for MCFC technology. FCE is reducing costs and increasing manufacturing capacity and is on the road to profitability. The full slide presentation is available as Appendix A.

DFC Opportunities, Dr. Mohammad Farooque, FuelCell Energy

At present, DFC products are cost-competitive, with government subsidies, in geographic areas with very high cost-of-electricity (COE). FCE is focusing its R&D efforts on near-term, targeted improvements to make DFC products cost-competitive in areas with high COE. Significant reduction in COE is needed to achieve increasing market penetration. The required decrease in COE can be achieved by (1) increasing power density, (2) extending life, and (3) lowering manufacturing costs. Immediate R&D goals are to:

- Increase power output of the MCFC stack, which is the building block for all the DFC products from 350 kW to 500 kW net
- Extend service life from five to ten years
- Reduce manufacturing costs by 20% by redesign and volume production.

The baseline MCFC stack design has a service life of five years. The two most important life-limiting factors are (1) nickel oxide dissolution from the cathode and its deposition as nickel metal in the electrolyte matrix and (2) electrolyte loss from the matrix, resulting in the intermixing and leaking of fuel and oxidant. The baseline MCFC stack represents two-thirds of the total power plant costs.

Opportunities for stack cost reduction include

- Streamlining of the cell assembly process to allow automatic cell assembly
- Developing “human touch”-free assembly lines
- Developing automated component joining techniques
- Developing automated cell stacking
- Improving electrolyte matrix manufacturing processes to provide higher yield.

Over the past seven years, FCE has accomplished a 240% reduction in the costs of manufacturing a megawatt of fuel cell stacks; however, further reduction is necessary. Since 1992, FCE has increased the output of the baseline stack by more than a factor of five. Figure 1 below shows the improvement in both gross DC and net AC output. Improvement has been achieved both through redesign of the stack and increased performance of the cell components. At present, the baseline unsubsidized COE for the DFC product is about 15 cents/kWh based on the current installed costs for a DFC 3000 and \$7.50/MMBtu for the natural gas. The current COE in California for commercial power is about 13 cents/kWh. A modest reduction of 3 to 4 cents/kWh in the COE for the DFC product line will result in significant market penetration and a good business case for the purchase of DFC products in areas with high COE without the necessity of government subsidies. The full slide presentation is available as Appendix B.

MCFC in Europe and Elsewhere, Dr. J. Robert Selman, Illinois Institute of Technology

In addition to the U.S., molten carbonate fuel cell (MCFC) technology has been under development in Germany, Japan, Korea, and Italy since the 1990s. Ansaldo Fuel Cells in Italy has signed a partnership agreement with Enel to build an integrated system (electricity, heat, and cooling) based on the Ansaldo MCFC technology. The Ansaldo technology is based on multiple 125 kW fuel cell stacks in a module. CFC Solutions, which is a business unit of MTU Friedrichshafen, a Daimler company, has partnered with FuelCell Energy to develop and market 250 kW MCFC systems in the EU. FCE provides the MCFC stack technology while CFC/MTU provides the balance of plant. One significant difference between the FCE and the CFC products is that the MCFC stack in the FCE product line are vertical, with individual cells parallel to the ground while CFC stacks are oriented horizontally with cells perpendicular to the ground. Work conducted by CRIEPI (Japan) has identified the two predominate life-limiting issues for the Japanese developers, nickel shorting and electrolyte loss. Degradation of MCFC power has two regimes, a region of gradual degradation caused by a slow, linear increase in ohmic resistance and electrode polarization followed by a region of rapid degradation believed to be caused by shorting and gas leakage across the electrolyte. Figure 2 is a generalized example of the decay in output voltage as a function of time.

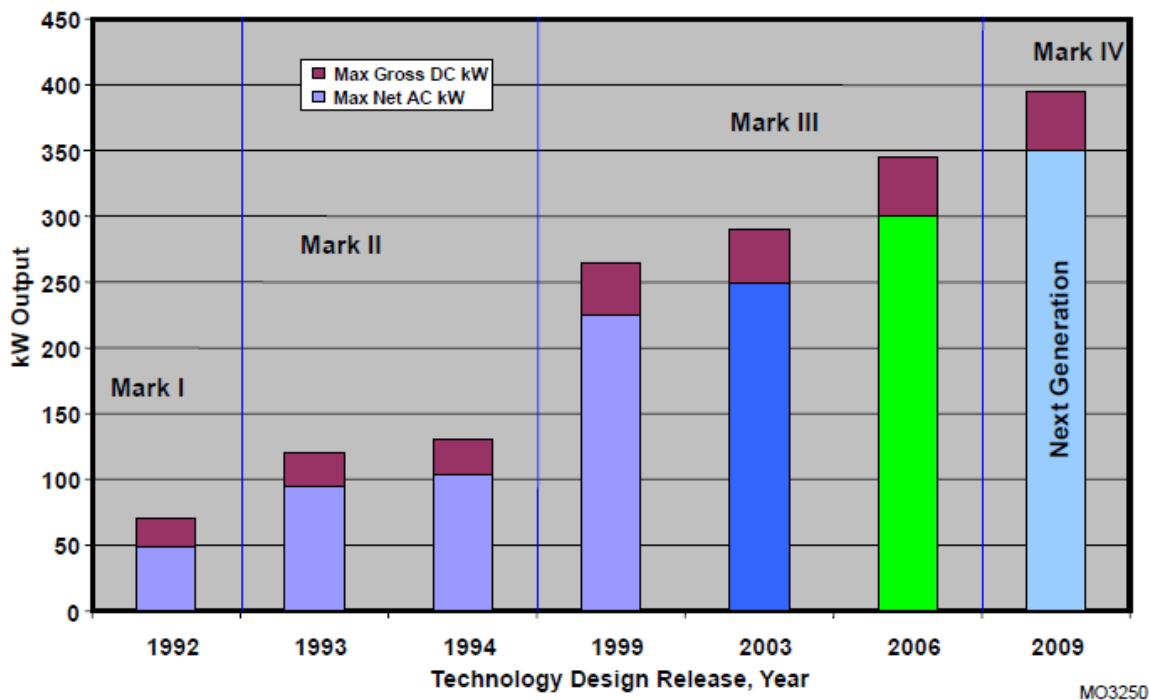


Figure 1: Improvements in power output over time for the baseline DFC stack (from Dr. Mohammad Farooque presentation, DFC Opportunities.)

Professor Selman pointed out that there was much discussion at an accelerated testing workshop held in Ulm, Germany, October 6 to 8, 2008, as to how the lifespan of a fuel cell system is defined. At what point along the performance curve in Figure 2 does one draw a line and declare end-of-life? The Ulm workshop also made the distinction between internal mechanisms leading to degradation of the fuel cell stack and external system failures and accidents that also can lead

to shortened lifetimes or stack failures. Examples of internal mechanisms include electrolyte loss, cathode dissolution, shorting, corrosion, and changes in component morphology at the microscopic level. Examples of external causes can include contamination and poisoning due to failure of the fuel cleanup system, thermo-mechanical stresses during load and thermal cycling, oxidation of the anode, or reduction of the cathode due to loss of flow of the fuel or oxidant. Accidental causes were defined as sudden loss of utility connections, failure of control systems, loss of fuel supply, unexpected loss of balance-of-plant components. Accidental causes result in the power plant going into rapid shutdown mode, which will induce thermo-mechanical stress that would not otherwise be present during a planned outage.

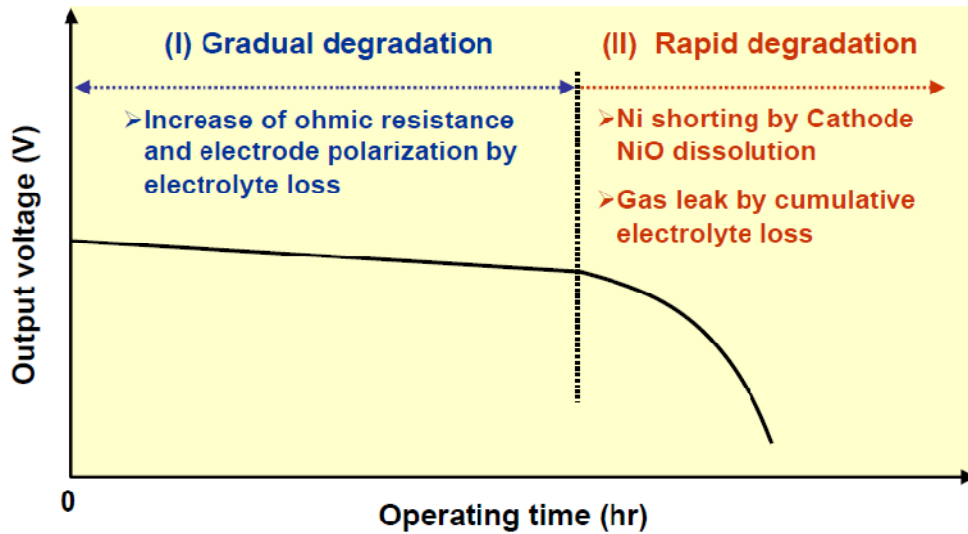


Figure 2: Generic depiction of performance as a function of time for an MCFC (from J. R. Selman presentation, MFCF in Europe and Elsewhere 2009).

The conclusions of the Ulm workshop with regard to MCFC are summarized as follows:

- A 30% to 50% increase in lifetime is required for the complete system.
- Stack outages are more often due to causes external to the stack such as control system failure, failure of the fuel processing system, or sudden loss of electrical load.
- Both internal and external mechanisms contribute to stack degradation and need to be factored into determining the degradation rate of the system.
- Need to adopt a standard protocol for assessing degradation rates.

The R&D recommendations from the Ulm conference are summarized as follows:

- Investigate solutions for problem of cathode dissolution and nickel shorting
- Investigate and develop methods to reduce the gradual increase in internal resistance
- Develop methods for mitigating the effects of corrosion
- Homogenize stack temperature across cell and from cell to cell in the stack.

There was a general consensus that the top two issues can and should be addressed by a combination of public and private research and partnership. Although there was no consensus, some of the developers attending the conference felt that the last two should be left up to the manufacturers to address because these were directly tied to intellectual property and know-how related to manufacturing. Professor Selman's slide presentation is available as Appendix C.

Breakout Sessions

Following the presentations, participants divided into two groups to discuss the information presented by FuelCell Energy and Dr. Selman. The two breakout groups were asked to focus on and recommend areas of research and development related to topics of (1) increased cell, stack, and system life and (2) overall cost reduction at the systems level. FCE staff participated in both groups and provided additional information on particular issues above and beyond what was in their presentations. Below are topical narratives that summarize the additional information and a list of approaches to finding a solution.

Focus Area: Increased Durability/Lifetime

Topical discussion consisted of materials interaction; operating conditions; and possible changes in surface, interface, and bulk chemistry responsible for long-term electrical and structural degradation. As mentioned earlier, areas of discussion included electrolyte loss and cathode dissolution.

Electrolyte loss: Due to a variety of factors, the volume of electrolyte in each cell in the MCFC stack decreases with time, leading to a slow increase in ionic resistance. There are four factors contributing to electrolyte loss: (1) electrolyte evaporation, (2) morphological changes in the electrolyte support, (3) chemical reaction between the electrolyte and the cell hardware, and (4) electrolyte migration.

1. Electrolyte evaporation: The electrolyte of the MCFC is nominally composed of a mixture of potassium and lithium carbonate held, by capillary forces, in a porous lithium aluminate matrix. The matrix is fabricated from lithium aluminate, LiAlO₂, - powders having particle sizes in the 1 to 10 micron range. The matrix is an un-sintered structure having only compressive strength. The best real-world analogue is wet beach sand that has sufficient compressive strength to support the weight of an automobile but has no sheer or tensile strength. At the beginning of life, during stack conditioning, sufficient electrolyte is loaded into the cells to completely fill the pores of the lithium aluminate matrix and approximately half-fill the porous electrodes. Over time, electrolyte is lost via evaporation at the electrodes.

Although both lithium and potassium carbonates have a very low vapor pressure at MCFC operating temperatures, an equilibrium exists between water vapor and carbon dioxide in the fuel and oxidant streams and carbonate and hydroxide ions in the molten electrolyte.



Under typical operating conditions of 1-atm pressure and 680°C temperature, potassium hydroxide has about an order-of-magnitude higher vapor pressure than potassium carbonate. As a consequence, over time, potassium hydroxide is preferentially removed from the electrolyte and carried away in the exhaust streams.

Suggested approaches to reducing electrolyte loss via evaporation include:

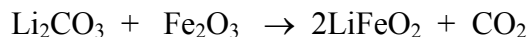
- Operation at reduced temperature
- Additives to the electrolyte to lower potassium activity
- Substitution of sodium or other cations for potassium
- Use of a ternary or quaternary electrolyte
- Development of a multi-dimensional map of how the various parameters affect electrolyte loss and choosing an operating point that corresponds to minimum loss.

2. Morphological changes in electrolyte matrix: Microstructural rearrangement on the atomic level of the lithium aluminate powders in the electrolyte matrix results in a slow increase in average pore size. Over time, as electrolyte is lost via evaporation, the largest of the pores in the electrolyte matrix open up and remain devoid of the molten electrolyte. The void spaces created in the matrix increase ionic resistance and can lead to the development of micro cracks, facilitating bulk gas flow through the matrix. Morphological change of the lithium aluminate is due to its very slight solubility in the molten electrolyte. This change is hypothesized a result of a process known as “Ostwald ripening,” where larger particles grow at the expense of the smaller ones. The end result is average particle size growth, which, in turn, causes a change in the pore size as well as the pore size distribution. The average increase in ionic resistance caused by loss of electrolyte from the electrolyte matrix is currently about $10 \text{ m}\Omega\text{-cm}^2/1000 \text{ hours}$. The rate of increase is approximately linear over the functional five- to seven-year life of the cell/stack. If stack life is to be doubled, the rate of increase in ionic resistance must be reduced to $5 \text{ m}\Omega\text{-cm}^2/1000 \text{ hours}$ or less. Suggested approaches for increasing electrolyte life and slowing the increase in ionic resistance include:

- Optimizing the lithium aluminate particle size and size distribution for long life
- Reformulating the lithium aluminate chemistry and structure to reduce the solubility
- Developing a fundamental understanding of the ripening process and how it is affected by gas phase composition in the electrodes and by the temperature
- Determining how the acid/base characteristics of the electrolyte affect the ripening process
- Revisiting the search for alternative materials to use as an electrolyte support
- Developing a multi-dimensional performance map that can correlate local operating conditions with both the rates of ripening and of ionic resistance increase
- Developing a mechanistic model for the ripening process and identify key parameters
- Understanding the mechanisms that cause morphological changes in the electrolyte matrix and how to arrest them.

3. Electrolyte Reaction with Cell and Stack Hardware: Lithium ions from the lithium carbonate in the electrolyte are selectively lost through a variety of chemical reactions with the

cell and stack hardware. Stainless steel, commonly used for fabricating interconnects and separator plates, will react with any oxygen-containing material to form a surface layer of mixed metal oxides at the elevated temperatures of the MCFC. Following acidic and basic fluxing processes, molten lithium carbonate can react with iron, nickel, and chromium oxides to form the corresponding lithium metal oxide, for example:



Fortunately, the iron and nickel compounds have very low solubility in the molten electrolyte and have good electronic conductivity, and so play the role of a passivating surface layer that prevents further corrosion of the hardware. Unfortunately, this process consumes lithium carbonate from the electrolyte.

Nickel oxide, NiO, is used as the cathode in the MCFC, because it has both good electrocatalytic properties and is a relatively good electronic conductor. However, nickel oxide heated in the molten electrolyte will incorporate a few atom-percent of lithium into its crystal structure. The lithium ions, which occupy interstitial positions in the NiO crystal structure, significantly increase the electronic conductivity of the cathode, which is highly beneficial. Incorporation of lithium in the NiO lattice, however, contributes to loss of the electrolyte.

The preferential consumption of lithium carbonate in these chemical reactions both decreases the electrolyte inventory and changes the Li/K ratio in the electrolyte. Suggested approaches to mitigating the loss of lithium from the electrolyte include:

- Preloading extra electrolyte into the cell/stack during assembly
- Assembling the stack using electrolyte with a higher Li/K ratio than optimum in anticipation of the lithium being preferentially lost
- Developing a protective coating for the stainless steel hardware that is inert with regard to reaction with lithium but is also an excellent electronic conductor.

4. Electrolyte Migration: The passivating surface layer formed by the reaction of lithium carbonate and the cell/stack hardware wets well with electrolyte and provides a pathway for electrolyte to migrate out of the electrolyte matrix. The result is that all stainless steel hardware on the cathode side of the cell as well as hardware on the exterior of the cell/stack that is in contact with wetted interior surfaces of the electrolyte matrix are coated with a thin film of molten carbonate electrolyte. A significant loss of electrolyte can occur if a pathway leading to an external electrolyte sink exists on the outside of the stack. Suggested approaches for reducing or eliminating electrolyte migration include:

- Using non-wetting materials for external hardware
- Developing a protective coating for internal hardware that is both passivating and non-wetting.

Cathode Dissolution: The cathode of the MCFC is a porous structure composed primarily of nickel (II) oxide into which a few atom-percent of lithium ions have been incorporated. Nickel oxide has a very slight solubility in the molten electrolyte of a few tens of ppm, depending on the conditions and the electrolyte composition. The solubility would not present a problem except

for the fact that the electrolyte near the anode side is highly reducing due to hydrogen diffusion into the matrix. Over the course of time, the dissolved nickel ions migrate through the electrolyte from the cathode by chemical diffusion and migrate toward the anode where they encounter a reducing environment. These nickel ions can be reduced to nickel metal within the electrolyte matrix. This reduction can occur on any surface that can mediate the electron transfer between dissolved hydrogen and the nickel ion. Once nickel deposits, it becomes a site for further deposition and slowly grows in size at that location. This growing deposit then becomes a sink for nickel in the electrolyte matrix and so a small flux of nickel moving from the cathode into the electrolyte is established. Cathode dissolution can impact fuel cell longevity in three ways: (1) over time the cathode slowly reduces in thickness as nickel oxide is transported into the electrolyte reducing active surface area, (2) over time the number and size of the nickel metal particles deposited in the electrolyte matrix increase, and (3) at the extreme, the nickel deposited in the electrolyte matrix can form an electronically conducting pathway bridging anode to cathode.

Considerable research was performed in the 1980s addressing cathode dissolution and as a result the fundamental mechanism is well understood. A wide range of innovative concepts were studied in the 1980s to mitigate the problem. Among them were development of alternative cathode materials, changes in the acid/base characteristics of the electrolyte, and addition of foreign materials that can serve as nucleation sites for depositing the nickel in noncritical locations. Sufficient success was achieved by a number of fuel cell developers such that cathode dissolution was removed from the list of important durability issues for a 40,000 hour stack life. However, as progress is made to push stack life to 10 years, cathode dissolution has surfaced again as an important durability issue. Suggested areas of R&D to address cathode dissolution include:

- Reformulating the electrolyte to broaden the range of compositions where nickel oxide solubility is at a minimum (the analog of using a buffer in aqueous chemistry)
- Continuing the search for alternatives to NiO for use as an MCFC cathode material
- Studying the effects of cathode microstructure on the rate of cathode dissolution
- Studying the impact of the nickel precipitates on the physical and chemical properties of the electrolyte
- Studying and documenting changes in cathode morphology as the result of dissolution
- Developing innovative cell and stack designs that reduce cathode dissolution and nickel ion transport
- Developing a comprehensive multi-dimensional model of the cathode and electrolyte matrix that can provide a better understanding of cathode dissolution and its impact on durability.

Focus Area: Cost Reduction

Cost reduction of stack components, balance-of-plant, fuel processing, and post conditioning was considered a topic of importance.

Balance-of-Plant Cost Reduction: There are several important opportunities for cost reduction in MCFC manufacturing. These opportunities include thermal management and integration, fuel processing and cleanup, quality control, quality assurance procedures, and stack conditioning.

1. Thermal management and Integration of Components: Fuel cells generate heat when they operate and that heat must be removed from the fuel cell stack to maintain a stable and uniform temperature. Two methods that have been effective for MCFC are sensible heat cooling and reactive cooling.

In the sensible heat approach, the fuel and oxidant streams are passed through the stack at several times the velocity required by the electrochemical demand for reactants. For example, under typical conditions, the oxidant stream may enter the stack at 630°C and exit at 680°C carrying the excess heat with it. Sensible heat cooling, in addition to requiring oversized heat exchangers to preheat the incoming oxidant stream, also requires that the oxidant flow be ramped up and down in lock step with the heat generation rather than electrochemical demand. It also requires larger turbo machinery to supply the higher flows with a concomitant increase in parasitic power losses.

In the second method, described here as reactive cooling, the steam-methane reforming (SMR) reaction occurs within the fuel cell stack rather than in a separate fuel processing reactor upstream of the stack. SMR is an endothermic reaction used in fuel cells operating with hydrocarbon fuels such as natural gas. By performing this reaction in special reforming units or plates incorporated at regular intervals in the fuel cell stack, excess heat generated by the electrochemical reaction is used to drive the reforming reaction. In other words, the heat generated by the electrochemistry is removed by the SMR reaction. The advantage of this approach is higher system efficiency. The disadvantage is a more complex stack design with reforming units interspersed among the fuel cells at regular intervals in the stack.

There are no obvious solutions to the challenges of heat management in the MCFC system. The issue of cost reduction can best be addressed by innovative design studies that focus on novel component configurations and improved system integration.

2. Fuel Processing and Cleanup: Unlike the PAFC, PBI, and PEM fuel cells, the MCFC is not sensitive to carbon monoxide or ammonia contaminants in the fuel stream. The MCFC, however, is highly sensitive to sulfur. Total sulfur, from all sulfur species in the fuel, must be less than one part-per-million by volume (ppmv) with the desired fuel specification being 0.1 ppmv or less. Odorization of hydrocarbon fuels is a requirement in the U.S., and virtually all of the odorant compounds used are sulfur-based. In the case of natural gas, a number of different odorant compounds may be blended together to cover a wide range of environments, everything from high molecular weight butyl mercaptan to highly volatile dimethyl sulfide. Total sulfur in natural gas may range from 10 to 40 ppm. Removing these odorants from the natural gas can be expensive. UTC Power uses a hydrodesulfurization reactor to convert the odorants into their constituent organic compounds and H₂S. The H₂S is then reacted with a scrubbing compound like zinc oxide. FCE uses adsorbent beds. However, no single adsorbent material can remove the wide range of odorant compounds used in the natural

gas industry. So, multiple adsorbent materials (beds) of activated carbon and molecular sieves are required.

Renewable sources of methane such as anaerobic digesters and landfills also introduce a variety of sulfur contaminants into the fuel as well as other contaminants, such as siloxane, not found in natural gas. Designing a cleanup system becomes almost a site-specific activity.

Contaminant removal processes need to be revisited and a more universal cleanup system developed that is cost effective, highly reliable, capable of removing sulfur to levels less than 100 ppb, and amenable to being fabricated by mass production methods.

3. Manufacturing Processes: The manufacturing processes for the repeat components in the fuel cell stack—electrodes, electrolyte matrix, current collectors, and bipolar separator plates—have been optimized as much as possible for limited production. High-speed manufacturing processes have not been needed to any great extent because of the limited market. Many of the QC/QA procedures are being performed manually with little opportunity for real-time feedback into processing equipment.

- An opportunity for cost reduction exists if automated measurement methods can be developed with sufficient speed and accuracy to adjust processing equipment on the fly and reduce rejection rates.
- In current limited production, many repetitive functions that could be performed by machine are being performed manually. The opportunity exists to speed production, reduce errors and costs, and improve QC/QA by implementing robotic assembly process.

4. Stack Conditioning: Conditioning of the MCFC requires approximately two weeks of specialized operation under controlled conditions. During the initial heating of the stack, a variety of physical and chemical processes take place.

1. Various organic binders used to fabricate cell components are exhausted from the cell/stack.
2. Electrolyte stored as a solid in the gas flow channels of each cell melts and wicks, by capillary action, into the electrodes and the electrolyte matrix.
3. Small amounts of lithium are incorporated into the nickel oxide cathode to increase electrical conductivity.
4. Passivated and electronically conducting surface oxide layers are formed on the bipolar separator plates.

Opportunities for cost reduction exist if the time required for conditioning can be shortened, although no specific suggestions were developed during the breakout sessions.

Summary of MCFC R&D Priorities

1. Research is needed to understand the causes of the microstructural changes in the electrolyte support material that led to early stack failure.
2. Research and development into the modification or reformulation of the electrolyte composition is needed to reduce loss of electrolyte from the cell stack.
3. Development of more robust cathode materials is needed to cut the rate of cathode dissolution by a factor of two or more.
4. Development of more cost-effective cleanup systems for fuel processing of biogas is needed to reduce both installed costs and maintenance costs.
5. Methods to mitigate the loss of lithium from the electrolyte that results from chemical reactions between the electrolyte and the cell and stack hardware are needed.
6. Automated methods for component manufacture and assembly, including real-time methods for QC/QA, need to be developed to reduce wastage, increase reliability, and lower labor costs.
7. The processes and methods used for initial system conditioning need to be reviewed and methods for shortening conditioning time developed.

Phosphoric Acid Fuel Cell Session

Introduction

On the afternoon of November 16, 2009, a Phosphoric Acid Fuel Cell (PAFC) Workshop was held at the Palm Springs, CA, Convention Center in conjunction with the Fuel Cell Seminar. The workshop was a joint activity sponsored by DOE's offices of Energy Efficiency and Renewable Energy (EERE) and Fossil Energy (FE). Attending from EERE was Fred Joseck and from FE Wayne Surdoval. Representatives from national laboratories, industry, and academia participated in the workshop. The objectives of this workshop were the following:

1. Provide an overview of the state-of-the-art and most recent technical progress for PAFC and polybenzimidazole (PBI) fuel cells
2. Identify critical areas, key barriers, and gaps in the current PAFC and PBI technology restricting commercialization
3. Identify opportunities for progress to reduce or eliminate the barriers and gaps impeding commercialization of PAFC and PBI fuel cell systems
4. Promote potential research collaborations and create or strengthen partnerships.

Three formal presentations were made followed by breakout sessions addressing R&D needs. John Ferro and Shridhar Kanuri of UTC Power, LLC and Emory De Castro of BASF Fuel Cell Inc. provided presentations on PAFC and PBI fuel cells, respectively. These background presentations clearly identified cost as a major factor impeding the commercialization of the PAFC and PBI fuel cell systems. Shridhar Kanuri (UTC Power) and Emory De Castro (BASF) also identified critical areas for advancing the PAFC and PBI technology in their presentations. Key barriers and gaps in fuel cell technology were identified and opportunities to advance the technology suggested.

Welcome and PAFC Session Overview

The purpose of this workshop session was to bring together technical experts from industry, academia, and the national laboratories to address the development of advanced PAFC and PBI technology. Industry experts were invited to provide technology and manufacturing overviews and to identify the issues that lie on the critical path to cost reductions, performance increases, lifetime increases, and commercialization. The organizers acknowledge the contributions of UTC Power and BASF for their presentations.

PAFC systems were the first commercial stationary fuel cell systems and have demonstrated the greatest durability for commercial systems with lifetimes in excess of 60,000 hours. The phosphoric acid stationary fuel cell system operating on natural gas has 40% fewer greenhouse gas emissions when compared to the average coal-fired power plant in the United States. The PAFC systems that also are configured to provide heat for cogeneration applications can achieve

overall heat plus electricity efficiencies >70%, further lowering the carbon footprint of the system.

The major challenge to PAFC systems is the high cost of materials; the high platinum content is particularly costly and represents 10% to 15% of the total PAFC system costs. Other material costs and processing costs also contribute to making the first cost of the PAFC system considerably greater than the average fossil-fueled steam turbine power plant. PAFC power plant cost of about \$4,500/kW makes the first cost prohibitive for many customers. The extended lifetime of the PAFC system permits a profitable return-on-investment after four to five years in premium power applications. Lifetimes in excess of 60,000 hours also increase profitability for the customer.

The Department of Energy Office of Fossil Energy has supported the development of PAFC in the past, and DOE's Office of Energy Efficiency and Renewable Energy (EERE) is supporting the development of PEM fuel cell systems. The focus of much of the EERE research has been for automotive applications. However, EERE efforts also have supported applications for backup power, materials handling (forklift trucks), and portable fuel cells. Recent technology breakthroughs resulting from the EERE PEM research programs may benefit PAFC and PBI fuel cell systems. These breakthroughs include the reduction of platinum content in PEM fuel cells, the development of alternative bipolar plate materials, and the development of reduced-cost balance-of-plant components. The EERE program also funds the development of advanced manufacturing methods for PBI fuel cells. These EERE-funded manufacturing projects may also be able to contribute to PAFC process advancements and lay the foundation for significant reduction in the first cost of PAFC and PBI systems.

Presentations

The following are summaries of the information provided in the presentations.

PAFC History and Successes, Mr. John Ferro, UTC Power, LLC.

John Ferro is the Manager of Product Development for UTC Power. His presentation focused on the UTC Power PureCell fuel cell system and its history dating back to the early 1970s. The 200 kW stationary PAFC system, the PureCell 200, is the most important PAFC accomplishment by UTC Power. Over 260 systems installed across 19 countries on five continents with more than 8.7 million hours of operation and more than 1.4 billion kWh of electricity generation have been achieved by the 200 kW PAFC system. The longest running system has operated over 64,000 hours and is operated by Toshiba at their Houston, Texas facility. Toshiba at one time owned 10% of UTC Power, and the two companies worked together to develop and market PAFC systems. The standard PureCell 200 is a grid-connected unit, operating in parallel with electric utilities. Dual-mode configuration also is available, and dual-mode enables the unit to operate grid connected or independent—switching between modes automatically or on command. The PureCell 200 produces 200 kilowatts of assured power, plus about 1.50 MM Btu/hr of heat at 140°F (60°C). UTC Power offered a high-grade heat option that will deliver 475,000 Btu/hr at 250°F (121°C) and 450,000 Btu/hr at 140°F (60°C); however, the quality of the heat will depend on the age of the power plant. UTC Power has broad and varied experience installing and

operating PureCell 200 systems on many different fuels: natural gas, hydrogen, landfill gas, and methane from an anaerobic digester. The PureCell 200 product line is no longer available as a product from UTC Power. It has been replaced by the new PureCell 400, which is now entering the market.

Three major subsystems are contained within the PureCell 200: the fuel processing section that converts fuel to hydrogen, the fuel cell stack that generates DC power from oxidation of hydrogen, and the power conditioner that converts the stack DC power to high-quality AC power. The critical materials for the cell stack are the platinum catalyst coated on carbon substrate and carbon-Teflon composite bipolar plates.

Failure modes for the PureCell 200 were identified by UTC Power in their presentation and are shown in Figure 3 and discussed below.

Acid Loss: Occurs because of the vapor pressure of the phosphoric acid under cell operating conditions is sufficiently high to allow slow evaporation of the electrolyte with the electrolyte vapors being carried away in the spent fuel and oxidant exhaust streams. Vapor pressure is a strong function of the operating temperature. Lower temperatures minimize electrolyte loss but can have negative effects on CHP performance and system power.

Cooler Plugging: Caused by accumulation of scale and deposits in the stainless steel tubing of the cell-stack cooling system.

Lower Voltage Limit: Is the minimum permissible stack performance. When cell-stack performance falls below this voltage limit, the stack is replaced. Low stack voltage is caused by three factors:

1. Steady state decay caused by catalyst agglomeration and corrosion of the catalyst carbon support materials.
2. Start-stop decay caused by carbon corrosion and possibly catalyst corrosion during both shut down and startup of the PAFC system; in particular, uncontrolled shutdown of the PAFC system is detrimental to PAFC performance. Under standard operating conditions, shutdown and startup procedures and operating conditions are controlled to minimize start-stop decay.
3. Contamination from impurities in anode feed; e.g., ammonia can induce performance loss and even failure of the PAFC of the cell stack.

The design approach for the next generation PureCell system invokes a modular approach with the development of a supply chain for manufacture of subsystem modules. Critical to the development of the next generation PureCell system is the reduction of the first cost of the PAFC system. Mr. Ferro's slide presentation can be found in Appendix D.

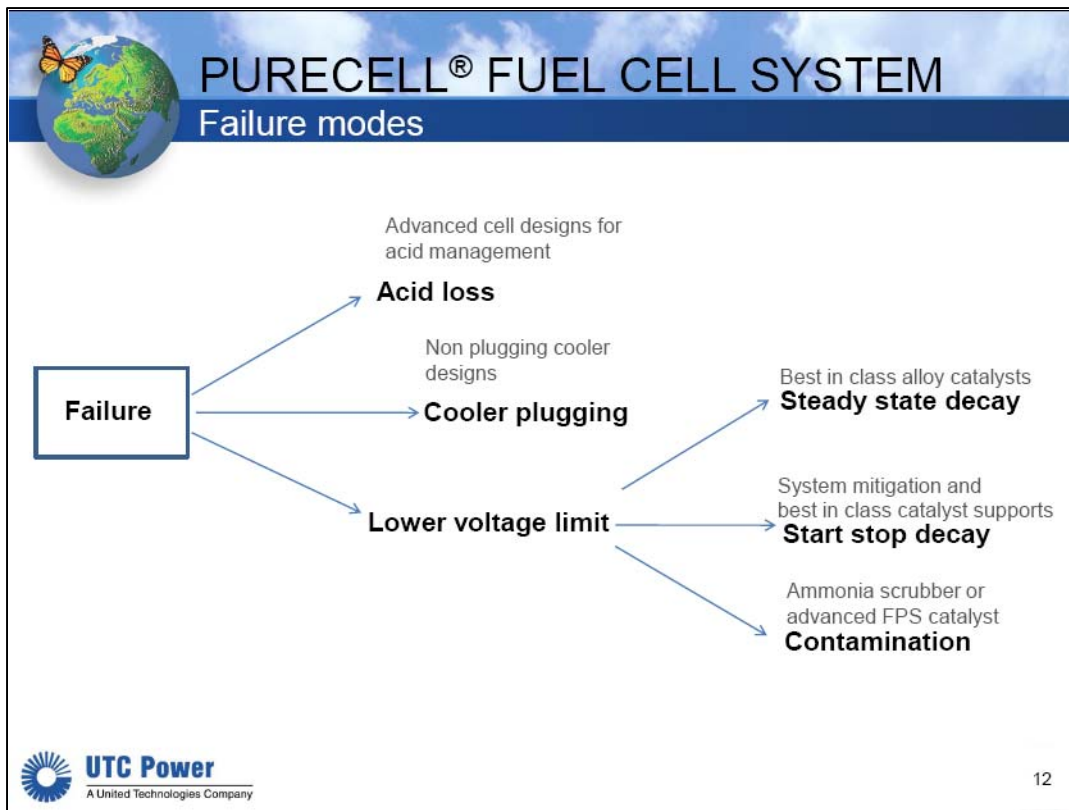


Figure 3: Failure modes for PureCell 200 (from J. Ferro presentation, PFAC History and Successes 2009)

PAFC Cost Challenges, Mr. Sridhar Kanuri, UTC Power, LLC

Sridhar Kanuri is Manager of PAFC Technology at UTC Power. His presentation emphasized cost challenges of the new PureCell 400 and identified cost reduction opportunities. Technology advances are required to reduce the cost and for UTC Power to reach its commercialization targets. The technology approaches identified by UTC Power to reach the commercialization target are development of:

1. Alternative electrolyte
2. More active catalysts
3. Low-cost manufacturing methodologies
4. Low-cost heat exchangers
5. Ammonia-free producing fuel processing system.

UTC Power identified the desired properties for an alternative electrolyte and many of these properties were introduced by UTC into the present PAFC system. The alternative electrolyte improvements are given in Table 1.

Table 1: Alternative Electrolyte Improvements to UTC Power's PAFC	
Improved Property	Value
Ionic Conductivity (S/cm)	> 0.65
Electrolyte Vapor Pressure (atm)	< 4.5×10^{-7} @ 175°C
O ₂ Solubility (mol/cm ³)	> 1×10^{-7} @ 175°C
Transference number	0
Anode poisoning	None

Eliminating anion poisoning and using electrolytes with vapor pressure lower than that of phosphoric acid would improve power plant efficiency by 6 percentage points; e.g., increase the beginning-of-life efficiency to 48% and reduce cost by 15% to 20%. The electrolyte improvement was identified as one the most important improvements for the phosphoric acid fuel cell system.

Anode Catalyst: The development of a more active anode catalyst that fulfills the following requirements was identified by UTC Power as an R&D need. However, the level of performance improvement or cost reduction associated with these improvements was not discussed.

- Catalyst/support stable at 150°C and 225°C.
- Carbon monoxide tolerant catalyst - at temperatures above 130°C platinum loadings in present PAFC systems have high CO tolerance. However, reducing platinum loadings by an order of magnitude or more may reduce CO tolerance of the anode.
- Stabilize active surface area of catalyst - agglomeration of the platinum crystallites either by surface migration or by Ostwald ripening reduces the active surface area of the anode catalyst over time; stabilizing the surface area may permit lower Pt loading at the anode.
- Low Pt loading at the anode - reduction of anode catalyst loadings for the PAFC system from 2.4 g/kW to levels similar to PEM fuel cells ~0.03 g/kW is considered an opportunity.

UTC Power suggested that metal carbides may be an alternative catalyst for PAFC anodes and should be investigated.

Cathode Catalyst: The development of a more active PAFC cathode catalyst with improved properties was also identified by UTC Power as an R&D need.

- Catalyst/support stable at 150°C & 225°C.
- Stable active surface area of cathode catalyst - agglomeration of the platinum crystallites reduces the activity of the cathode catalyst over time. Reducing or eliminating graphitized carbon support corrosion would improve the stability of the cathode catalyst surface area; stabilizing the surface area should permit much lower Pt content at the cathode.

- Increased mass activity of the cathode catalyst - UTC Power identified research supported by EERE for PEM fuel cells that provide a new cathode catalyst structure for a platinum - palladium "alloy" that yielded a ten-fold increase in the mass activity compared to platinum alone.
- Low Pt usage at the cathode - reduction of the cathode catalyst loadings for the PAFC system from 5.2 g/kW to levels similar to PEM fuel cells ~0.13 g/kW is considered an opportunity.

Manufacturing: UTC Power identified the present PAFC electrode manufacturing process as capital intensive and showed that the development of low-cost electrode manufacturing concepts would result in a reduction in first cost. A reduction in the cost of gas diffusion layers (GDL) could be achieved by a combination of lower cost materials and alternative manufacturing processes. UTC Power suggested that low-cost carbon composite fibers or carbonized cellulose based fibers and cotton based fibers should be investigated as GDL materials.

Heat Exchangers: Improvements in heat exchanger materials and designs are recommended by UTC Power. Development of heat exchangers following concepts used for automotive radiators could provide lightweight and compact heat exchangers with a low pressure drop on the gas side. UTC Power anticipates heat exchanger designs following automotive radiator design concepts would result in lower costs because of existing volume production and the "simple" structure of the automotive radiators.

Ammonia Production in the Fuel Processor: The PureCell 400 is required to use a scrubber to remove ammonia from the fuel entering the cell-stack in those applications where the nitrogen content of the natural gas supplied to the system exceeds 1% by volume. The source of the ammonia is nitrogen in the natural gas that reacts with hydrogen produced in the methane-steam reforming process to form ammonia. The penalty is a reduction in the stack voltage caused by the formation of ammonium phosphate in the electrolyte. The ammonium phosphate impedes the transport of protons in the PAFC fuel cell. UTC Power recommends R&D to develop non-ammonia producing fuel processing catalysts. Mr. Kanuri's slide presentation can be found in Appendix E.

PBI-Phosphoric Acid Based Membrane Electrode Assemblies: Status Update,
Mr. Emory De Castro, Executive VP of BASF Fuel Cells

Mr. De Castro's presentation covered the growth of BASF Fuel Cells (BASF) from the initial company, E-TEK, through the interaction with Celanese to form PEMEAS, to the acquisition of PEMEAS by BASF. As a leading supplier of membrane electrode assemblies (MEA), fuel cell catalyst, reformer catalysts, and gas diffusion material to the emerging fuel cell industry, BASF is an established manufacturing company with a global presence and a sound financial base.

BASF Celtec-P is a gel-type PBI (polybenzimidazole) membrane containing phosphoric acid that has a low solid content and is a core technology for BASF. Hydrogen bonding of the phosphoric acid with PBI may help the membrane retain phosphoric acid as shown in Figure 4.

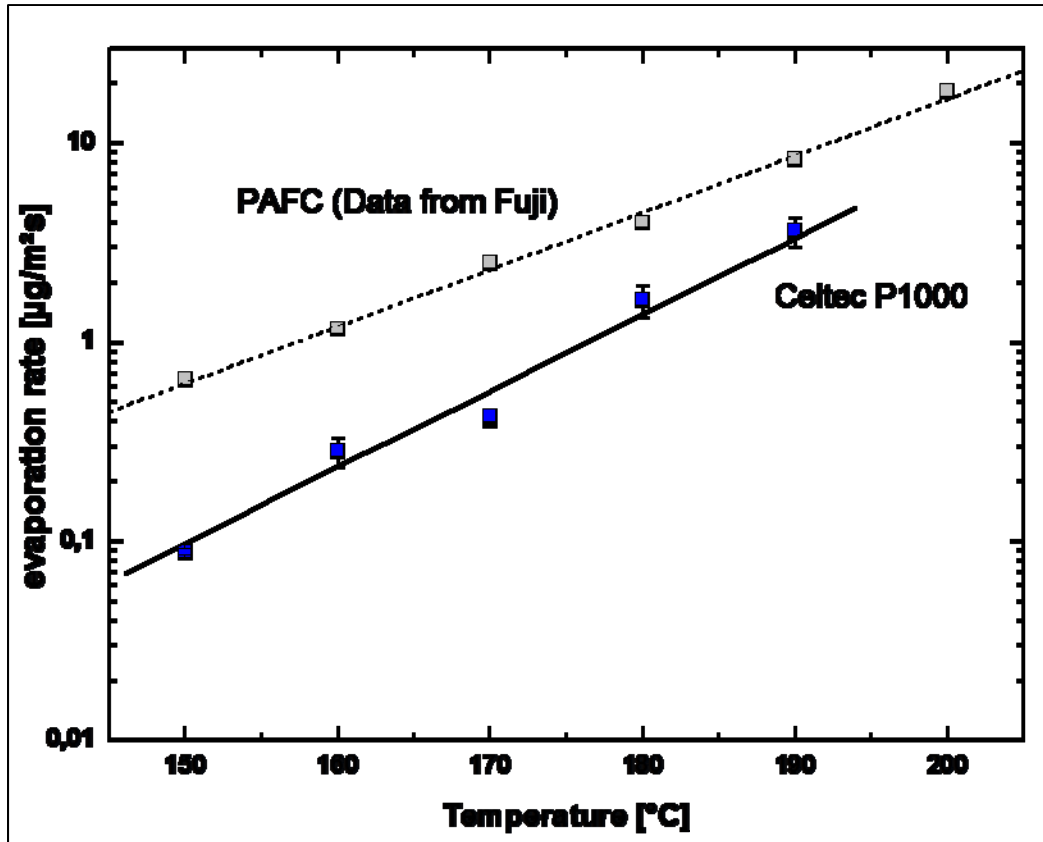


Figure 4: Reduced evaporation of phosphoric acid from Celtec P1000 compared to Fuji Electric PAFC (Data provided by BASF.)

BASF continues development of the mechanical properties of the membrane to improve resistance to creep. A PBI membrane with low creep properties will permit high-speed roll-to-product processing for membrane fabrication.

Celtec-P membrane electrode assembly (MEA) is BASF's integral part of the core technology with PBI membranes. The Celtec-P MEAs operates at temperatures between 120°C and 180 °C, tolerating large concentrations of carbon monoxide and being able to run independently of humidification. A characteristic of the Celtec-P MEA is high sulfur tolerance. Three Celtec-P MEA products for different applications have been developed by BASF:

1. Celtec-P 1000 for back-up power and auxiliary power units that operate in the power range 250 W to 10 kW
2. Celtec-P 2000 for stationary applications, including CHP that operate in the power range 750 W - 10 kW
3. Celtec-P 3000 for micro fuel cells operating in the power range 10-100 W.

R&D Needs for PBI: Suggestions for continuing R&D relating to the PBI/phosphoric acid cathode are:

- Elimination of the strong adsorption of phosphate ions at the platinum that reduces access of oxygen to the Pt catalyst. The development of alloys more resistant to phosphate anion adsorption was suggested by BASF. New tools for understanding the adsorption of the phosphate anions and for alloy development are available, such as XAFS and XANES. Greater understanding of the catalyst structure and improved synthetic techniques developed for low temperature PEM cathode catalysts may offer routes to an improved catalyst.
- Increasing the oxygen solubility in phosphoric acid. The addition of additives to the phosphoric acid; e.g., addition of perfluorosulfonimide.
- Improvements in cathode stability during start-stop operation can be obtained with modification of the carbon support materials and improving the catalyst-support interaction.

BASF manufactures all subcomponents used in the production of the Celtec MEA. Starting with platinum metal, carbon cloth or paper, and polymer monomers, BASF makes electrocatalyst, fabricates gas diffusion electrodes, synthesizes polymer films, and assembles MEAs via a “pick and place” robotic laminator.

BASF also offers catalysts for fuel processing, including catalysts that incorporate sulfur removal adsorbents, reforming catalysts, shift catalysts, and highly selective catalysts for CO removal. These products can be used for auto-thermal and steam reformers. BASF Selectra Series D adsorbents and catalysts are used to remove sulfur before the fuel is fed into the auto-thermal or steam reformer. The BASF reformer catalyst Selectra Series S includes a high-temperature shift catalyst and a low-temperature shift catalyst. A new generation of high-temperature CO shift catalysts using precious metal instead of base metal has outstanding performance and stability. The high-temperature shift catalysts Selectra Series are resistant to deterioration caused by oxygen breakthrough from the upstream reformer during start-up. The low-temperature shift catalysts strongly adsorb traces of sulfur compounds from the reformat stream and protect the fuel cell catalyst from sulfur poisoning.

The Selectra Series R catalysts are reformer catalysts that are resistant to frequent load changes and start/stop cycles. The Selectra Series R catalysts operate at high space velocity, enable compact reformer design, are tolerant to liquid water, and tolerant to air.

Selectra Series CO catalysts are highly selective catalysts for CO removal that prevent poisoning of the fuel cell anode by CO. BASF offers two different catalytic approaches to CO protection:

1. Catalysts for the CO-preferential oxidation and
2. Catalysts for the CO-selective methanation. They can be used in a single stage reactor for the reduction of CO content. Reduction from 8,000 ppm down to 1-2 ppm is possible.

The BASF slide presentation can be found in Appendix F.

Breakout Groups

The participants divided into two groups to discuss the information presented by BASF and UTC Power. The two breakout groups were challenged to recommend areas of research and development for the following two PAFC/PBI fuel cell systems areas: (1) cell stack and cell stack components R&D (Table 2) and (2) manufacturing and balance-of-plant R&D (Table 3)

Table 2: Highlights of PAFC Cell Stack & Cell Components Breakout Groups	
Issue	Recommendation from Breakout Groups
Anion adsorption	<p>Alternative electrolyte development</p> <ul style="list-style-type: none"> • Acid variation of $\text{Li}_2\text{B}_{12}\text{F}_{12}$, for lithium batteries very good conductivity • Perfluorinated additives to improve conductivity; variation of the perfluorosulfonimide reported by BASF • Review previous work; e.g., GRI efforts by Dan Scarpiello in 1990
Increased catalytic activity	<ul style="list-style-type: none"> • Catalyst alloys that impede anion adsorption • Platinum-free anode catalyst (UTC Power reported tungsten carbide as a potential anode catalyst)
Increased durability and eliminate steady state decay	<p>Catalyst supports</p> <ul style="list-style-type: none"> • Non-carbon catalyst supports • Stable, high surface area supports • Carbon support modifications that prevent platinum sintering
Analytical testing of H_3PO_4 / PBI systems	<p>Fundamental studies</p> <ul style="list-style-type: none"> • Catalyst stability • Understand and control Ostwald ripening • <i>In-situ</i> characterization of catalyst and electrodes; XANES • Develop methods for evaluating mesoscopic electrode structure • Fundamental studies of phosphate adsorption • Fundamental studies of the effect of surface structure on catalyst performance • Fundamental studies of reformer catalysts that do not form ammonia in presence on nitrogen and hydrogen
Electrolyte studies	<p>Electrolyte management</p> <ul style="list-style-type: none"> • Additives to increase the O_2 solubility in H_3PO_4 • Review work by Dan Scarpiello in 1990 • Modify PBI to reduce creep and acid loss
Cell stack	<p>Mechanical properties - reduce creep of all cell components through material and design changes.</p> <p>Develop new bipolar materials</p> <ul style="list-style-type: none"> • Polymer stable at H_3PO_4 / PBI operating conditions • Reduce Teflon content • Develop new compounding resins for bipolar plates; replace phenolic resins <p>Low-cost substrate materials - reduce cost and improve manufacturing</p>
Manufacturing	<p>Reduce stack condition times</p> <ul style="list-style-type: none"> • Fundamental study to determine what changes are occurring during conditioning

Table 3: Highlights of PAFC Cost Reduction & Balance-of-Plant Breakout Groups	
Cost factors	Fuel processor ~20% of cost Platinum catalyst ~10% to 15% of cost Cell Stack ~40% of cost Materials:
Fuel processor	Cleanup <ul style="list-style-type: none"> • Sulfur • CO cleanup a function of operating temperature • Ammonia reduction; 1% nitrogen acceptable • Ammonia cleanup very costly; single biggest cost of fuel processor • Hydrogen reclamation - at 80% utilization do you recycle hydrogen back to the anode inlet or use hydrogen to fire the SMR reactor? • Removal of H₃PO₄ vapor from hydrogen if using it to fire SMR • Fuel processor produces 1,000 kg hydrogen per day • Fuel processor is a scaled-down commercial unit • Fuel processor life needs to be 10 years
R & D needs:	Prevent ammonia poisoning <ul style="list-style-type: none"> • New catalyst Methods of stabilizing platinum <ul style="list-style-type: none"> • Stabilize carbon support • Stabilize catalyst layer - leverage from PEM low-temperature efforts Benefits of recycling platinum <ul style="list-style-type: none"> • Develop new, low-cost recycling chemistry
Manufacturing processes	Develop new cost-effective methods for manufacturing electrodes <ul style="list-style-type: none"> • Current methods are time and capital cost intensive Material cost and material processing costs need to be reduced <ul style="list-style-type: none"> • Teflon is a costly stack material • High-temperature processes are costly; e.g., graphitization and carbonizing Development of in-line quality control procedures <ul style="list-style-type: none"> • Decrease waste in the manufacturing process
Performance	Ultimate / alternative electrolyte to reduce anion adsorption and increase oxygen solubility-diffusivity product <ul style="list-style-type: none"> • Increase cell voltage • Improve power density

Summary of PAFC R&D Priorities

1. Both the industry presenters and the breakout session participants agreed that first cost, consisting of capital equipment, manufacturing processes, installation, and warranty, needs to be reduced. In addition, technology improvements need to be addressed to increase the performance of PAFC/PBI fuel cell systems. Performance improvements may lead to reduction of the first cost by increasing the power density of the cell stack and reducing the number of cells in the stack.
2. Both industry and other participants agreed that anion adsorption limits cathode catalyst performance and, hence, PAFC/PBI fuel cell system performance. A consensus recommendation was for R&D to eliminate anion adsorption either through electrolyte modification, development of an alternative electrolyte, or development of improved cathode catalyst.
3. It is recommended that development of manufacturing processes for low-cost electrode and MEA manufacturing be addressed. Quality control procedures need to be developed to reduce waste and rework. New and faster methods of conditioning cell stacks and power plants are needed.
4. It is recommended that materials research and development programs be initiated to discover lower cost materials for the cell stack and the balance-of-plant components. This would include new polymers for processing bipolar plates and the replacement of Teflon in the cell stack.
5. Fuel processing research to develop steam-methane reforming catalysts that do not produce ammonia from nitrogen impurities in the fuel should be initiated.
6. Research and development to identify new electrode catalyst and catalyst support materials are critical for stable performance over the extended life of PAFC/PBI fuel cell systems.
7. Fundamental studies are needed to define *in situ* and *ex situ* analytical tests for characterizing the properties of catalyst and electrode structures.

Acknowledgments

Workshop organizers wish to acknowledge the support of the U.S. Departments of Energy's Office of Energy Efficiency and Renewable Energy and Office of Fossil Energy for their support and participation.

Appendix A
DFC Technology Status
Mr. Pinakin Patel, FuelCell Energy, Inc.



FuelCell Energy

DFC Technology Status

Pinakin Patel

Mohammad Farooque

FuelCell Energy, Inc.

3 Great Pasture Road

Danbury, Ct 06813

reliable, efficient, ultra-clean



DFC power plant is an enabler for broad distributed generation

- Distributed generation puts power where it's needed
- Increases power reliability
- Near zero emissions allow units to be sited almost anywhere – even polluted urban areas
- Reduces need for central generation plants
- Reduces grid congestion and need for new transmission lines
- Distributed generation enables smart grid
- Balances the grid with 24/7 power
- Meets requirements for low carbon technology
- Smaller projects enable faster permitting, financing, and execution

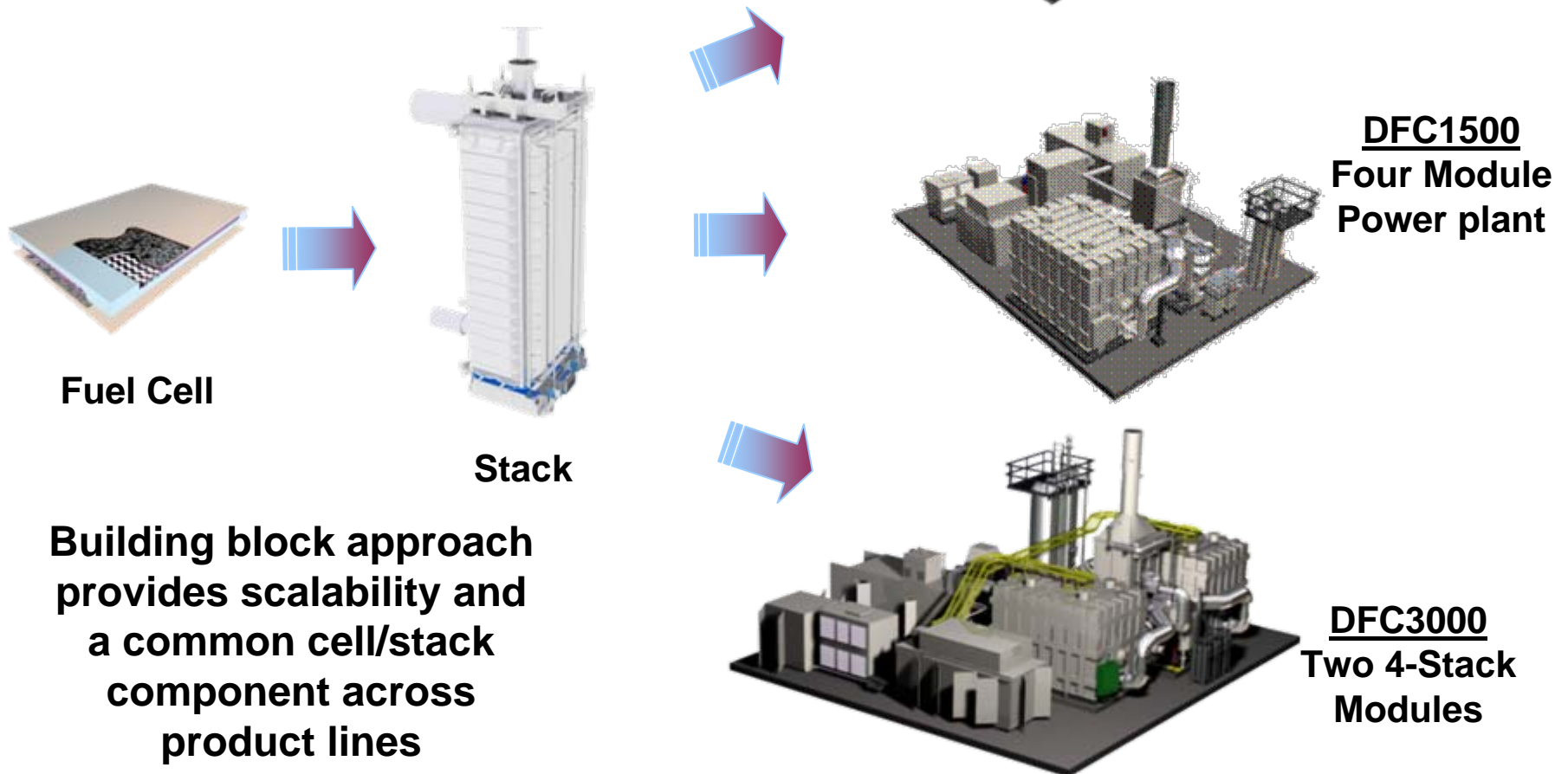


600 kW at M&L Commodities



FuelCell Energy

FuelCell Energy Products





DFC Typical Applications



Average-Sized Grocery Stores,
300-Bed Hotels

300 kW



1.4 MW



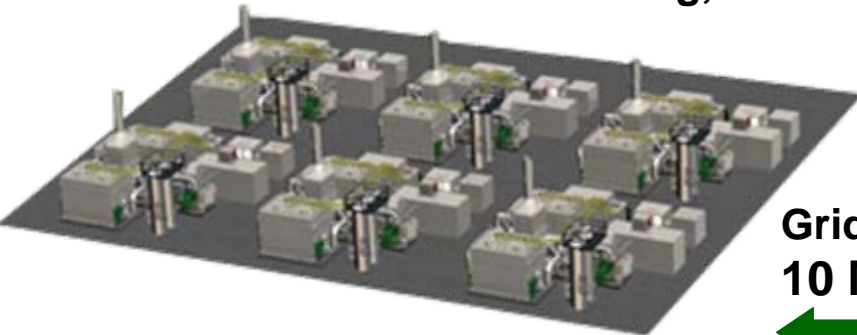
1000-Bed Hotels, Convention Centers,
Wastewater Treatment, Food/Beverage



300-Bed Hospitals, Manufacturing, Universities



2.8 MW



Grid Support, RPS
10 MW +

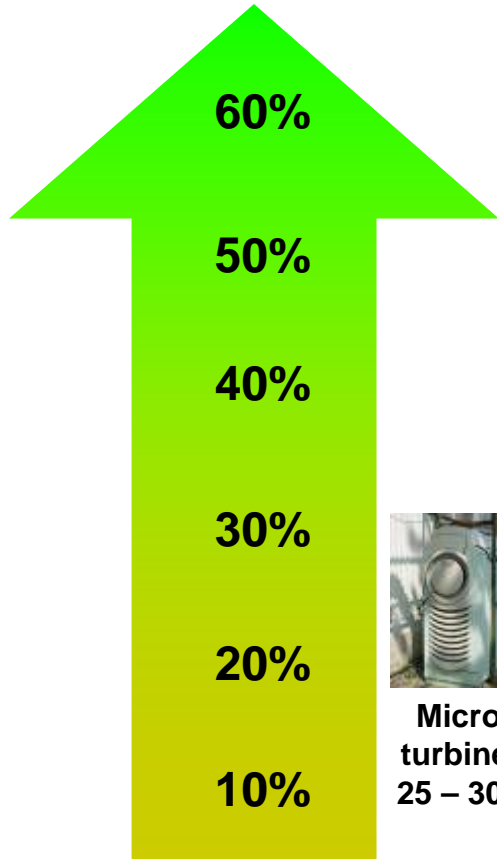




High Electrical Efficiency

DFC power plants offer the highest efficiency of any distributed generation technology

Fuel to Electrical Efficiency



Micro-turbines
25 – 30%



Small Gas Turbines
25 – 35%



Natural Gas Engines
30 – 42%



Direct FuelCell (DFC)
47%



DFC-ERG
DFC/Turbine
58 – 65%



FuelCell Energy

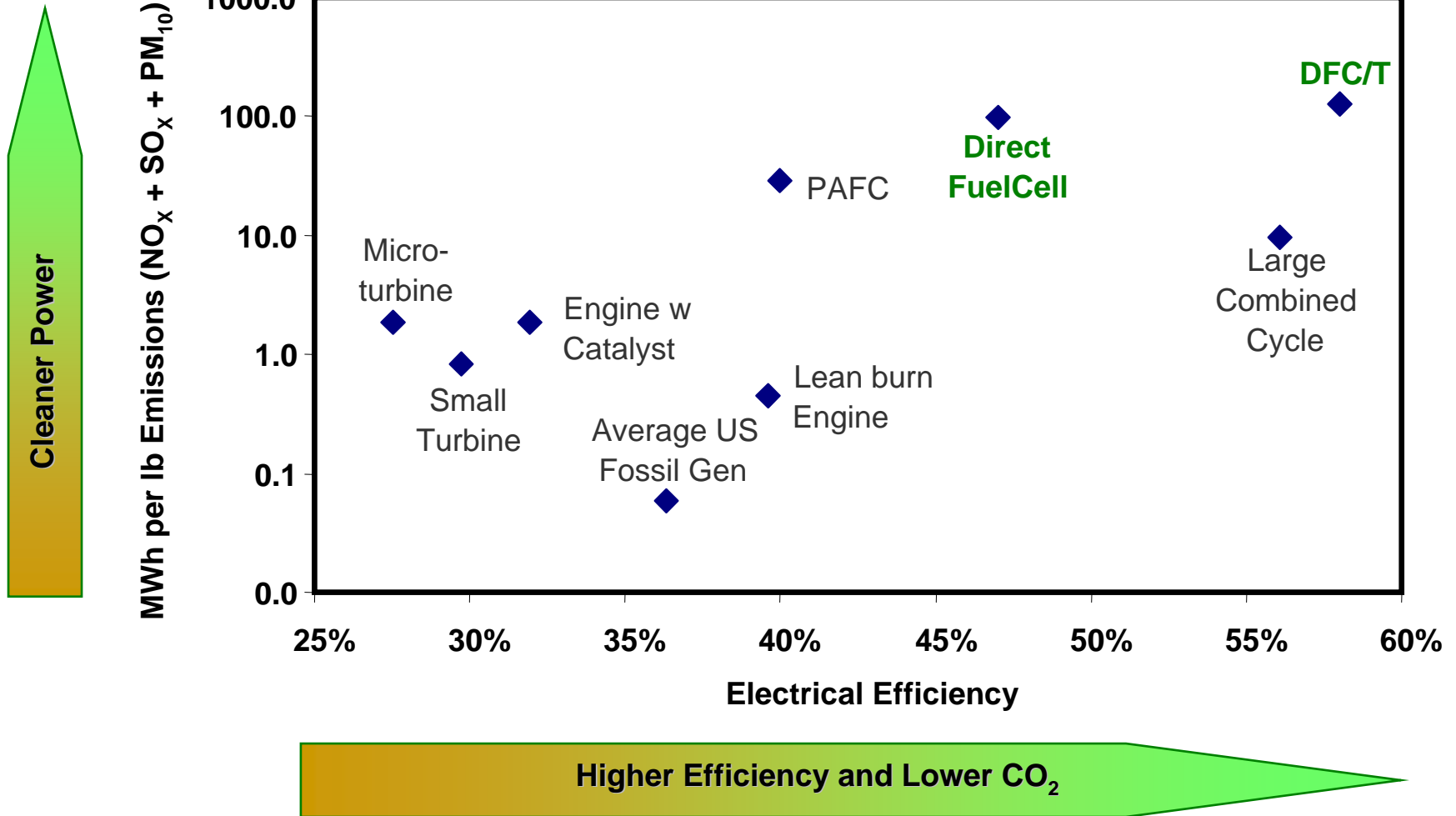
Direct Fuel Cell Emissions Compared to Others

	CO₂ (lb/MWh)	NO_x (lb/MWh)	SO_x (lb/MWh)	PM₁₀ (lb/MWh)
Average US Fossil Fuel Plant	2031	5.06	11.6	0.27
Average US Generation	1408	3.4	7.9	0.19
Typical Small Gas Turbine	1494	1.1	0.008	0.08
DFC (Baseline products)	980	0.01	0.0001	0.00002
DFC Potential (at 65% Efficiency)	680	0.007	0.00007	0.00001

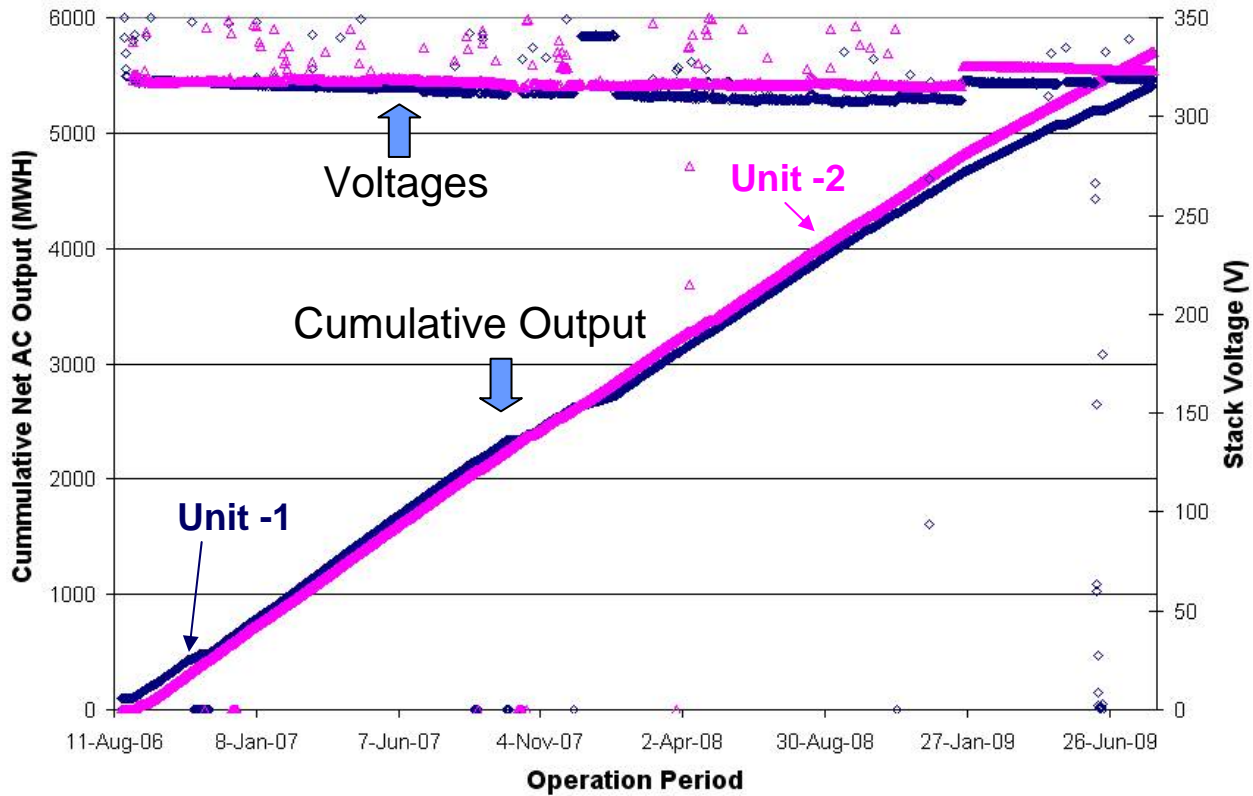


FuelCell Energy

DFC: Cleanest Power at the Highest Efficiency



Source for non-DFC data: PAFC data from product brochure; Other data from "Model Regulations For The Output Of Specified Air Emissions From Smallscale Electric Generation Resources Model Rule and Supporting Documentation", October 15, 2002; The Regulatory Assistance Project report to NREL




Both stacks at the Camp Pendleton site met life goals



FuelCell Energy

Typical Operating Point of a 2.4 MW Power Plant



DFC3000 POWER PLANT MAIN MENU  8/17/2009
8:11:27 AM

Power Plant Load Rated

	ACTUAL	ISO RATED
DC Power	2607 KW	2566 KW
Gross AC Power	2573 KW	2463 KW
BOP Load	58 KW	63 KW
Altitude Correction	0 KW	0 KW
Stack Auto Derate	0 KW	0 KW
Net AC KW Output	2415 KW	2400 KW

SYSTEM INFORMATION:

ICONICS VERSION: 11
PLC LOGIC VERSION: 55.0
MODULE A SERIAL NUMBER: B1220-013
MODULE B SERIAL NUMBER: B1220-014

POWER PLANT LOCATION:
MPC 2 - Yulchon, Republic of Korea

MODULE A			MODULE B		
	DC Voltage	DC Current		DC Voltage	DC Current
STACK AB	623 V	1046 A	STACK AB	625 V	1046 A
STACK CD	631 V	1032 A	STACK CD	625 V	1046 A
AVERAGE	627 V	2078 A	AVERAGE	625 V	2093 A
Runtime	1169 Hrs		Runtime	1169 Hrs	



FuelCell Energy

Multi-MW Scale Fuel Cells



4.8 MW Fuel Cell – Pohang, Korea



FuelCell Energy

DFC Edge in Biogas Applications

- **More power for given amount of biogas:** Higher efficiency than any other generation at typical digester facility sizes
- **Good heat to power ratio for digester support:** Fuel cell makes enough heat to support digester operation
- **Avoids generation of NO_x and other pollutants** from flare or from other generation technologies





FuelCell Energy

King County
Seattle



**1 MW Municipal Wastewater Treatment Plant
First Site with Online Fuel Switching**



FuelCell Energy

Kirin Brewery
Project



First SubMW Digester Gas Project, Running on Biogas from Beer Production



FuelCell Energy

Sierra Nevada Brewery

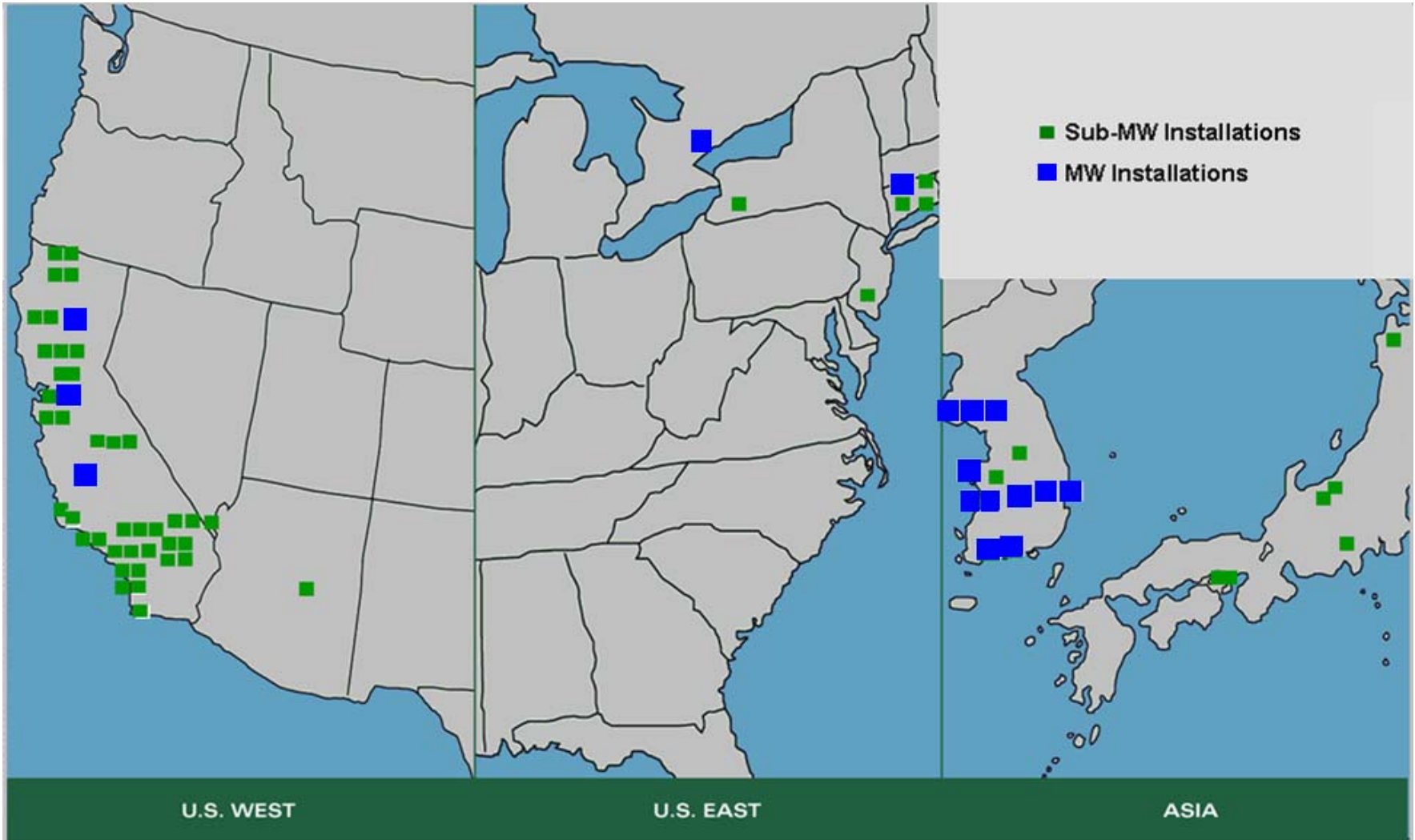


Site with Power Generation in excess of ADG Supply
First Site with Automated Fuel Blending



FuelCell Energy

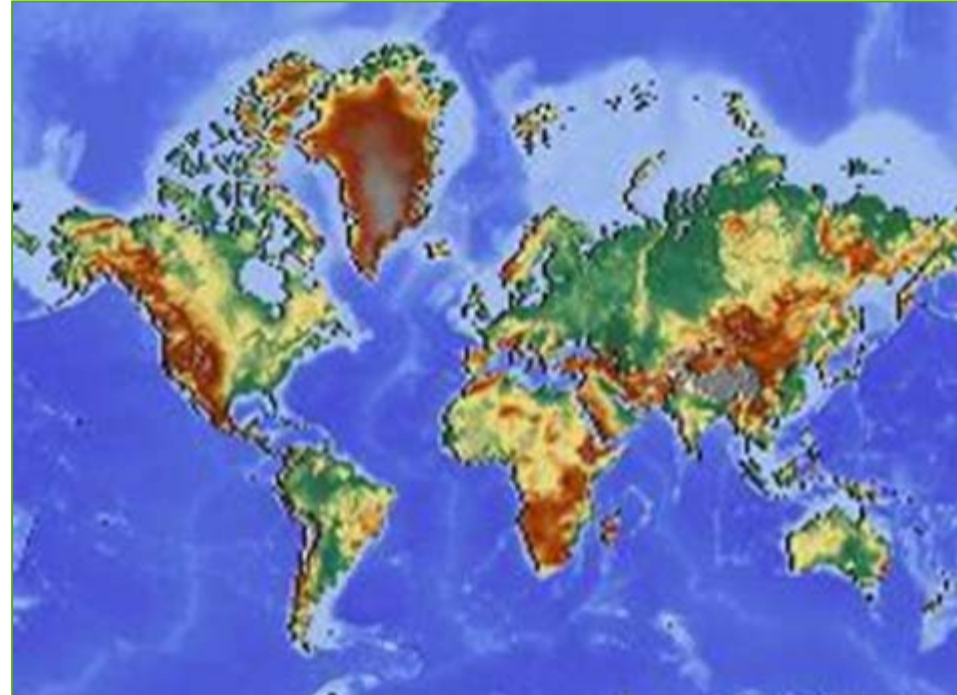
MW and Sub-MW DFC® Worldwide Installations





Markets

- 95 MW installed/backlog
 - Japan/Korea: 72 MW
 - California/West Coast: 15 MW
 - Northeast/Canada: 5 MW
 - Europe: 2 MW
- Targeted applications
 - Grid Support: 69 MW
 - Renewable/Wastewater: 9 MW
 - Manufacturing: 7 MW
 - Hotels: 3 MW
 - University & Hospitals: 2 MW
 - Government: 3 MW
 - DFC-ERG: 2 MW





- Production and delivery capabilities meet current demand
- State-of-the-art manufacturing in Torrington, CT
- 70 MW capacity
- Production rate of 30 MW/year
- Strong supply chain in place
- Expansion plan to achieve 150 MW capacity





New Products: DFC ERG Status

- DFC-ERG provides heat for natural gas pipeline letdown operations
 - Byproduct heat warms gas to prevent freezing as pressure is let down from transcontinental pipelines to local lines
 - Excess electricity sold to the grid
- Improved economics and lower carbon emissions due to ~60% electrical efficiency
- First site commissioned in Toronto
- Four sites pending under Connecticut RPS program
- Market opportunity estimated at 250-350 MW in Toronto, California and the Northeast U.S.



2.2 MW DFC-ERG in Toronto



FuelCell Energy

Products Under Development: DFC/T Fuel Cell Turbine Hybrid System

- **Fuel cell waste heat drives unfired turbine**
- **Electrical efficiency increased from 47% to 58-60%**
- **Field tested in DFC300 based subMW system**
- **Commercial product being designed based on DFC3000, 3.4 MW rating**
 - **First unit approved under CT Project 100**

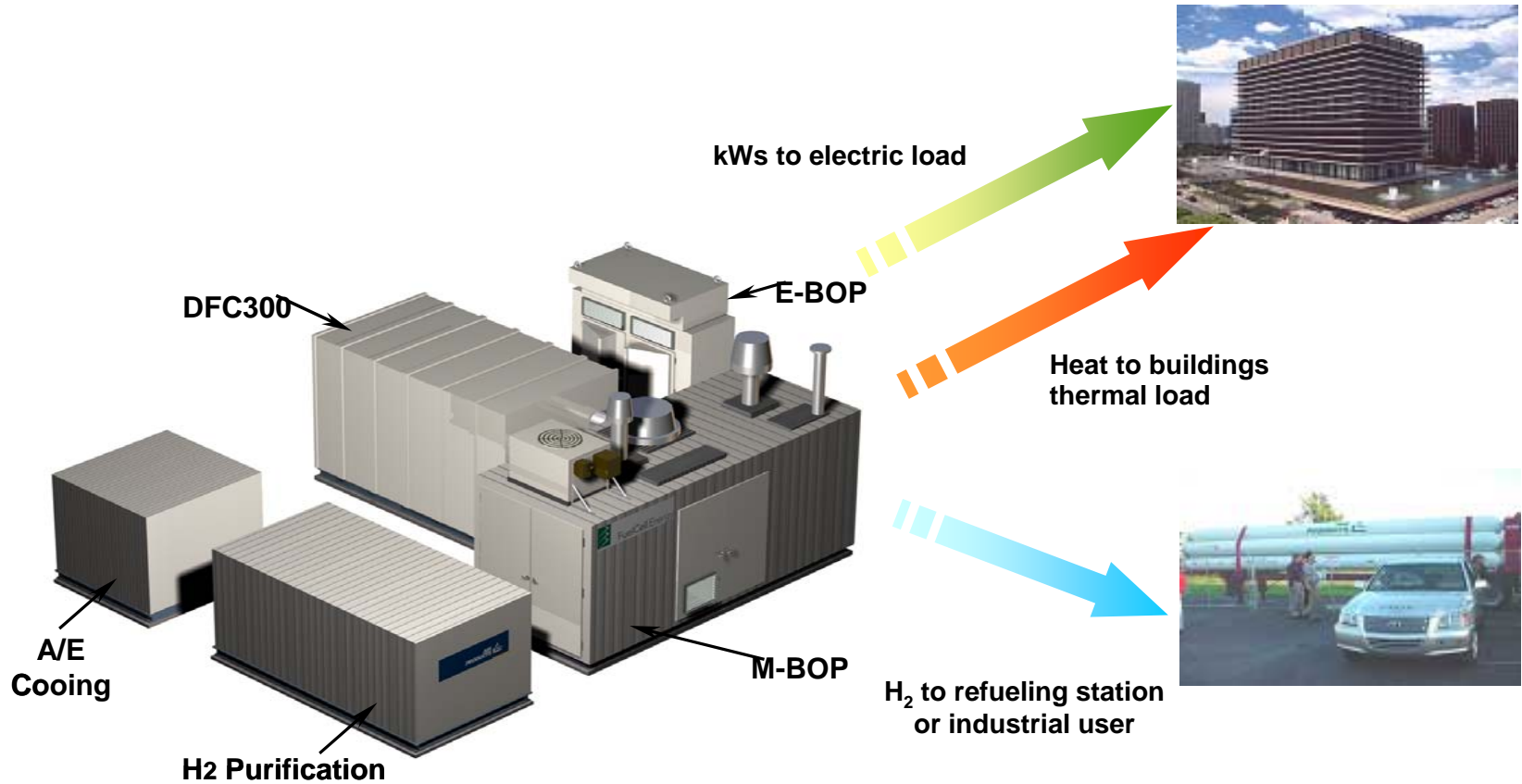


Billings, MT field test



FuelCell Energy

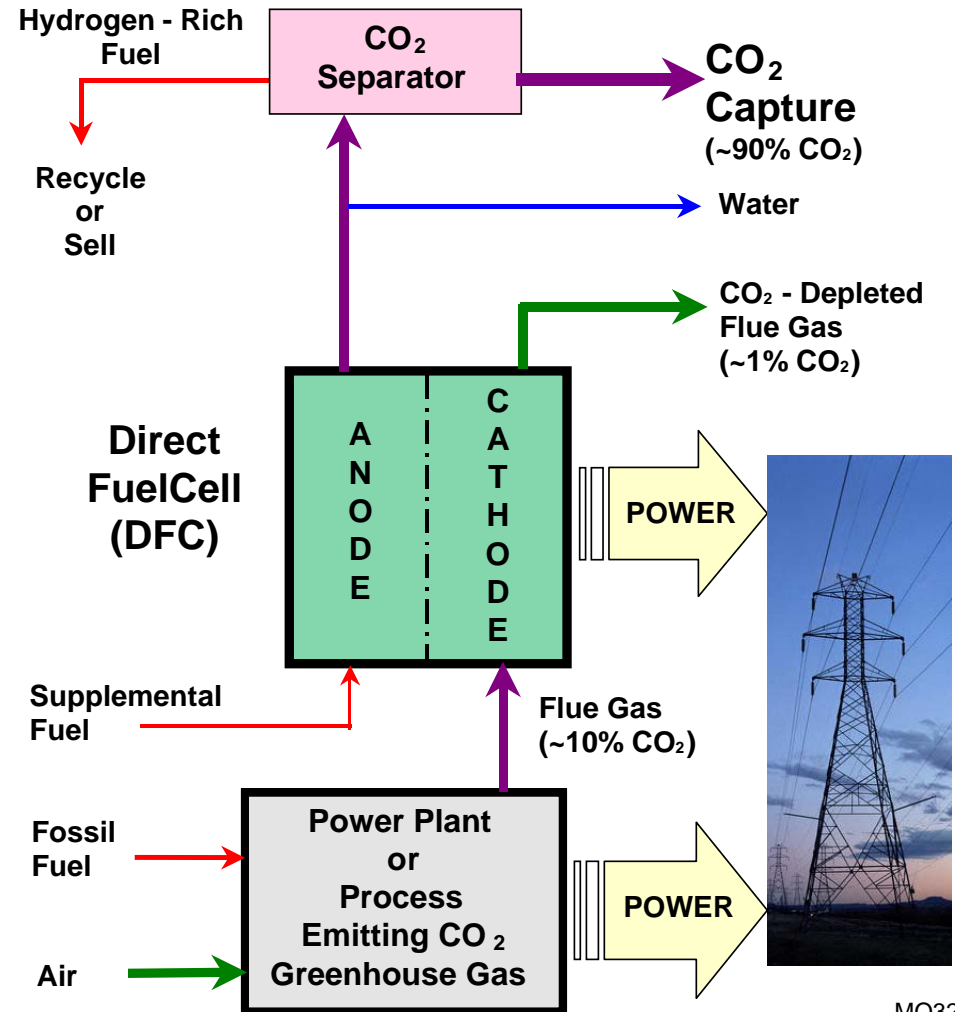
Products Under Development: Electricity and Hydrogen Co- production





Products Under Development: Electricity Co-production and Carbon Separation

- Exhaust from fossil fuel plant used as DFC oxidant
- CO₂ from fossil fuel plant transferred and concentrated for efficient sequestration
- Produces additional power, unlike other carbon capture concepts





➔ **DFC system has shown excellent performance in separation of carbon dioxide, in the study of various types of coal fueled power plants**

PLANT TYPE	Net Power MW		CO2 to Environment lbs/MW hr	
	w/o DFC	with DFC	w/o DFC	with DFC
Pulverized Coal (PC) Steam Plant	200	341	1838	108
ACFB Steam Plant	200	353	1997	113
IGCC Plant	200	327	1657	101

DFC provides additional power

> 90% CO₂ separation from the greenhouse gas (per unit energy produced)

* Preliminary results prior to input from fuel cell test results



- 300 kW, 1.4 MW, and 2.8 MW size products for CHP applications
- Product performance expanding markets
- Customers/applications providing repeatable order flow – Asia, California, Connecticut
- RPS and South Korean markets creating multi-MW volume (84% of the installed and backlog volume in Asia) .
- Established manufacturing capability to meet current and future demand
- Cost reduction and volume on path to profitability



Pohang, Korea



FuelCell Energy



- Higher electrical efficiency than competing technologies (approaching 50% in simple cycle distributed generation applications)
- Fuel flexible (NG, biogas, propane, coal-bed methane, and methanol)
- Modular
 - Easily siteable at load centers (simple connections to grid and fuel infrastructure)
 - Near-zero NO_x, SO_x and low CO₂ emissions as well as quiet operation
 - Reliable, 24/7 power
- High grade waste heat for combined heat & power (CHP; overall efficiency can achieve 90%)
- Competitive advantage on renewable biogas over other technologies
- Enabler for transformational technologies
 - High efficiency (58-65%) combined cycle systems in small size range (DFC/T)
 - Co-production of electricity and hydrogen (DFC-H₂)
 - Co-production of electricity from coal and CO₂ separation
 - High efficiency energy (>60%) recovery generation (DFC-ERG) system



FuelCell Energy



Cell Package and Stack



Single-Stack Module



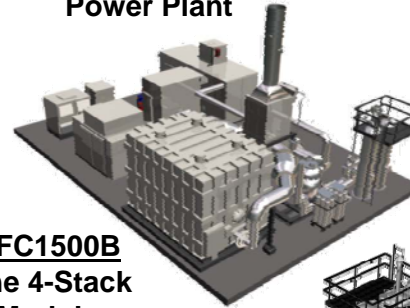
Four-Stack Module



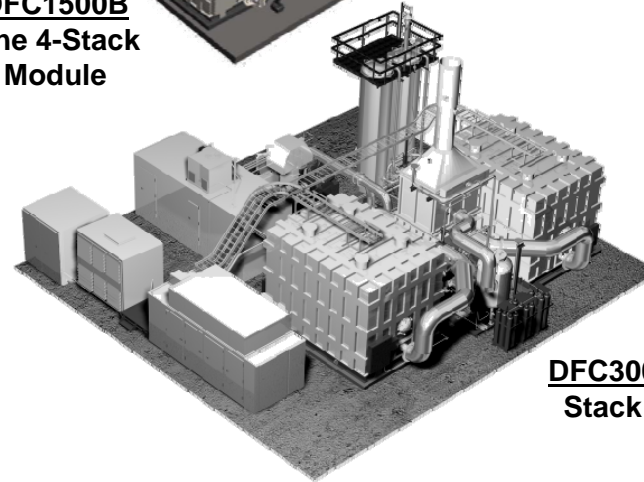
DFC300
Single Module
Power Plant



DFC1500A
Four Module Power Plant



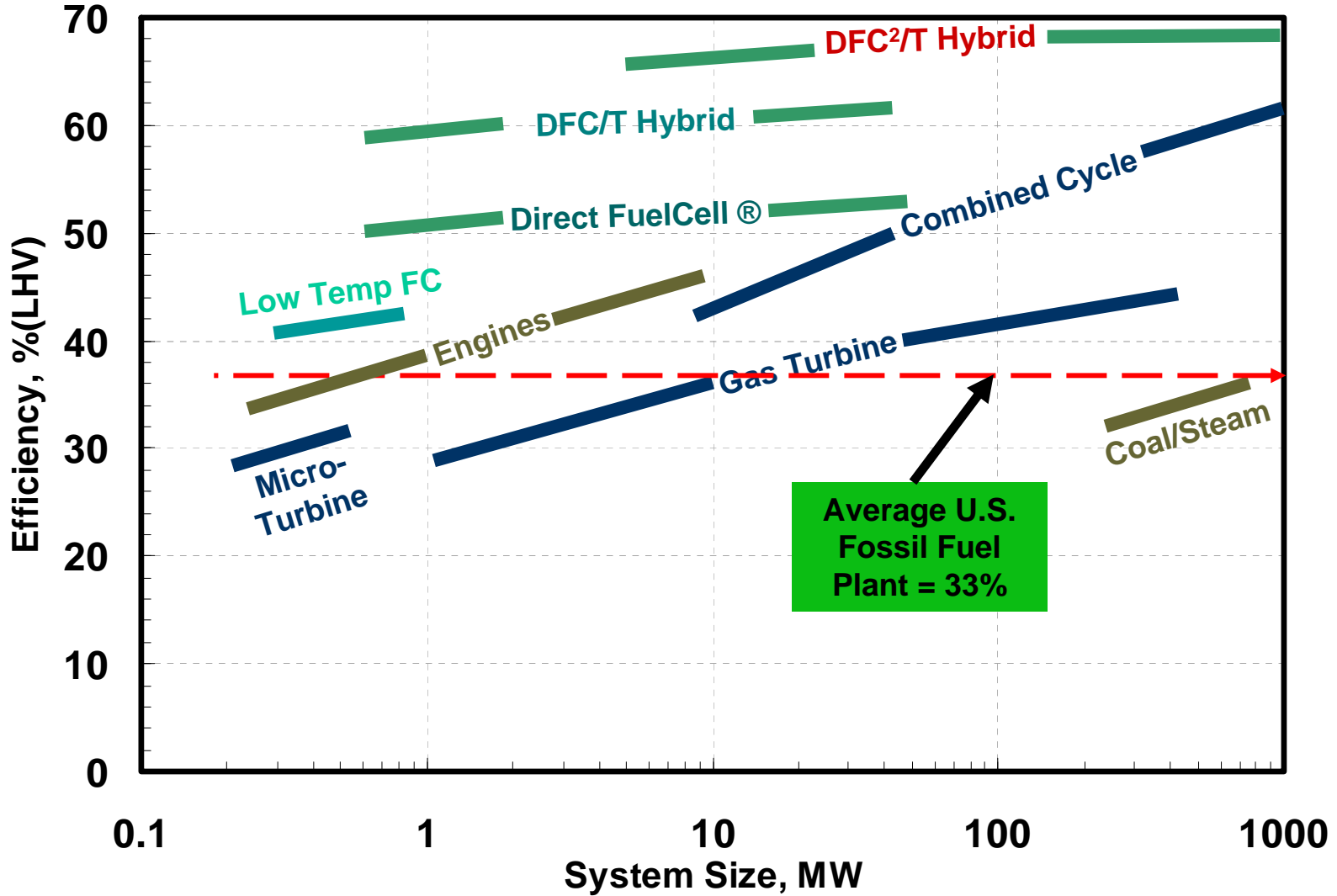
DFC1500B
One 4-Stack
Module



DFC3000: Two 4-
Stack Modules



Direct Fuel Cell Efficiency Comparison with Competition





FuelCell Energy

DFC Production Readiness

- Production and delivery capabilities meet current demand
- State-of-the-art manufacturing in Torrington, CT
- 70 MW/yr capacity
 - Current production rate 30 MW/year
- Strong supply chain in place
- Expansion plan to achieve 150 MW capacity



Torrington, CT



Danbury, CT

Appendix B
DFC Opportunities
Dr. Mohammad Farooque, FuelCell Energy



FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

DFC Opportunities

**FuelCell Energy, Inc.
3 Great Pasture Road
Danbury, Ct 06813**

reliable, efficient, ultra-clean



FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

Direct Fuel Cell Challenges

- Baseline products cost-competitive with government subsidy at locations with very high cost-of-electricity
- Company sponsored R&D focusing on marginal gains to make the DFC products cost-competitive in regions with high cost-of-electricity



FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

Direct FuelCell Opportunities

- Needs large scale market penetration to enjoy the fruits of this transformational technology
- Needs drastic reduction in cost-of-electricity to achieve large scale deployment
- Requires high risk research to achieve the required COE reduction (increase power density, enhance life and lower cost)
 - Increase stack power from 350 net kW to 500 net kW
 - Enhance stack service life from 5-yr to 10-yr
 - Additional 20% cost reduction by design and volume production



FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

DFC Life Improvement Opportunities

- **Baseline design life 5-yr**
- Life (5-yr) limiting factors
 - NiO dissolution from cathode and deposition in the matrix
 - Electrolyte loss from matrix causing gas leakage and cell internal resistance increase
- Desired life 10-yr for wide spread commercial success



FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

Performance Improvement Opportunity

- Stack output has increased by a factor of three over last twelve years
- **Current stack output is 350 kW net AC**
- Another 40% increase is achievable
 - New cathode development will be required to achieve the desired goal



FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

Stack Cost Reduction Opportunity

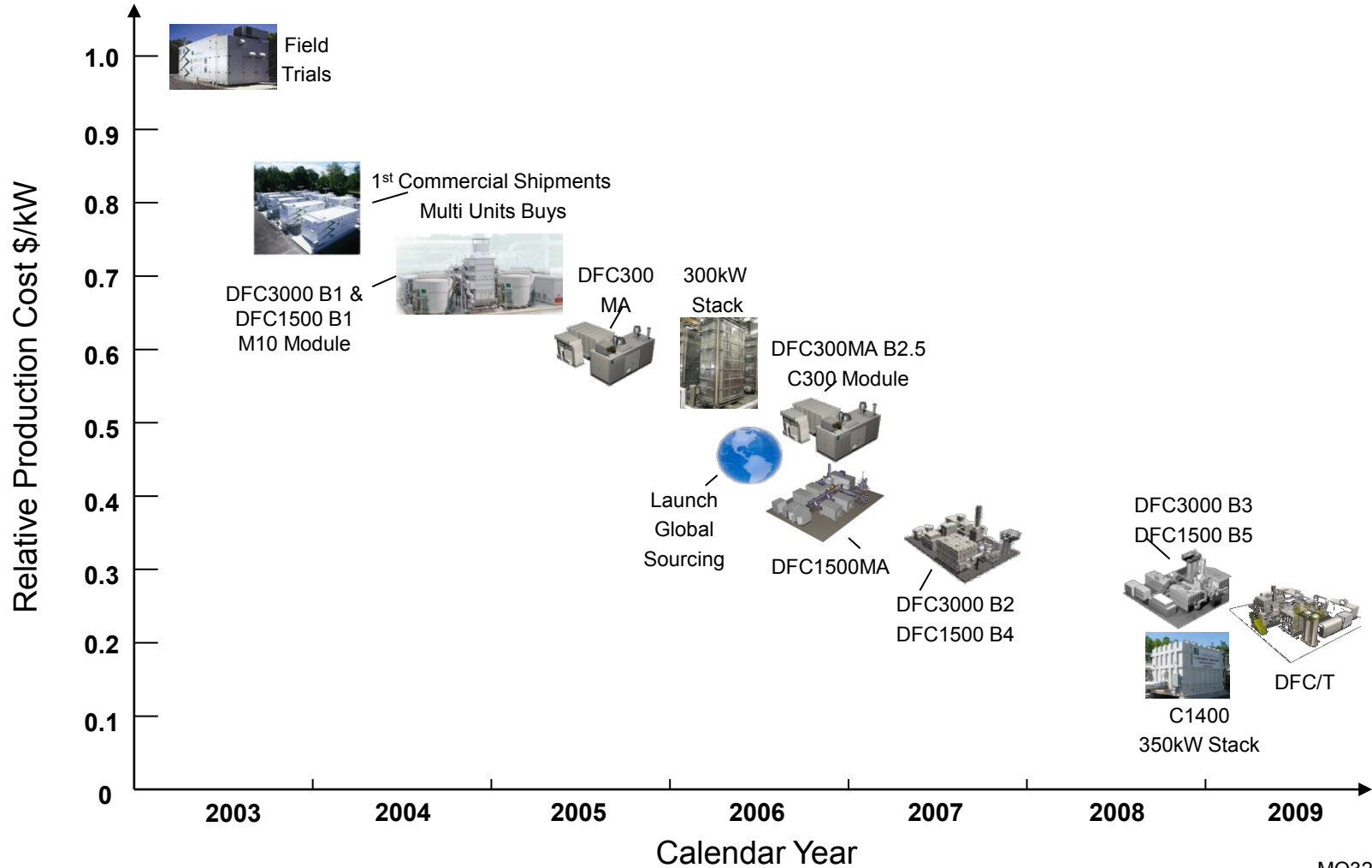
- **Stack module cost is ~two-third of the plant cost**
- Low hanging opportunities:
 - Stream lining of cell assembly process allowing automatic cell assembly
 - Develop human touch free assembly line concept
 - Develop automated components joining techniques.
 - Demonstrate cell components assembly without human touch
 - Matrix manufacturing process improvement to allow higher yield



FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

The History of DFC Products Cost Reduction

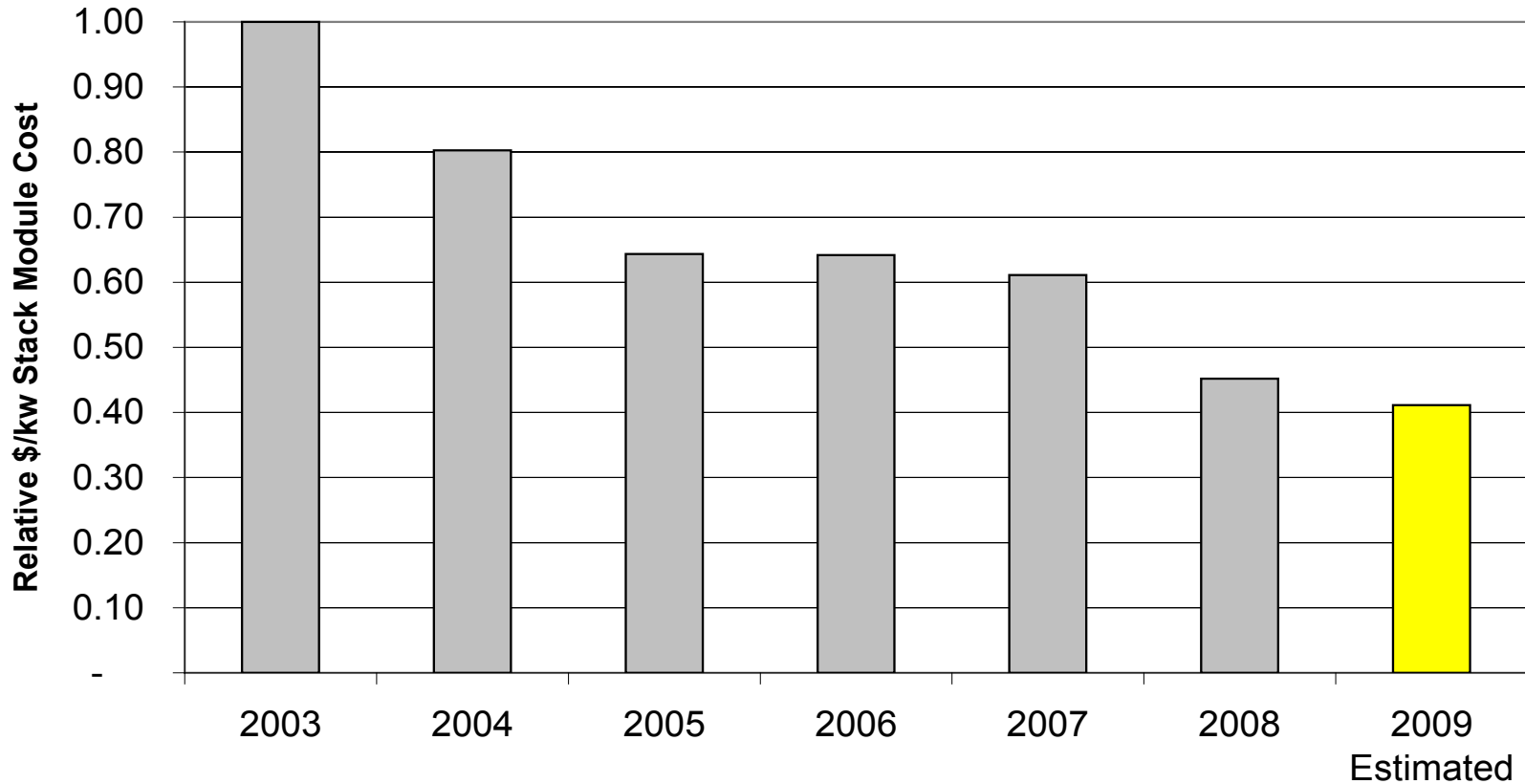




FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

Normalized Direct Fuel Cell MW Module Cost Reduction Progress

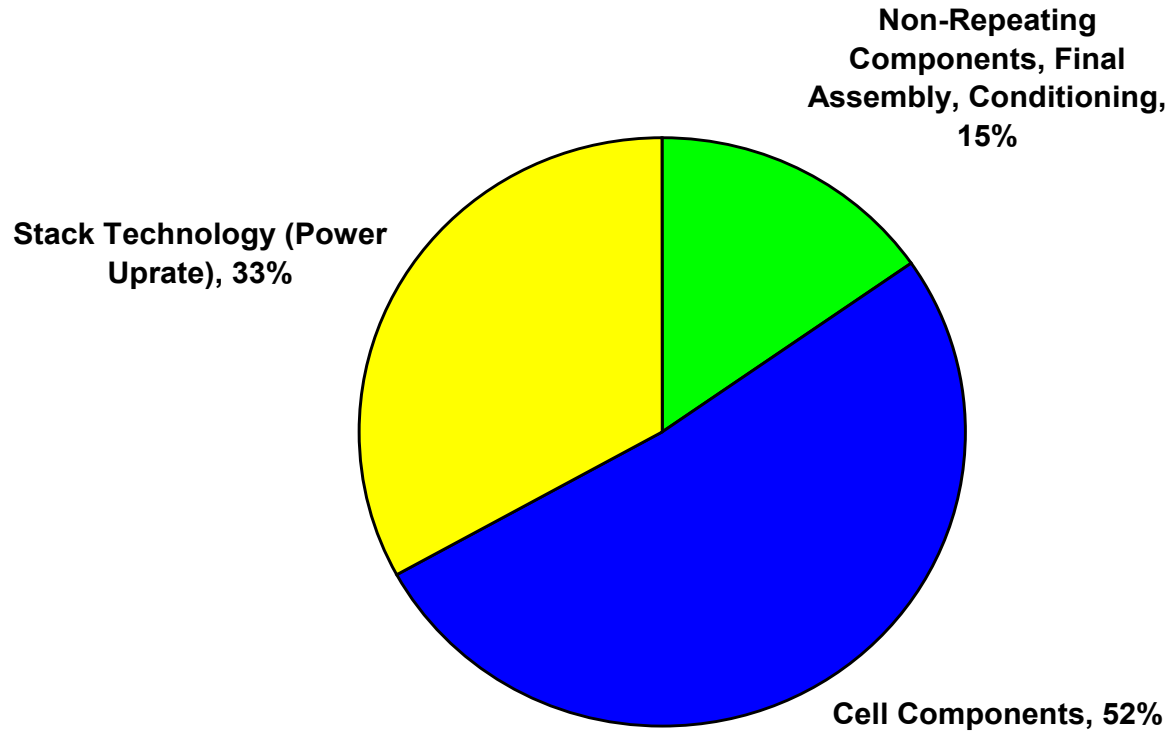




FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

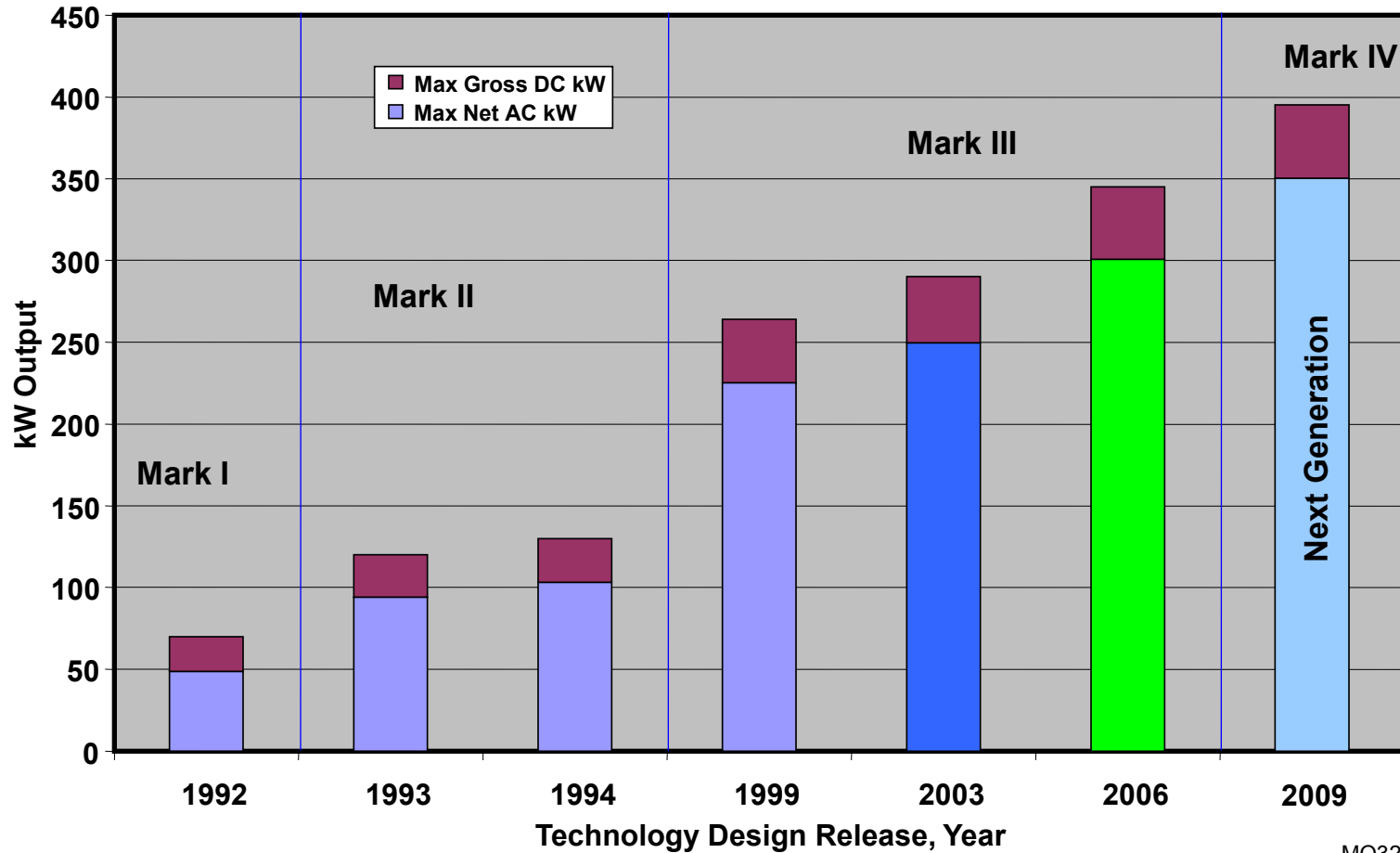
Source of Realized Cost Savings DFC Module (2003 – 2009)



MO3246



Full-size Stack for Output Improvement Over the Years

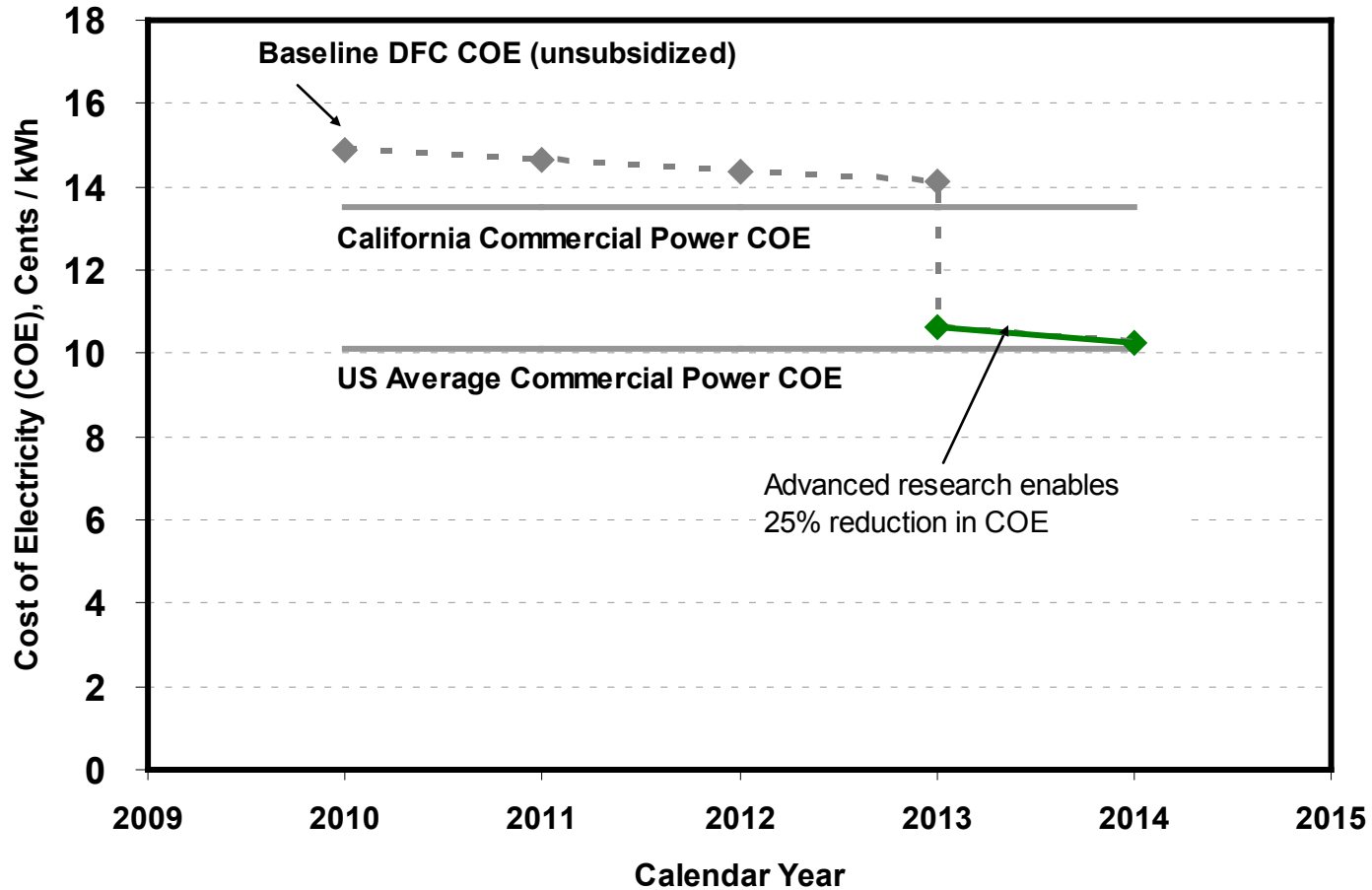




FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

DFC Cost-of-Electricity Reduction by 40% Performance and 100% Life Improvements



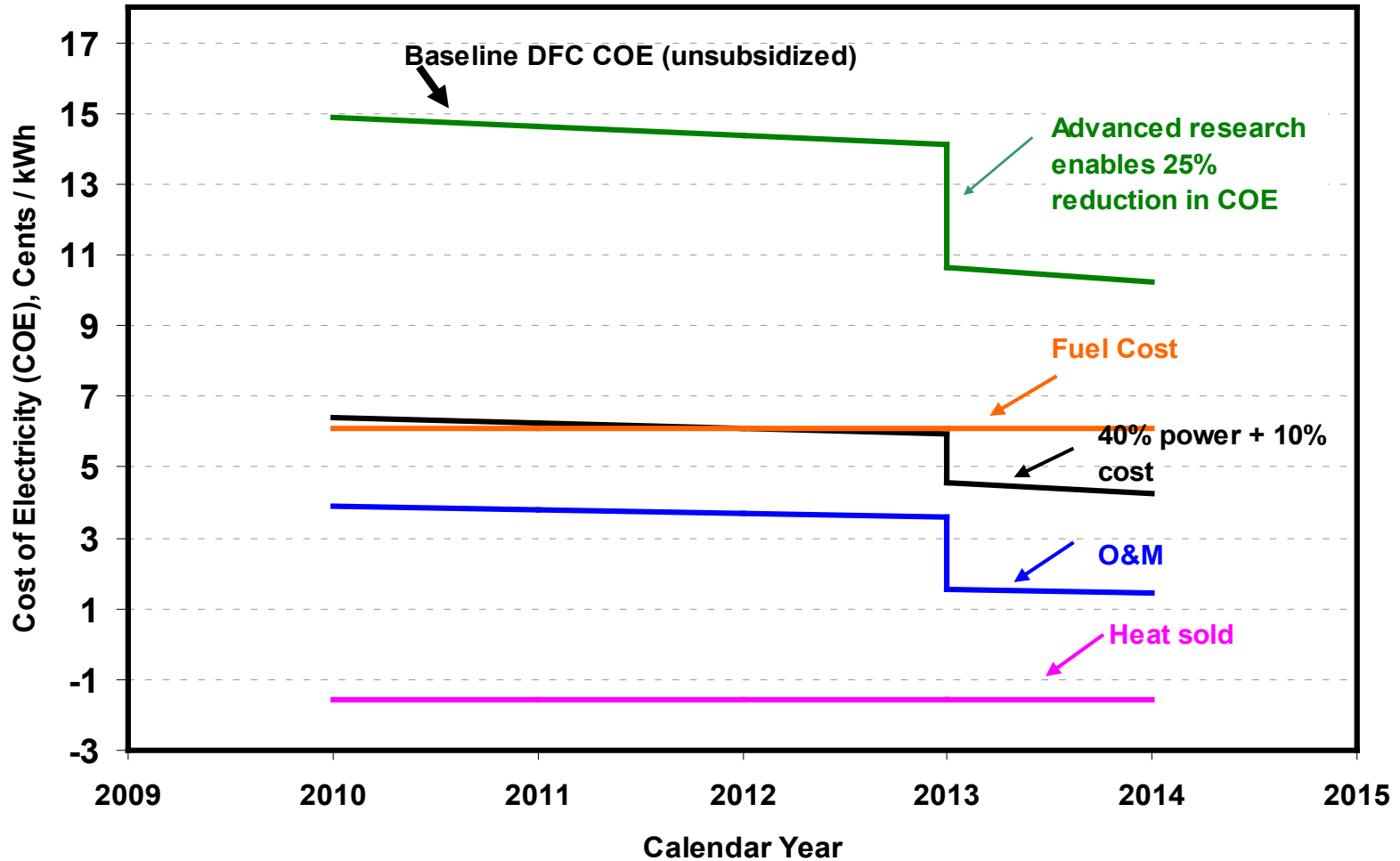
DFC COE based on installed cost for DFC3000 product. Capital costs amortized over 15 years, fuel cost at \$7.5/MMBtu



FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

Cost of Electricity Breakdown

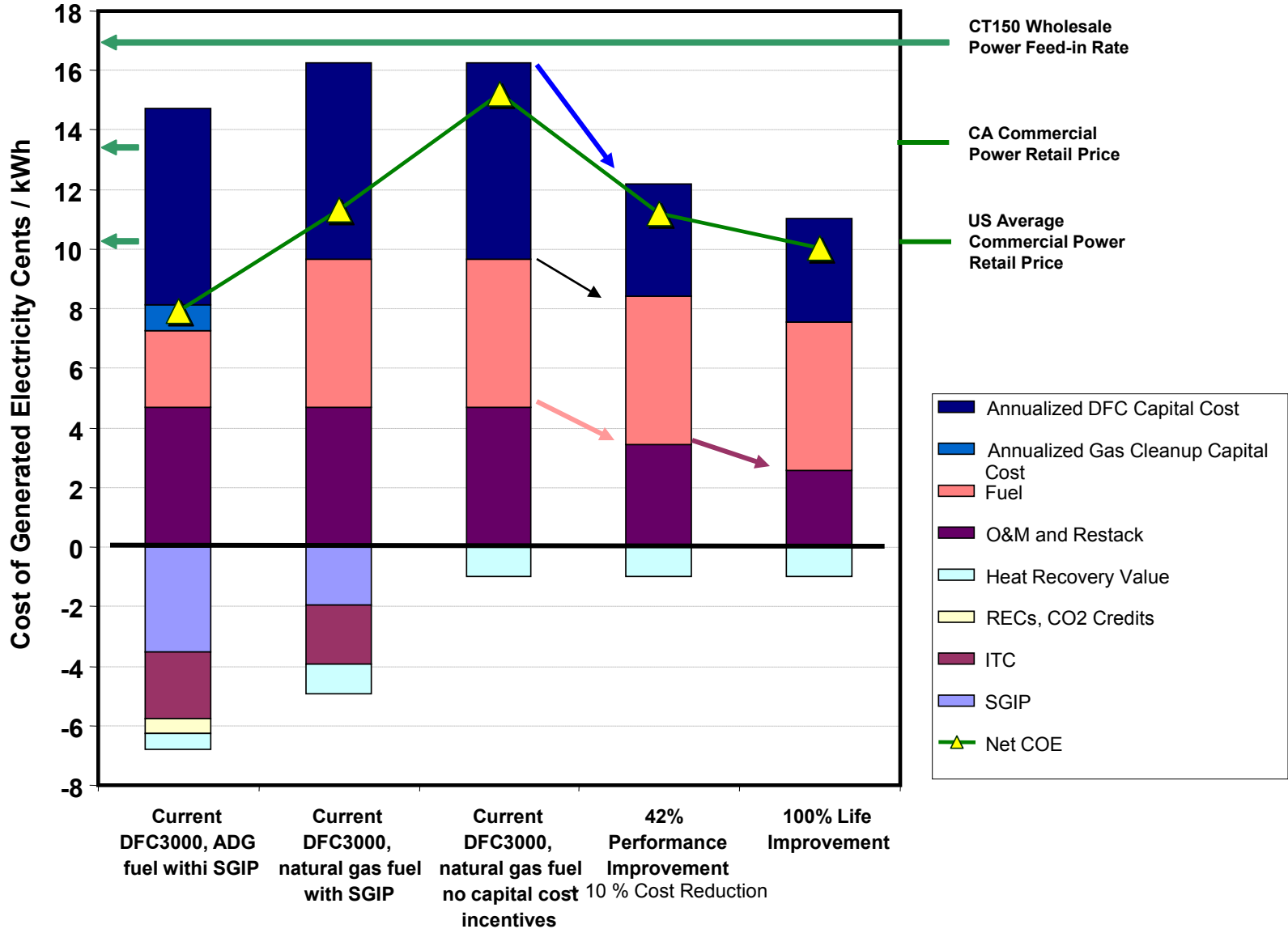




FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

Impact of Target Improvements: Opens Up Unsubsidized Markets





FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

Potential Impacts

Wide spread adaptation of the DFC will result from drastic COE (~3-4 cents/kWh) reduction and will lead to immeasurable national benefits. Simply 0.2% capture of the total capacity will lead to:

- **Reduces GHG emissions by ~20 million tons of CO₂ per year) to combat climate change**
- **Saves fuel (~50 million barrels of oil equivalent per year) improving energy security**
- **Ensures US leadership in the energy technology field**
- **Creates ~300,000 new green technology jobs**
- **Generates billions of dollars (~\$10 billion) in foreign sales**



FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

Appendix



FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

Estimation of Impacts

Assumptions	USA	Rest of the World	Total
Total Installed Capacity in 2006 ¹ , MW	964,000	3,048,000	4,012,000
Replacement Market, 3% per year	28920	91,440	120,360
Growth Market, 1.0% USA ¹ and 2.2 % rest of the world ²	9,640	67,056	76,696
Toatl New Installations, MW	40,000	160,000	200,000
Yearly DFC Capture starting 2015, 5% of US market and 3% of World Replacement Market, MW	2,000	4,800	6,800
% penetration of the Total	0.21	0.16	0.17
Fuel Cell Sale , \$X10 ⁶ (\$1800 per kW)	3,600	8,640	12,240
Fuel Cell Stack Replacement + Maintenance (15%), \$10 ⁶	540	1,296	2,000
Total business, \$10⁶	4,000	10,000	14,000
Job (direct+indirect) creation, # (23 jobs per \$10⁶)³	100,000	200,000	300,000
Total Fuel Cell Power Per Year (@ 90% Capacity factor), MW-hr	15,770,000	37,840,000	53,610,000
CO ₂ Emissions Avoided,million tons per year	5	12	18
SOx Emissions Avoided	0.06	0.14	0.19
Nox Avoided	0.02	0.06	0.08
PM ₁₀	0.0019	0.00	0.01
Fuel Savings, million barrels/yr oil equivalent	10	30	50

1. Energy Information Administration International Energy Annual 2006

2. EIA Press release, April 14, 2004, "World net electricity consumption nearly doubles over the projection period, from 13,290 billion kilowatthours in 2001 to 23,072 billion kilowatthours in 2025" (estimated to be 2.2%)

3. Projected by Chris Bentley of FCE

Appendix C
MCFC in Europe and Elsewhere
Dr. J. Robert Selman, Illinois Institute of Technology

MFCF in Europe **(and elsewhere...)**

J. Robert Selman



Illinois Institute of Technology
Chicago, IL

Work MCFC-PAFC R&D

Palm Springs, CA

Nov, 2009

Outline

1. *Status of technology, players*
2. *Life time, performance decay, failure*
3. *R&D priorities*
4. *Fundamental research*
5. *Concluding remarks*

1. Status of technology, players

Developer	Operating pressure (atm)	Reforming	Manifolding	Module	Plant size/target (kW)
FCE (USA)	1.0	Internal	External	Single or multistacks	300–3,000
GenCell (USA)	1.0	Internal (indirect)	Internal	Single stack	40–120
CFC Solutions/MTU (Germany)	1.0	Internal	External	Hotmodule (horizontal stack)	250–1,000
AFCo (Italy)	3.5	External	External	Twin-stack (two 125-cell stack integrated with reformer in a can)	125–1,000
KEPRI (Korea)	3.5	External	Internal	Building-block	250
IHI (Japan)	3–10	External	Internal	Building-block	300

Modified from: M. Farooque and H. Maru, Enc. Electrochem. Power Sources

Major and minor R&D in carbonate FC technology

Developer or Institution	Location	Development	Fundamental research
FCE	Danbury, CT, USA	Yes	No
IIT	Chicago, USA	No	Yes
MTU	Munich, Germany	Yes	Some
AFCo	Genoa, Italy	Yes	Some
ENEA	Rome, Italy	No	Yes
KEPRI	Daejeon, Korea	Yes	Yes
Doosan HI	Daejeon, Korea	Yes	?
Hanbat U	Daejeon, Korea	No	Yes
CRIEPI	Kanagawa, Japan	Yes	Yes

Various Universities in Europe, for example, KTH (Sweden), U. of Magdeburg (Germany), ENSC Paris (France), U of Pisa (Italy) / fundamental research up to early 2000s' – some continuing at low level.

Universities in US (other than IIT): U of South Carolina (up to early 2000s'; status?), U of Connecticut (status?)

- Est. Jan. 2003
- Located near Munich (D)
- Research & Development
- Power plant assembly and test
- Pilot cell manufacturing
- 20 test sites (total 5 MW) in Europe



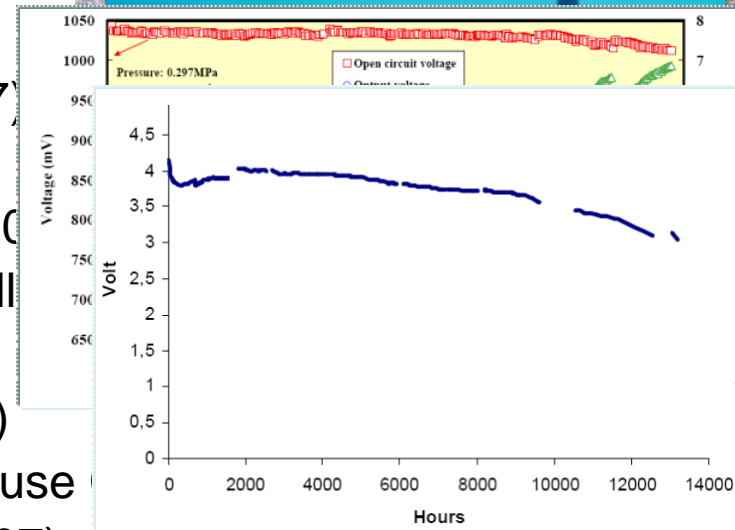
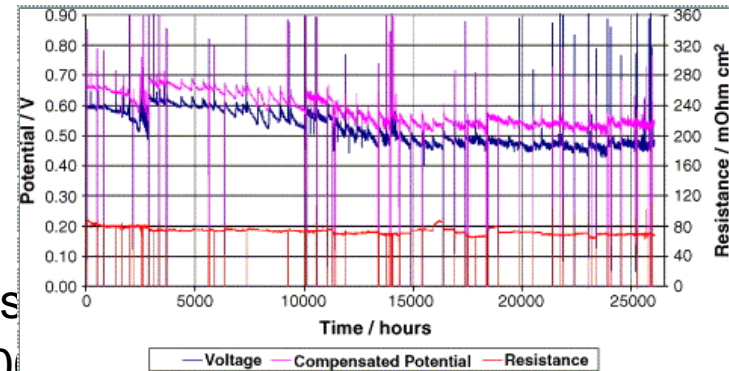
The durability issue comparison with other fuel cells

DoE lifetime targets for 2010:

- 5000 h for mobile applications
- 40 000 h for stationary applications

Current reported lifetimes:

- PEMFC
 - application: 2000 h (Mercedes Benz FC Bus)
 - laboratory: 26 000 h (GORE, single cell, 2007)
- PAFC
 - application: 66 000 h (UTC PureCell, 2007)
- MCFC
 - application: 30 000 h (CFC, Magdeburg, 2007)
 - laboratory: > 60 000 h (CRIEPI, single cell, 2007)
- SOFC
 - application: 10 000 h (Hexis, planar, 2007)
 - application: 30 000 h (Siemens-Westinghouse, tubular, 1997)
 - laboratory: 14 000 h (Topsoe, planar, 2007)
 - laboratory: 70 000 h (Westinghouse, tubular, 1997)



Generally recognized needs for MCFC

1. Increased power density $J \Rightarrow$ need finer μ -structure of porous electrodes.

Largely left to development

2. Longer cell life \Rightarrow need lower $T \Rightarrow$

*red. corrosion,
more stable morphology,
red. volatility;*

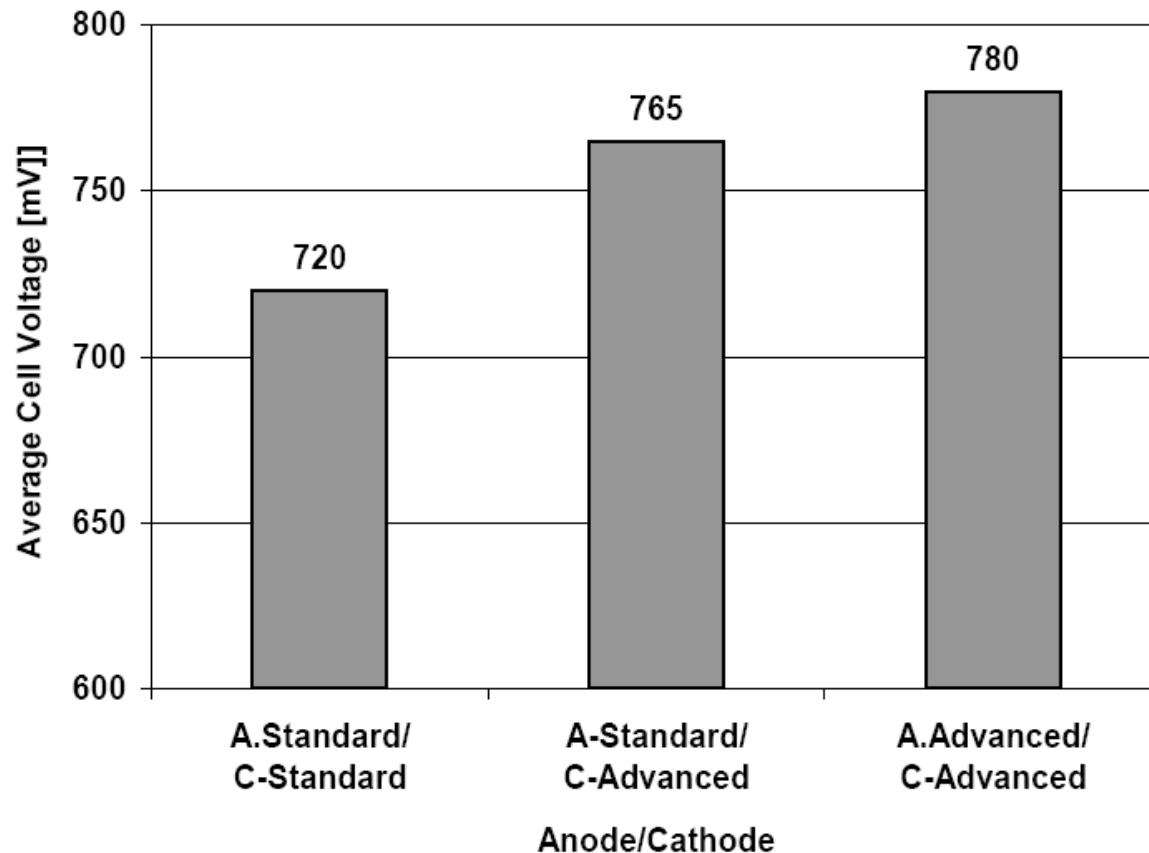
*but decr. electrochem. activity/real area ,
decr. conductance of oxide scales,
decr. wetting of electrodes,
incr. NiO dissolution*



Lifetime, performance decay, failure

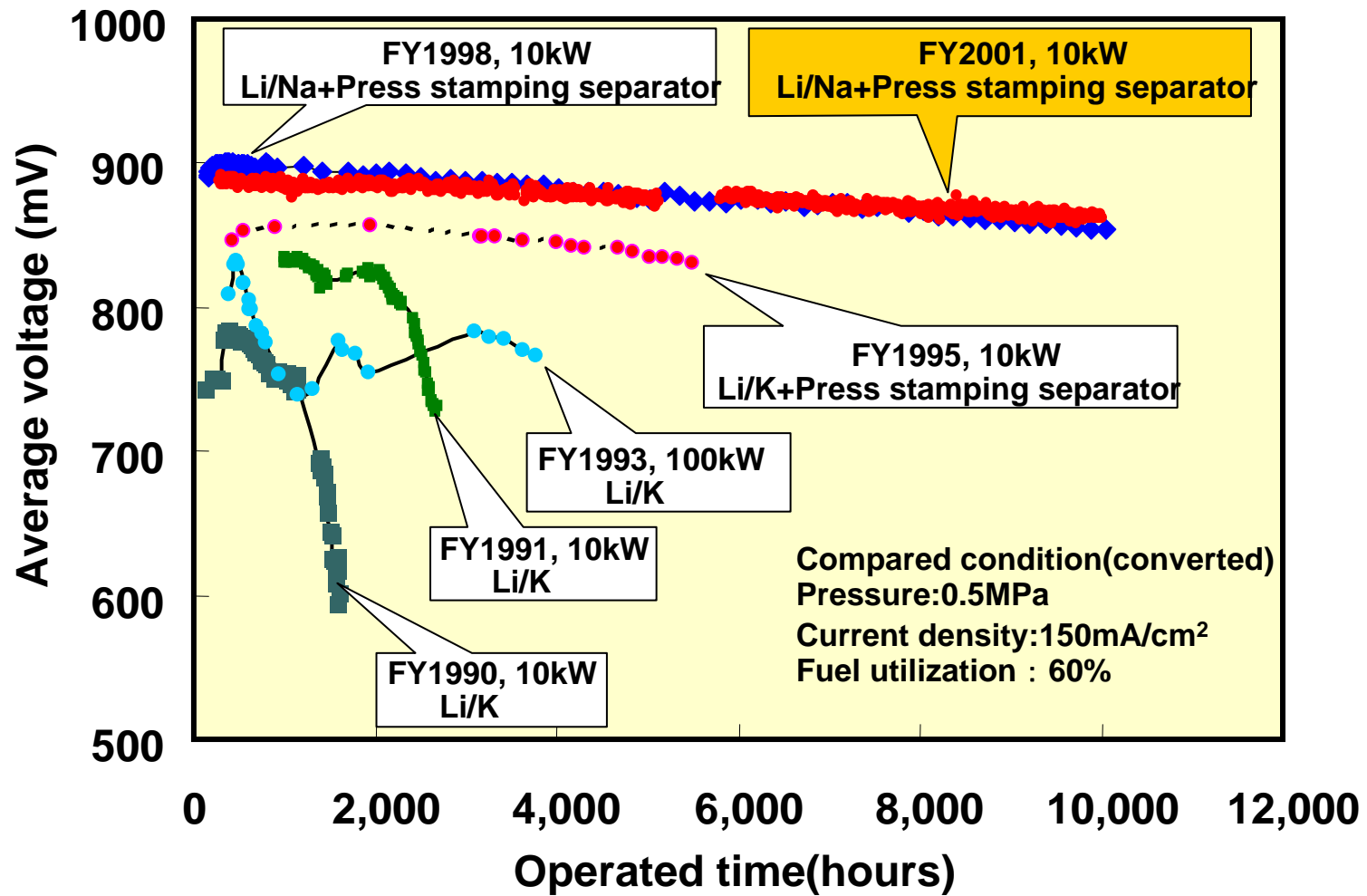
Joint effort of European Community

Advanced anode and cathode performance (MTU 2009)



Full scale tests (1000 h runtime, 120 mA/cm², 70% fuel utilization, medium cell temperature 620°C, system gases)

Dramatic advances in performance + stability of MCFC stacks (Japan) 1990-2001

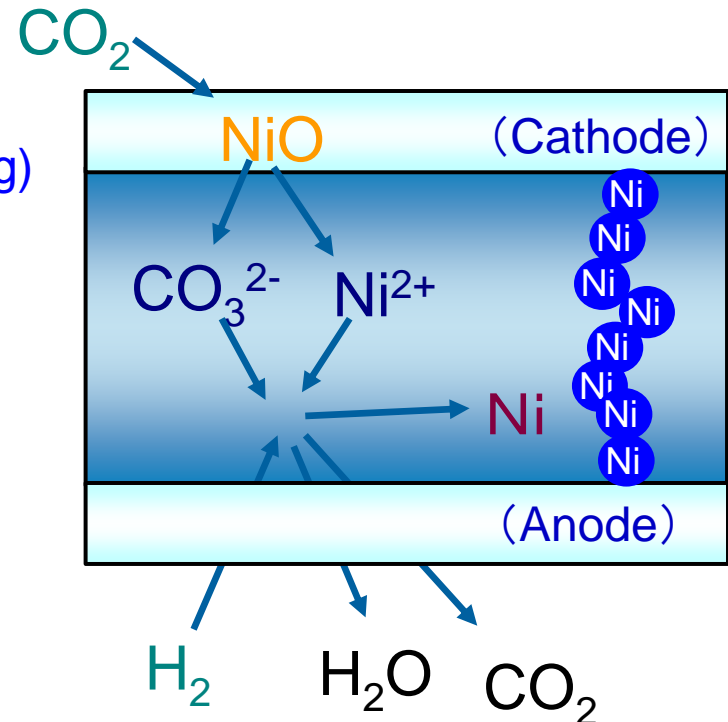
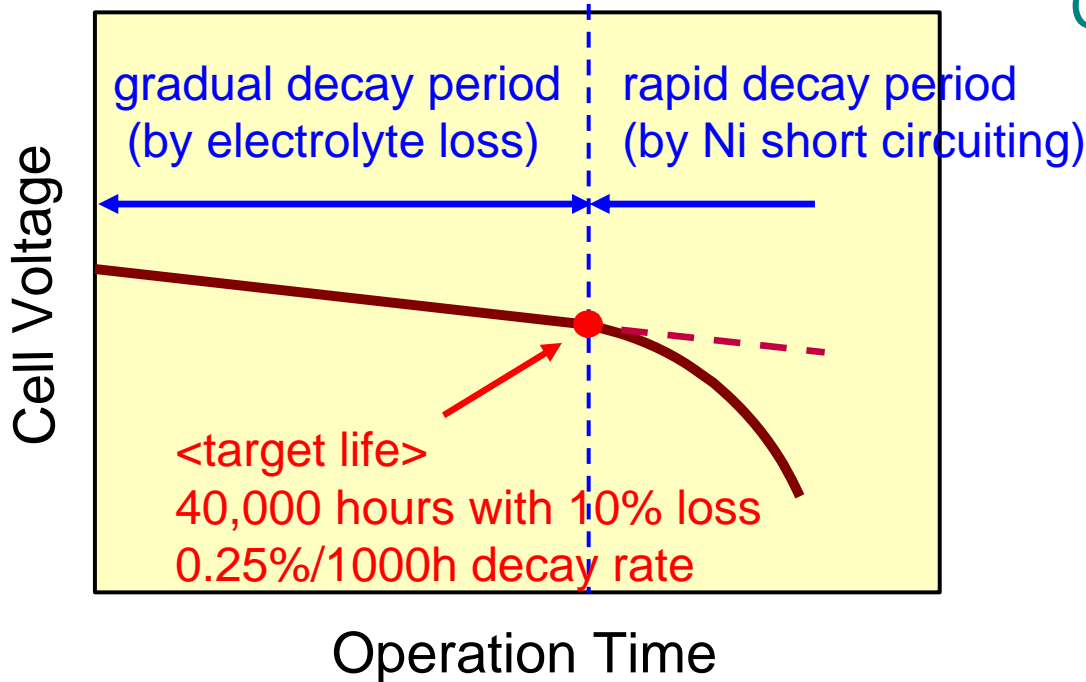


2. Life time, performance decay, failure

Adopting 40,000 hours longevity as a target , CRIEPI (Japan) has carried out two kinds of tests to identify the degradation mechanisms of the MCFC.

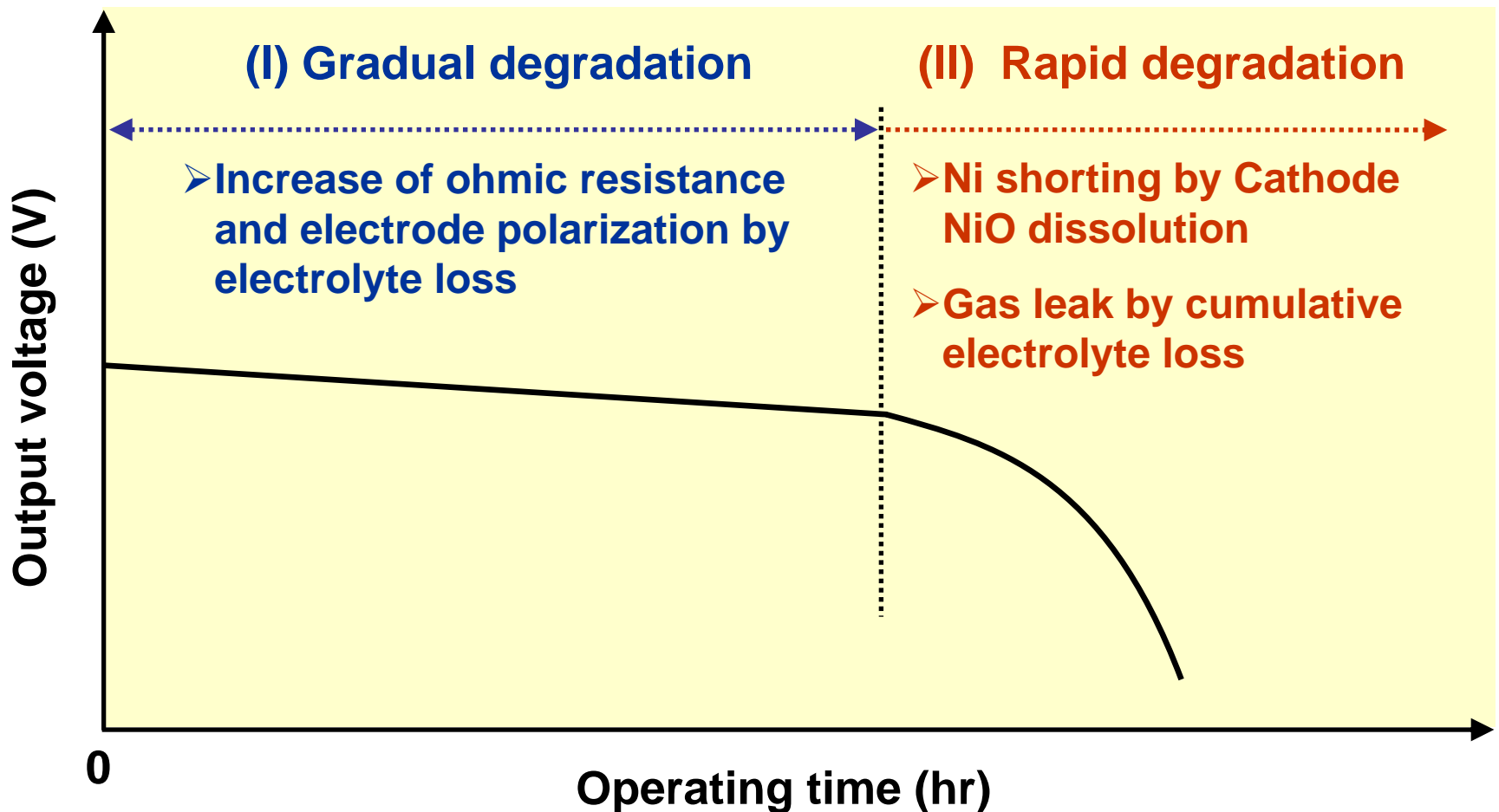
- 1. Accelerated testing in Ni shorting**
- 2. Testing of long term electrolyte loss**

Life extension of MCFC



- Suppression of Ni Shorting
- Low Ni solubility electrolyte

Schematic of MCFC performance degradation to time (at a constant current)



The durability issue

From Workshop, Ulm (2008)

DoE lifetime targets for 2010:

- 5000 h for mobile applications
- 40 000 h for stationary applications

What is needed?

30-50% increase in lifetime

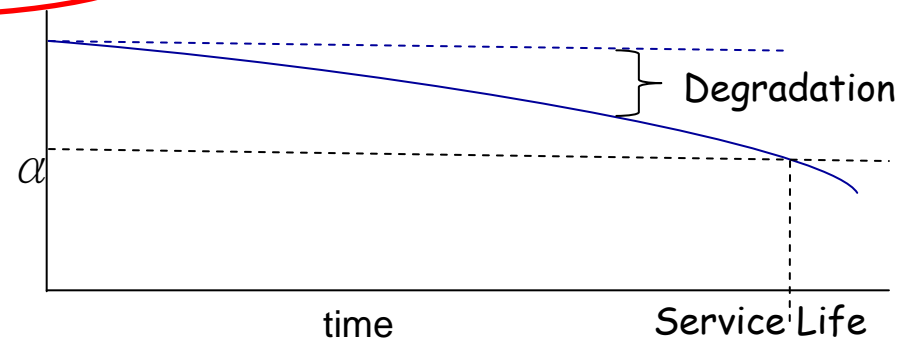
But what is lifetime?

One of the definitions under discussion within TC 105 WG1 for the second edition of TS 62282-1 terminology:

The cumulative period of time that a fuel cell/stack may operate before its output deteriorates below a useful minimum value

Degradation

Service life



Degradation

or *The process of decline in performance due to accumulation of operating time*

Differentiate causes of degradation (=life shortening) between:

Technical “innate” causes:

- Changes in morphology and hydrophilicity
- Changes in phase and chemical bonding
- Interdiffusion of materials
- Corrosion
- Thermomechanical stress

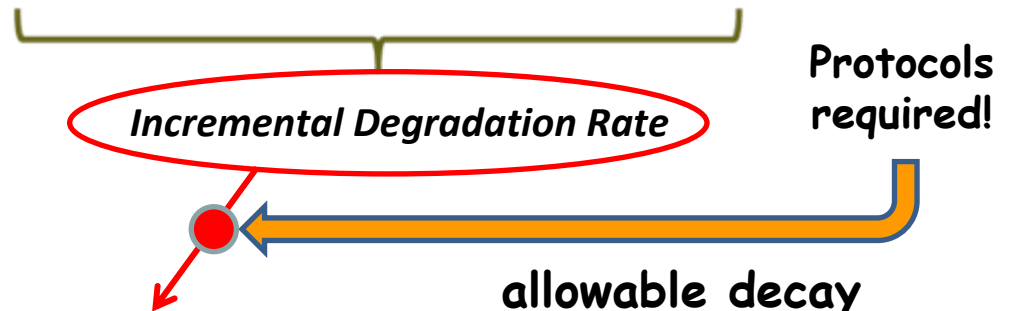

Base Degradation Rate

Applied causes:

- Thermal cycles
- Load cycles
- Reduction-oxidation cycles
- Poisoning

Accidental causes:

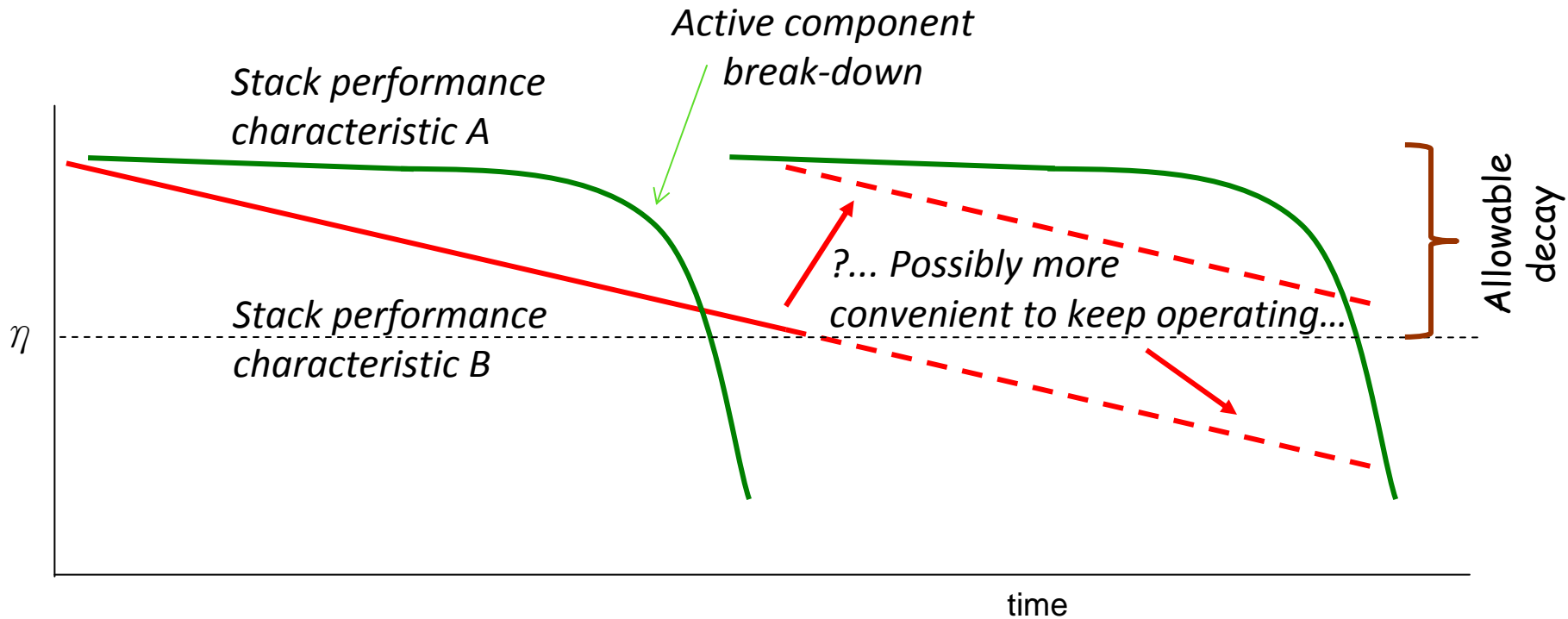
- BOP failures
- Utility failures
- Control failures
- Fuel supply failures



$$\text{Base Degradation Rate} * \text{Correction factor } (>1) = \frac{\text{allowable decay}}{\text{service life}}$$

Degradation

What about the economical implications...



→ **Compromise between output, efficiency, maintenance and investment costs**

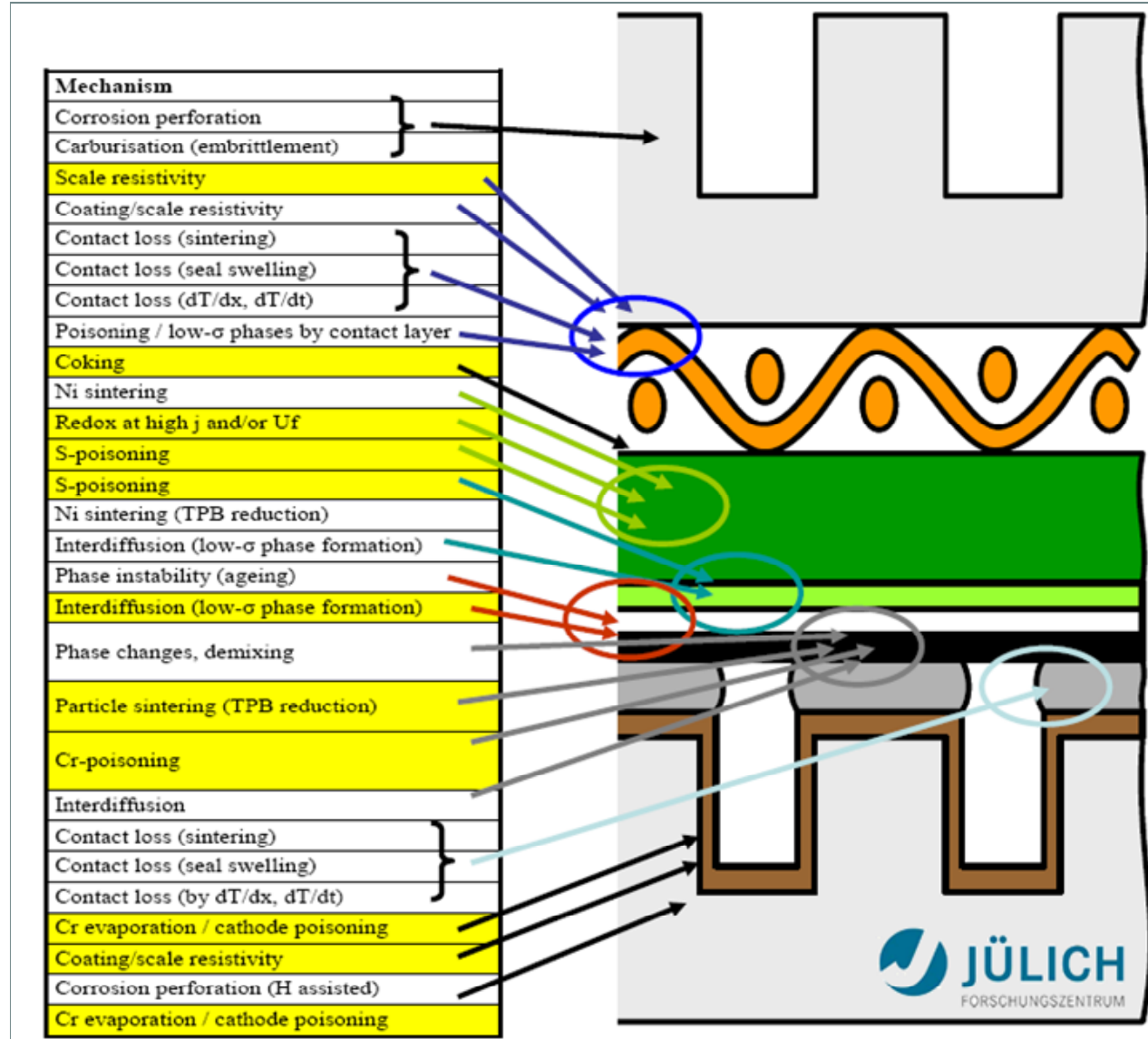
Degradation

Technical “innate” causes:

- Changes in morphology and hydrophilicity
- Changes in phase and chemical bonding
- Interdiffusion of materials
- Corrosion
- Thermomechanical stress



Base Degradation Rate



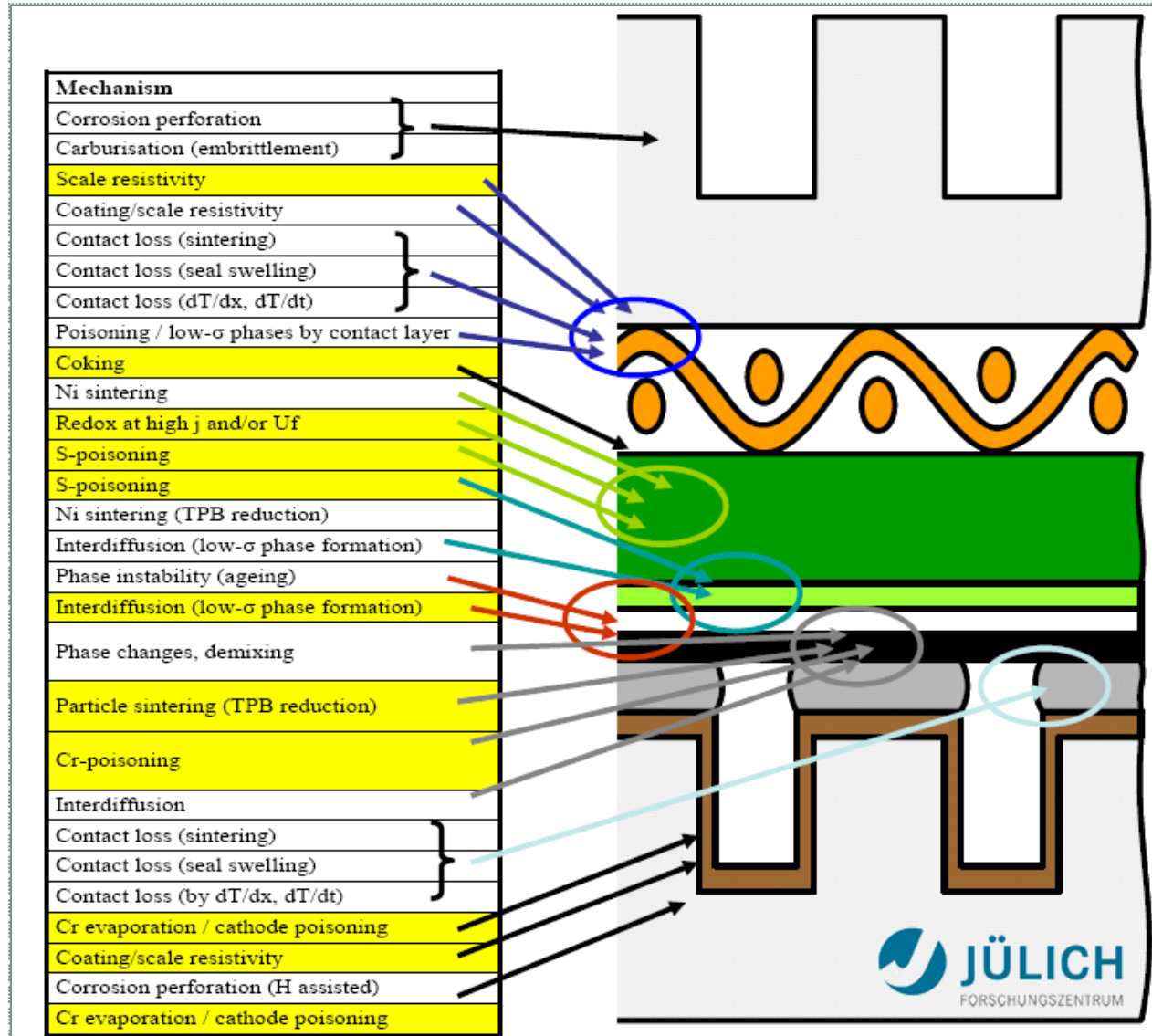
Degradation

- Resultant of all innate decay mechanisms
- comparable conditions
→ comparable degradation
- independent of the way it is measured

Battery: charge capacity

Lubricant: chem-phys properties

Jet engine: SFC (Specific Fuel Consumption = fuel flow/net thrust)
Base Degradation Rate



Forging a common standard

End user viewpoint:

Power system
efficiency (electric &
thermal) requirements

Utilisation pattern

Reliability
expectancy/
maintenance

Economic
demands

R&D viewpoint:

Understanding of
lifetime limiting
phenomena

Modelling and
lifetime
prediction

Innovative
component
testing

Technology
validation



Conclusions

(Workshop Fuel Cell Accelerated Testing, Ulm 2008)
(for MCFC)

- 30-50% increase in lifetime required
- Target lifetimes are intended for **systems**
- Stack outage usually due to **externalities** (rarely “end-of-life”)
- Degradation composed of innate, applied and accidental causes
- Applied and accidental stresses should be accounted for in standard protocols
- Must find compromise between **intuitive** and **intrinsic** degradation definition
- ...to adopt a common standard that can be evaluated by end-user

Good luck!

3. *R&D priorities*

- Priorities by company (see next table)
- Type of challenge :
 - Type 1: for example, cathode current collector (CCC) decay
 - Mechanism known
 - Solution known
 - Need for optimization (both technical and economic)
 - Type 2: for example, cell shorting by Ni dissolution
 - Mechanism known
 - Several possible solutions \Rightarrow need for further investigation to find the best or most suitable
 - Type 3: for example, long-term rise of internal resistance
 - Effect known
 - Need to investigate the mechanism and to find solution
- Approach: public vs private (confidential)

“Towards An Additional 20,000 Hours”

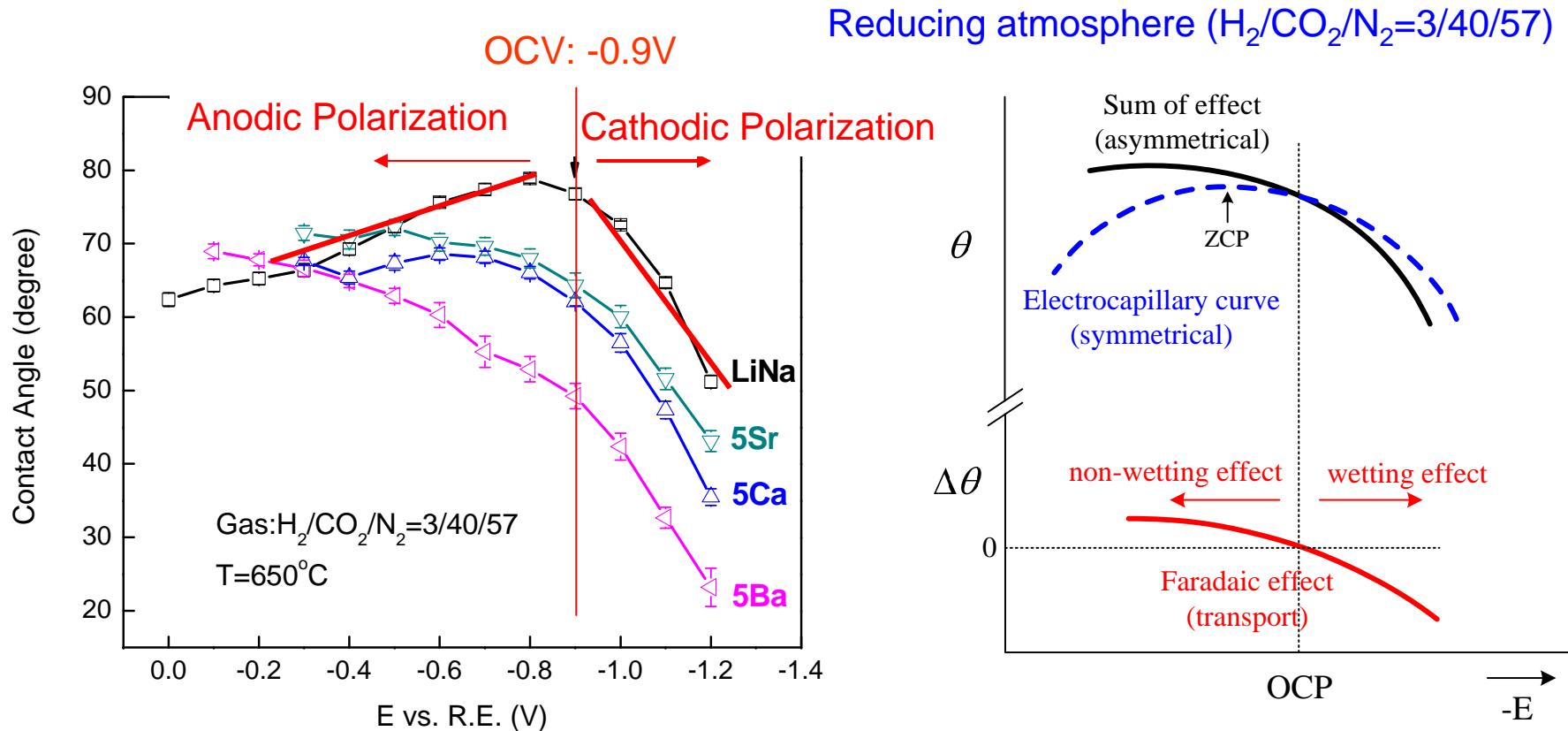
Degradation issue priority	Type 1. Optimize known solution (tech and econ)	Type 2. Select among possible solutions	Type 3. Identify mechanism and solutions	Public vs Private
FCE				
1		Cathode dissolution		Public (solubility, matrix solidity)
2		Internal resistance increase	Internal resistance increase	Public
3	CCC material stability			Confidential
MTU				
1	Stack Temperature homogenization (vertical & horizontal)			Confidential (active cooling systems)
2	CCC material stability			Confidential (improved materials)
3	Component thermomechanic response to stack deformation			Confidential (component thermomechanic properties)

“Towards An Additional 20,000 Hours” (cont’d)

Degradation issue priority	Type 1. Optimize known solution (tech and econ)	Type 2. Select among possible solutions	Type 3. Identify mechanism and solutions	Public vs Private
AFCO				
1			Fundamental material-behaviour in off-design conditions	Public (material robustness, kinetic reaction)
2		Ni shorting		Public, all-round research
3	CCC material stability			Public (improved materials)
KIST				
1		Stack Temperature control (vertical & horizontal)		Confidential (separator design, manifolding, operating variables)
2		Matrix stability		Public (raw material, thermodynamic properties, phase diagrams)

4. Fundamental research

(example: wetting by molten carbonate under polarization, Ping-Hsun Hsieh, IIT 2009)



Why/how does the melt chemistry affect CA under cathodic and anodic polarization?

5. *Concluding remarks*

- Incremental improvement strategy has been very effective in improving life time.
- Combination of high power density with long(er) life time remains a major challenge.
- Radical innovation is now on the backburner, but must receive more attention. For example, 1. smart use of nano-materials and micro-composites (Bin Zhu a.o.). 2. development of non-wettable or controlled-wettable materials.
- Re-emerging field for innovation: DCFC (direct coal FC) – in the USA: LLNL, SARA, SRI, a.o.

Appendix D
PAFC History and Successes
Mr. John Ferro, UTC Power, LLC



PAFC History and Successes

John Ferro

Manager Product Development



UTC Power

A United Technologies Company

john.ferro@utcpower.com



AGENDA

Company overview and history

System description and applications

Failure modes and life analysis

Summary



UNITED TECHNOLOGIES CORPORATION

Revenues: \$58.7 billion (2008)

Commercial & Residential Building Systems, Aerospace & Transportation, Industrial systems



UTC Power



Carrier



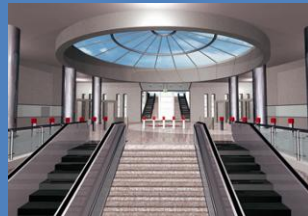
Hamilton Sundstrand



Sikorsky



UTC Fire & Security



Otis



Research Center



Pratt & Whitney

18th largest U.S. manufacturer (2009 list, *Industry Week*)

37th largest U.S. corporation (2009 list, *Fortune*)

61st largest publicly held manufacturer in the world
(2009 list, *Industry Week*)



UTC Power

A United Technologies Company



UTC POWER

Markets

Transportation
fuel cells



Space & defense
fuel cells



Stationary
fuel cells



Global sales



5 continents
19 countries



PURECELL® FUEL CELL SYSTEM

Stationary fuel cell history



1976
1 MW - PAFC



1984
4.5 MW - PAFC



1991
11 MW - PAFC

PureCell Model 400




2009
400 kW

2001 - 2005
150 kW PEM



1988 - 1992 1992 - Present
200 kW - PAFC 200 kW - PAFC



 \$290 MM from DOE for PAFC*
Main focus areas: Durability & CHP

1968
4 kW - PAFC



1971 - 1973
12 kW - PAFC



1975 - 1986
40 kW - PAFC



1970

1975

1980

1985

1990

1995

2000

2005

2009

2002 - Present
5 kW H₂ PEM



UTC Power

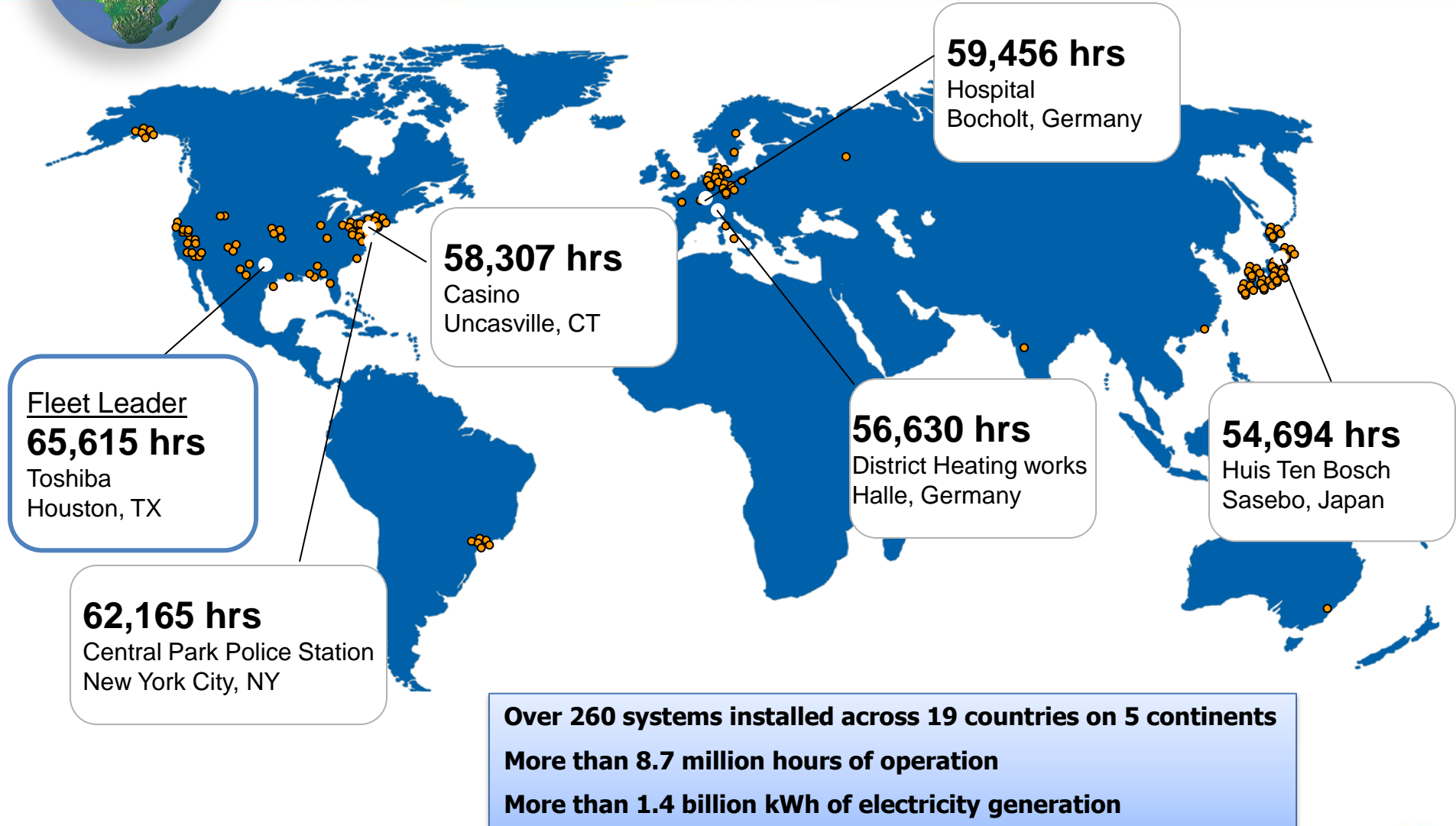
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* Reference: "FETC Perspective on the DOE Stationary Power Fuel Cell Program," Rita A. Bajura, 1997



PURECELL® FUEL CELL SYSTEM

Worldwide fuel cell deployment and experience

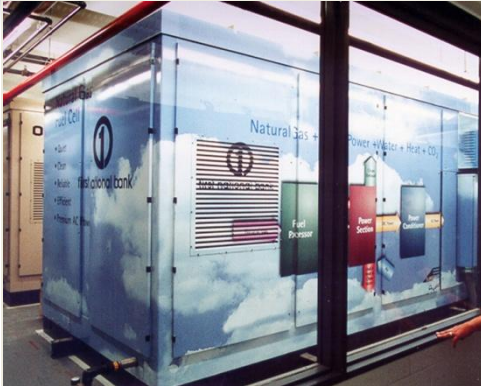




PURECELL® FUEL CELL SYSTEM

Flexible fuel cell application and varied experience

Assured Power



*First National Bank of Omaha
Nebraska*

On-Line Emergency Power



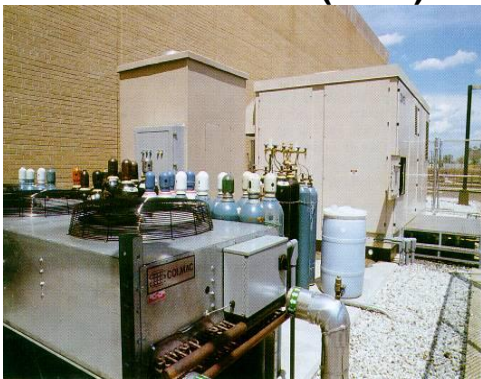
*Verizon Communications
New York*

Green CHP Power



*Whole Foods Market
Connecticut*

Renewable Fuel (ADG)



*Wastewater treatment plants
New York, New York*

Indoor CHP Power



*Mohegan Sun Resort & Casino
Connecticut*

Off-Grid Power



*Central Park Police Station
New York*



UTC Power

A United Technologies Company



PURECELL[®] FUEL CELL SYSTEM

Three main sections – fuel processor, stacks, & power conditioner

Fuel Processor

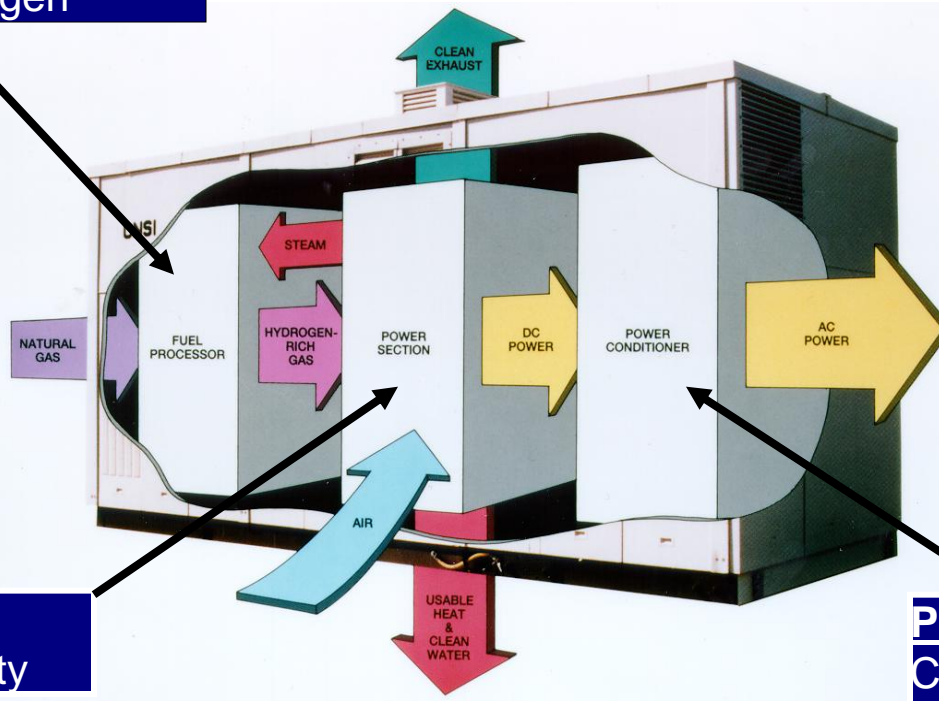
Converts fuel to hydrogen

Fuel Input

98.9 Nm³/hr
natural gas

Fuel Cell Stack

Generates DC electricity



Electric Output:

400 kW, 480 V, 60 Hz
400 kW, 400 V, 50 Hz

Power Conditioner

Converts DC power to high quality AC power

Internal heat exchanger provides:

1.50MM BTU/hr @ 60C, or

0.68MM BTU/hr @ 121C with balance at 60C



UTC Power

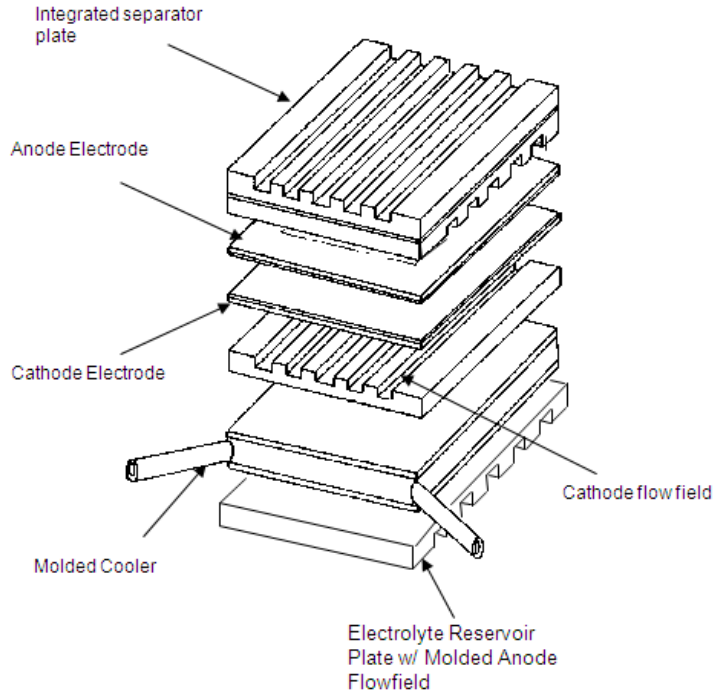
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PURECELL® FUEL CELL SYSTEM

Cell stack assembly

Repeat assembly



8 cells per substack

34 substacks per CSA

Cell stack assembly (CSA)



Molded carbon Teflon® composite for bipolar plates and coolers

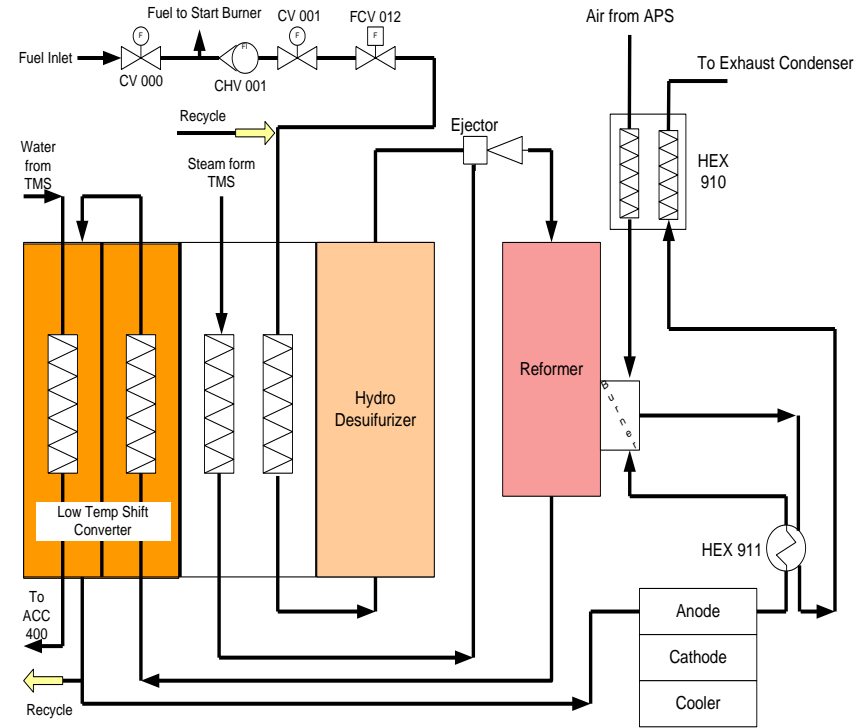
Carbon substrates coated with catalyst layers

Cell active area = 0.5 m²



PURECELL[®] FUEL CELL SYSTEM

Fuel processing system



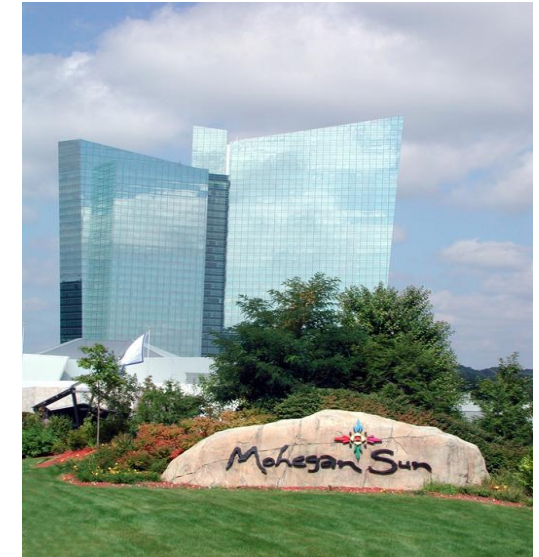
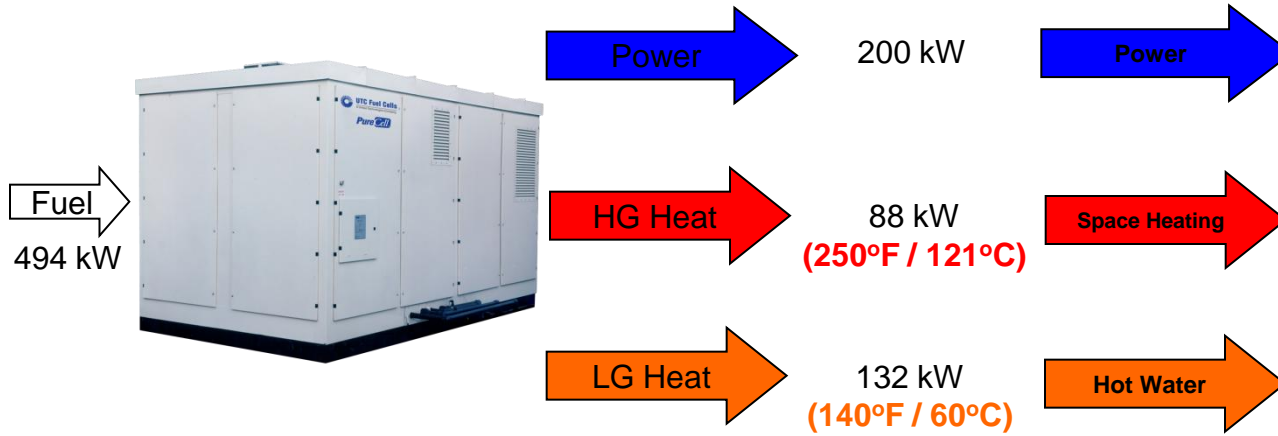
FPS converts fuel into a hydrogen-rich, sulfur-free, gas for CSA

CSA provides required heat for the endothermic fuel processing steam reforming



PURECELL® FUEL CELL SYSTEM

Mohegan Sun facility



$$\text{Maximum Efficiency} = \left(\frac{200 + 88 + 132}{494} \right) = 85\%$$

Efficient use of high grade and low grade heat

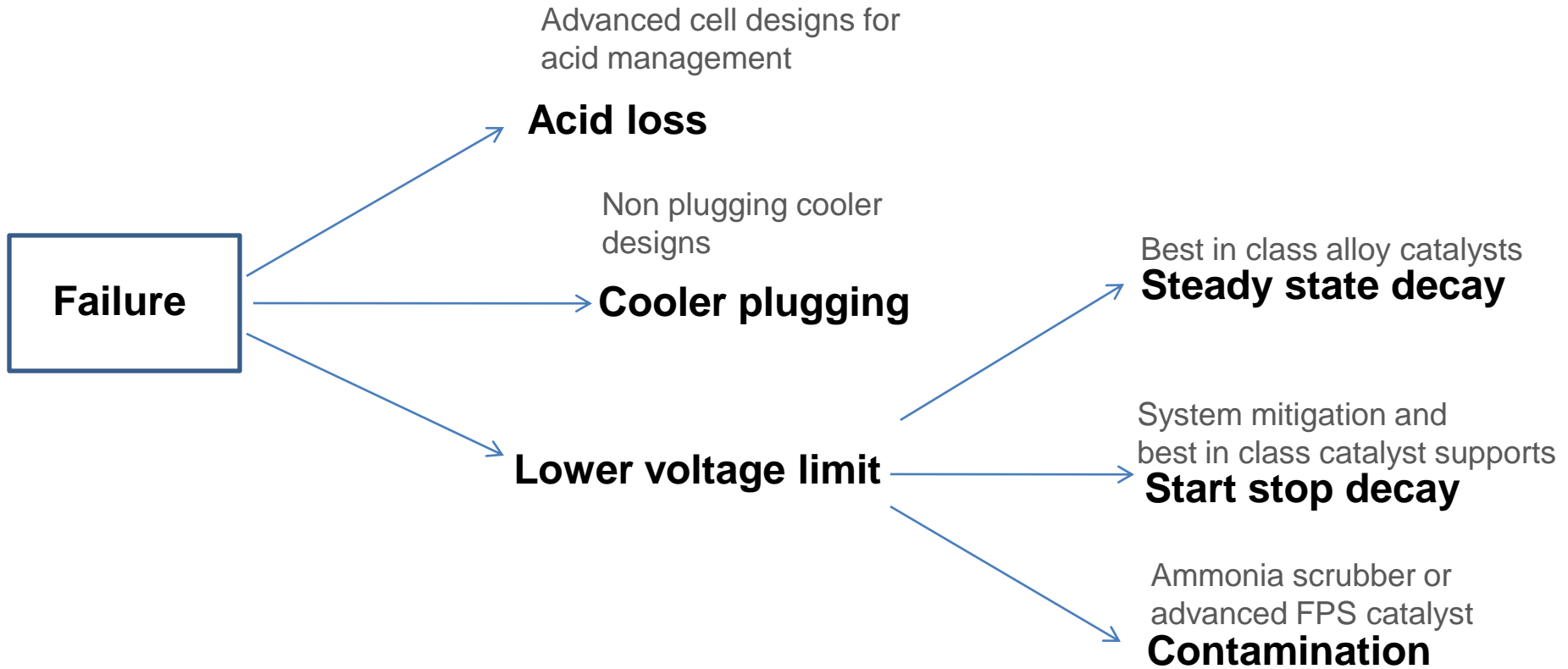
Customer needs heating all year long

Effective integration



PURECELL[®] FUEL CELL SYSTEM

Failure modes

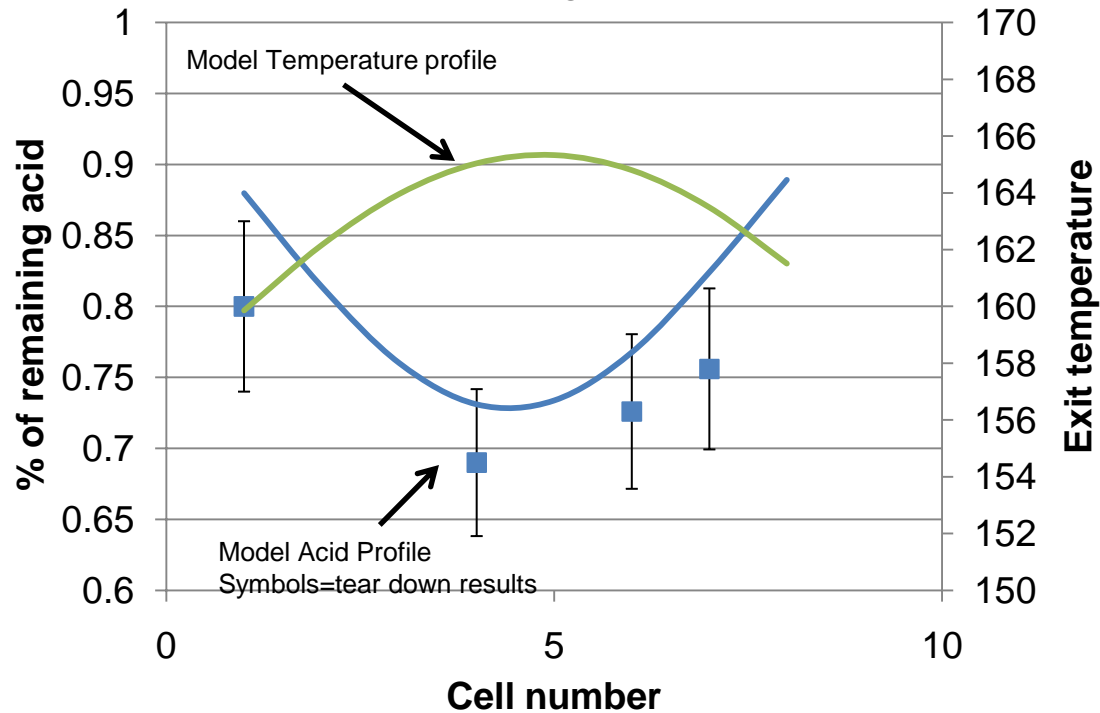




PURECELL[®] FUEL CELL SYSTEM

Post test acid inventory

Model predictions and post test acid inventory data after 43k hrs off-grid operation



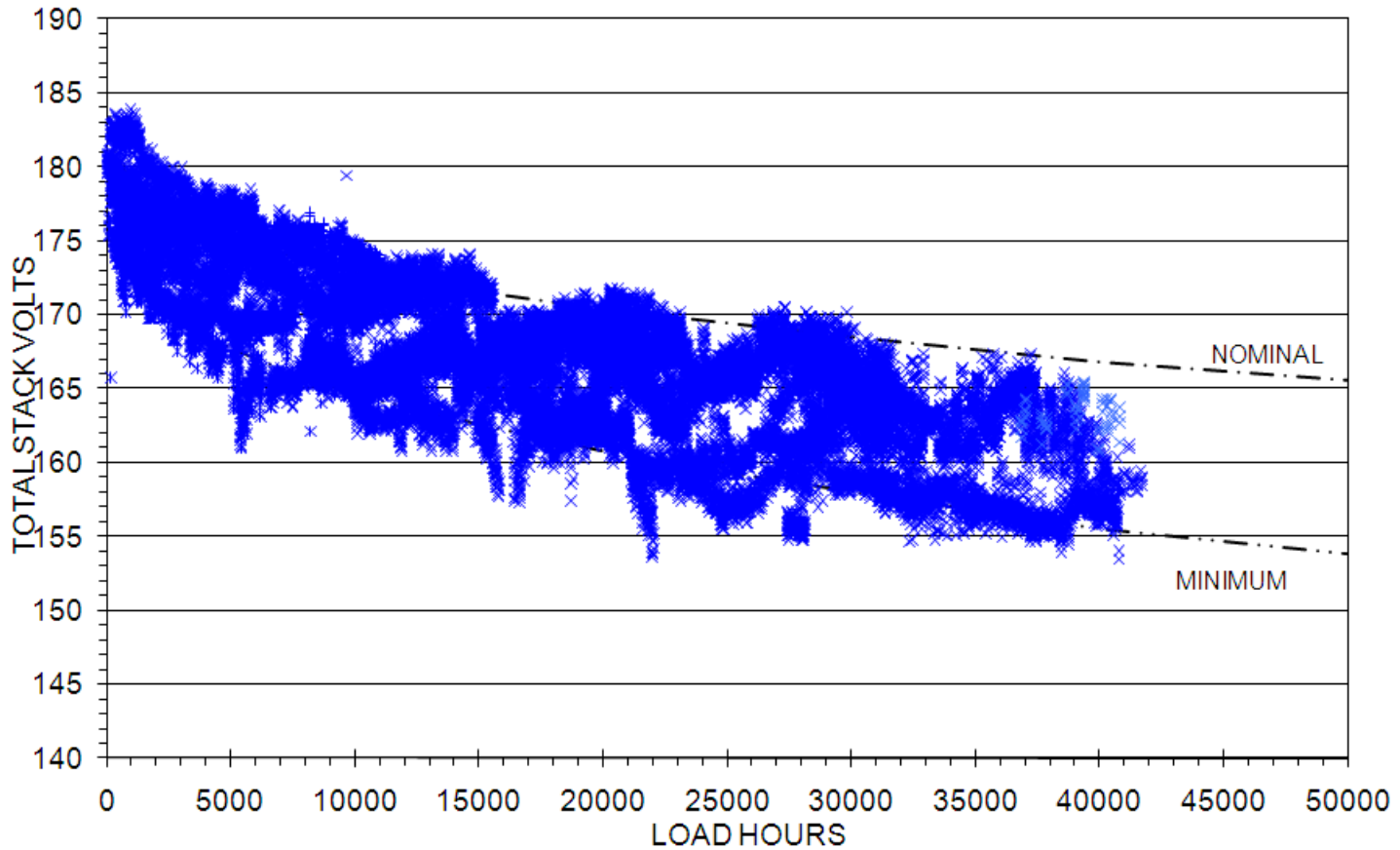
Understanding of acid movement fundamentals is the key enabler for product performance



PURECELL[®] FUEL CELL SYSTEM

Fleet decay performance

Performance at 200 kW



Performance band due to operational and site characteristics

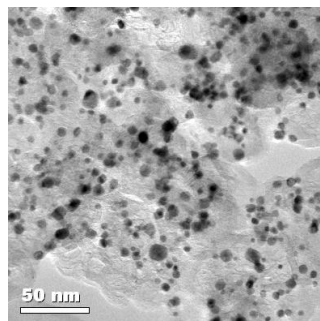


PURECELL[®] FUEL CELL SYSTEM

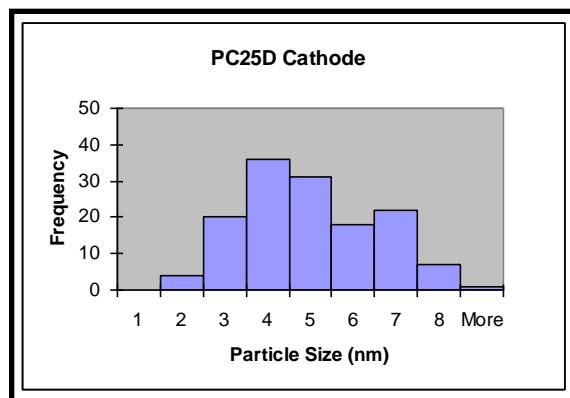
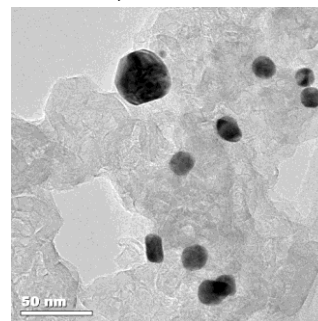
Catalyst decay

Analysis of field operated components demonstrates catalyst agglomeration

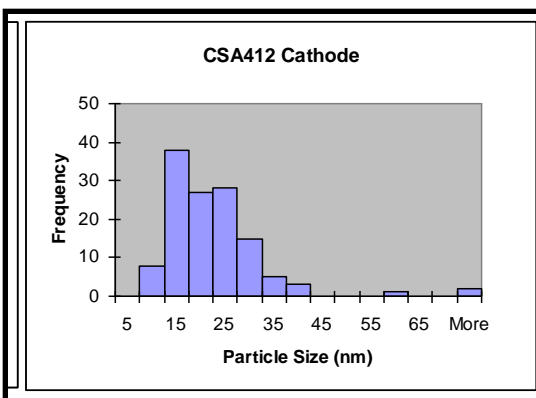
New



43,000 hr



ECA: 50 m²/g
Average diameter: 4.5nm



ECA: 6.5 m²/g
Average diameter: 19.9 nm

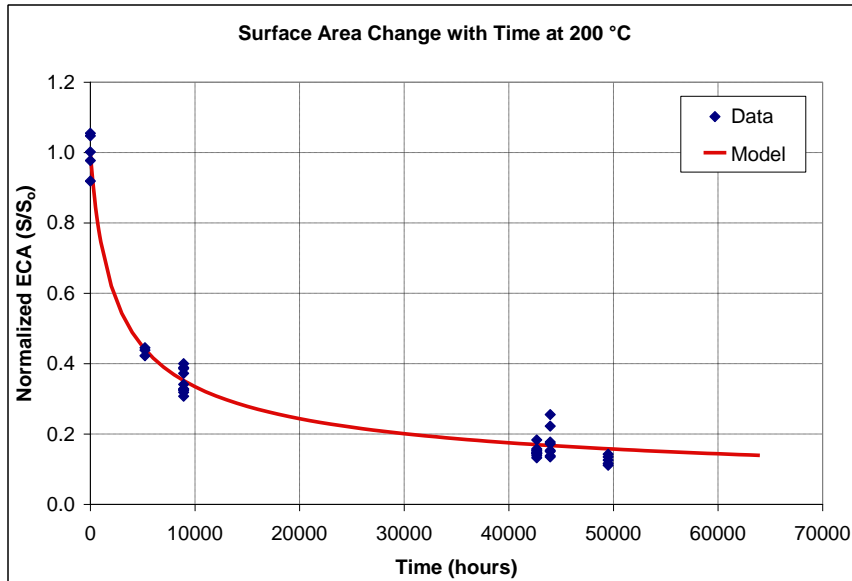
ECA=Electrochemical area



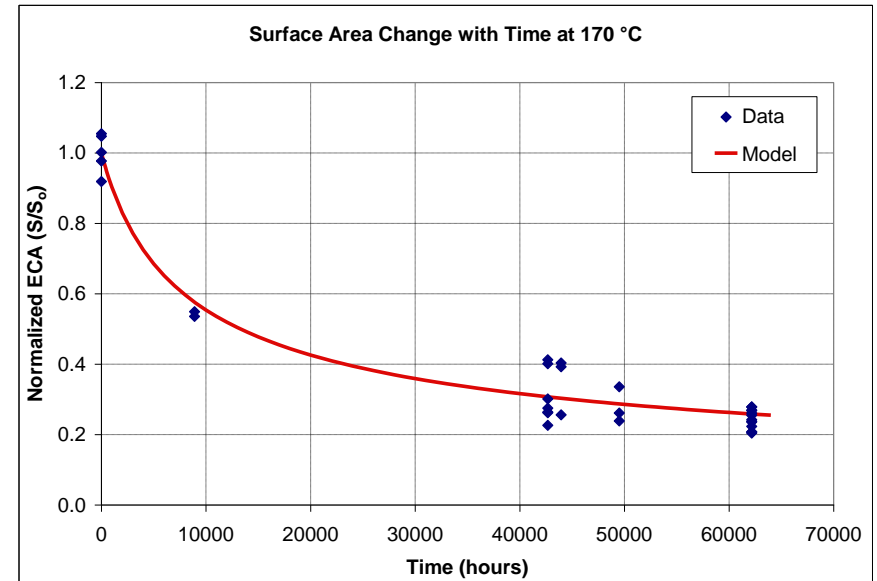
PURECELL[®] FUEL CELL SYSTEM

Surface Area with Time

200 °C Data vs. Model



170 °C Data vs. Model



Modeling accounts for catalyst decay mechanisms

Good model correlation with field data out to 60,000+ hours



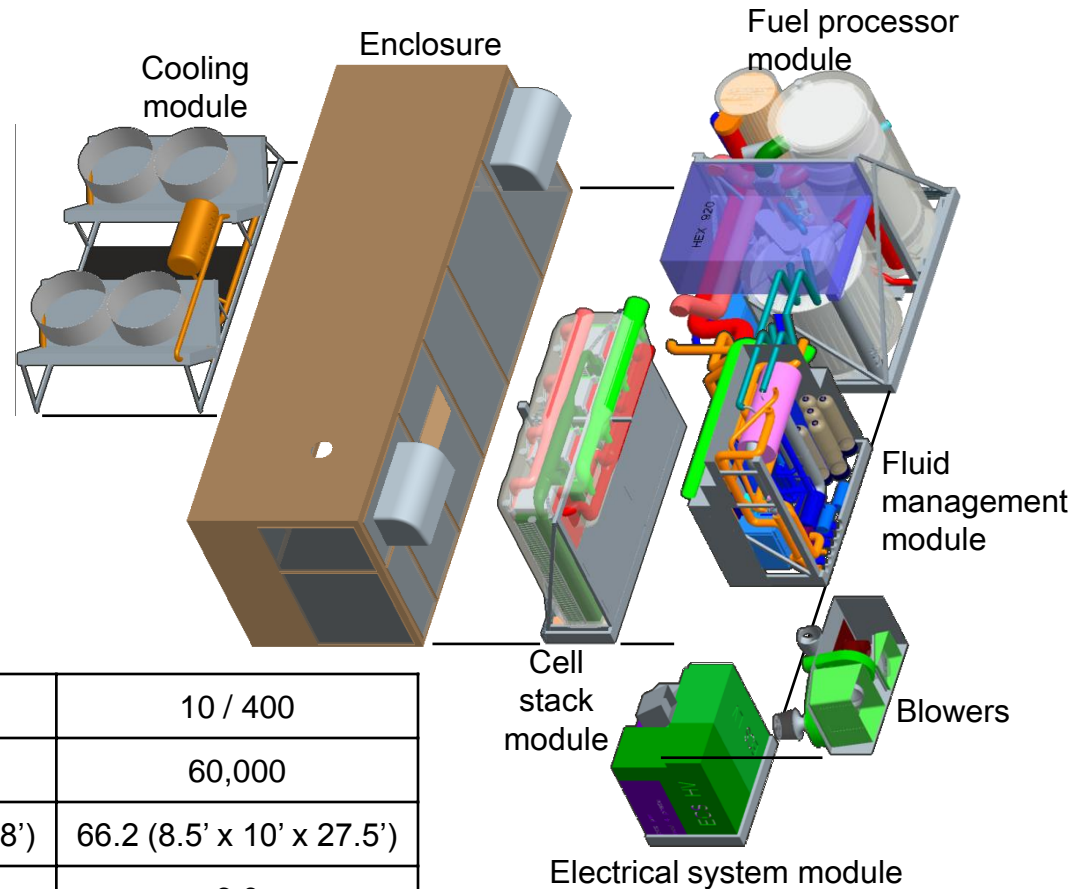
PURECELL® FUEL CELL SYSTEM

Next generation powerplant

Approach

Collaborative designs

Supply chain module sourcing



Life (years) / Power (kW)	5 / 200	10 / 400
Weight (lb)	40,000	60,000
Volume (m ³)	48.4 (9.5' x 10' x 18')	66.2 (8.5' x 10' x 27.5')
Power density (kW/m ³)	3.9	6.0

PureCell™
Model 200

PureCell™
Model 400

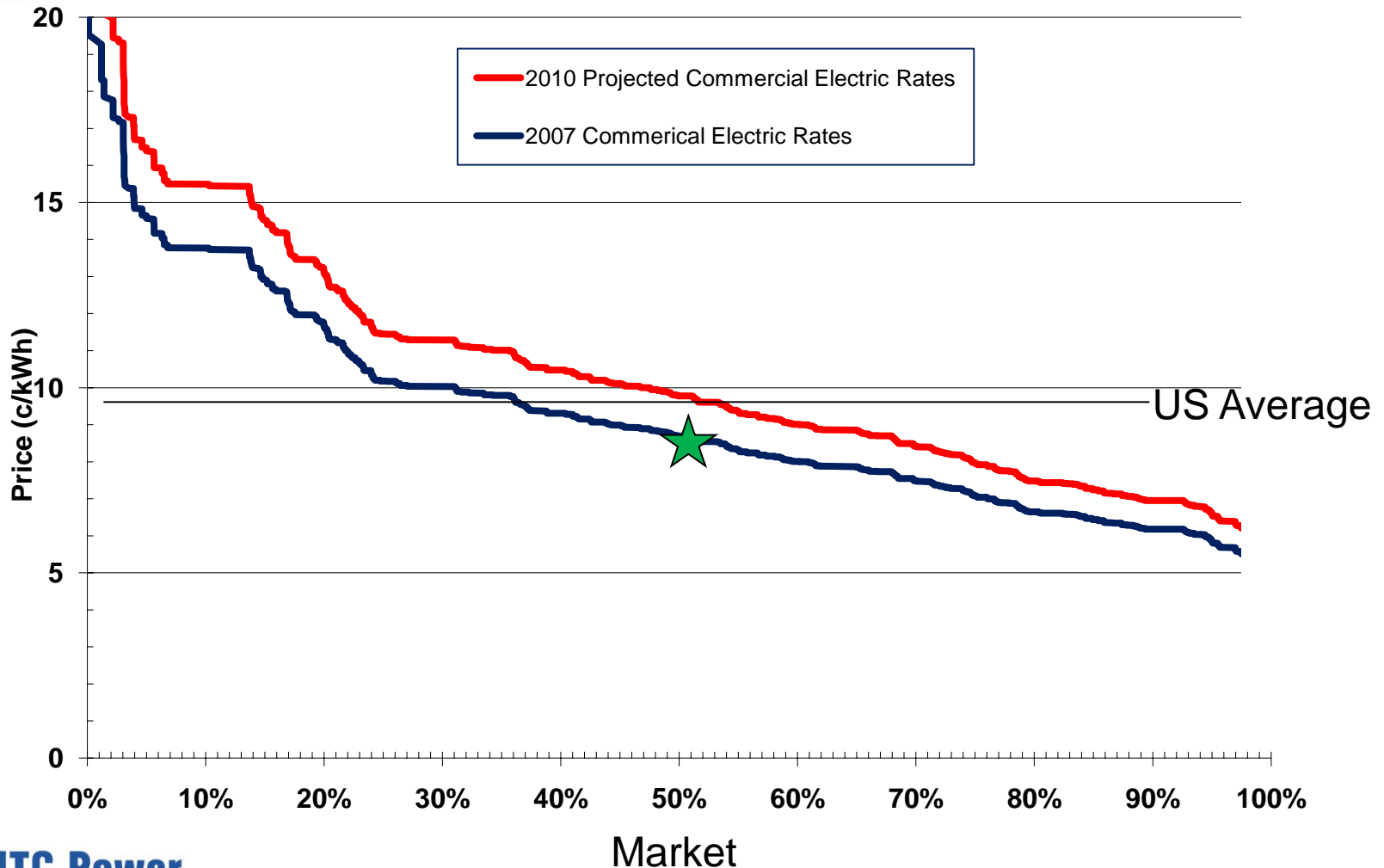


UTC Power

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DISTRIBUTION OF U.S. GRID RATES 2007 and 2010 (projected) commercial rates





PURECELL[®] FUEL CELL SYSTEM

Summary

PAFC offers high durability and total efficiency

Durability performance is driven by fundamentals based modeling and post tear down analysis correlation

PAFC has been a technical success in many market segments and applications

Next generation 400 kW powerplant leverages sound technology to close gaps to true commercialization

However, first cost is still a challenge.....

Appendix E
PAFC Cost Challenges
Mr. Sridhar Kanuri, UTC Power, LLC



PAFC Cost Challenges

Sridhar Kanuri

Manager, PAFC Technology



UTC Power

A United Technologies Company

*Sridhar.Kanuri@utcpower.com



AGENDA

Purecell® 400 cost challenge

Cost reduction opportunities

Summary



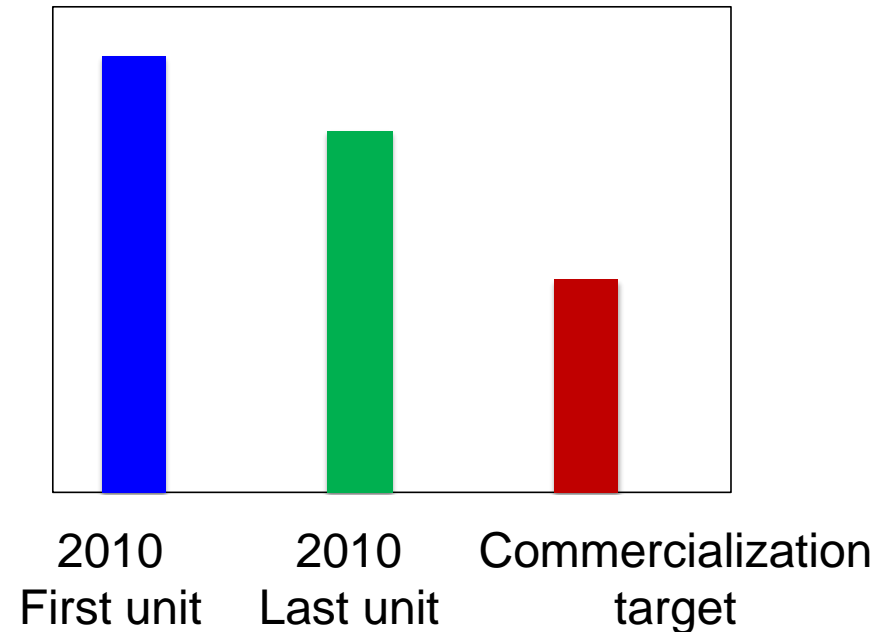
PURECELL[®] FUEL CELL SYSTEM

Powerplant cost

2010 cost reduction is being accomplished by incremental changes in technology & low cost sourcing

Technology advances are required to reduce further cost and attain UTC Power's commercialization targets

First cost

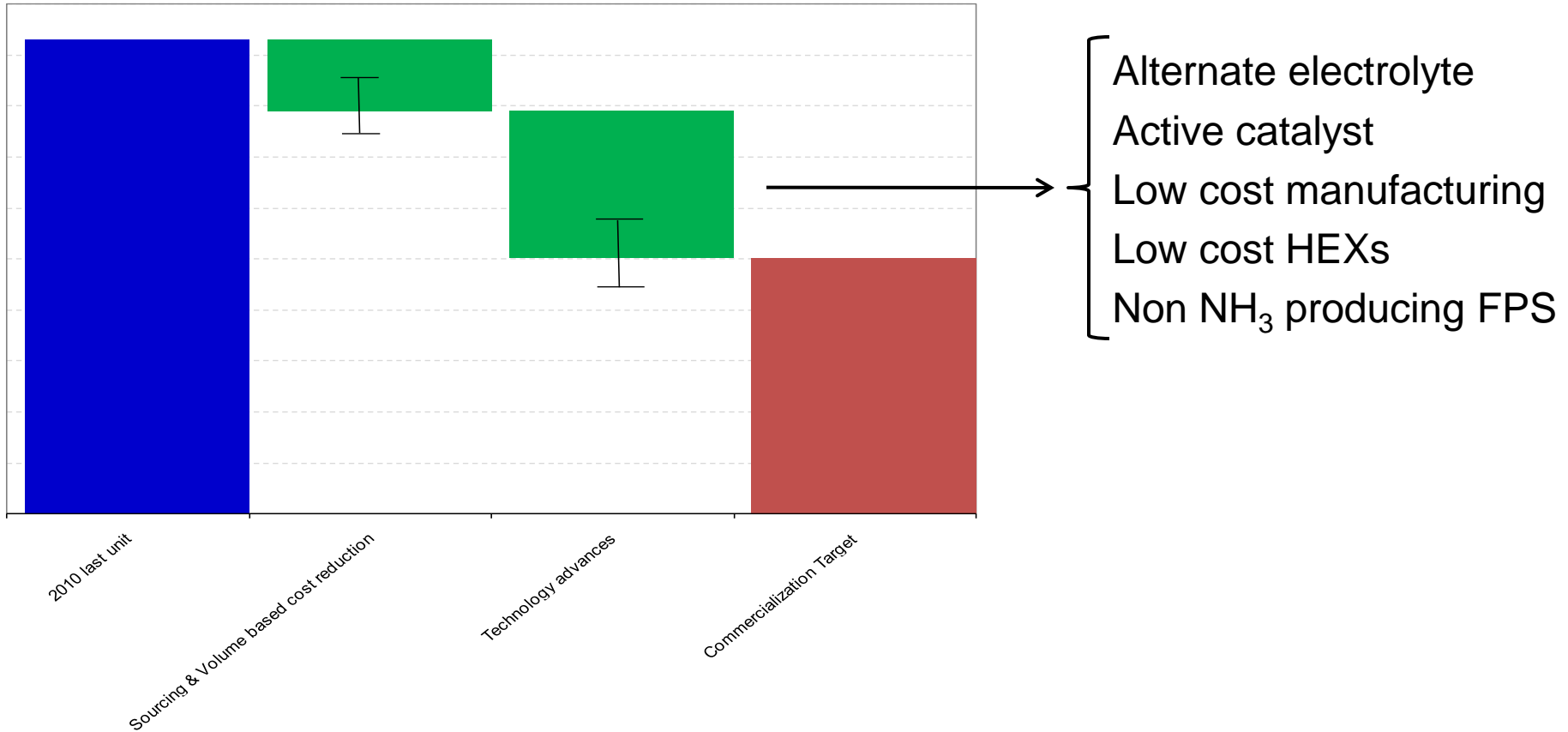




PURECELL[®] FUEL CELL SYSTEM

Powerplant cost

Cost reduction



Significant technology advances are required to meet commercialization targets



PURECELL[®] FUEL CELL SYSTEM

Alternate electrolyte

Property	Desired	PAFC
Operating temperature (C)	150 – 250	150 - 250
Ionic conductivity (mho/cm)	> 0.65	0.65
Vapor pressure (atm)	~ 0	4.5×10^{-7} @ 175 C
O ₂ solubility (mol/cm ³)	high	1×10^{-7} @ 175 C
Transference number	0	0.11
Anion poisoning	None	Phosphate poisons catalyst
Electrochemical stability	No decomposition products between 0 – 1.2V	H ₃ PO ₄ is very stable
Material compatibility	Compatible with fuel cell materials (Ex: Carbon, Teflon, SiC, Catalyst)	Very compatible with fuel cell materials
Freeze tolerance	-30 C – 250 C	-30 C – 250 C

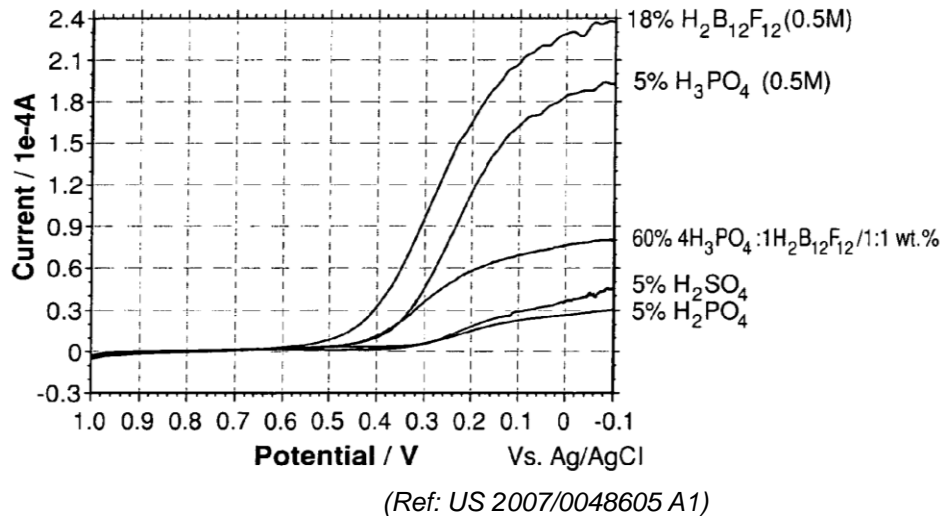




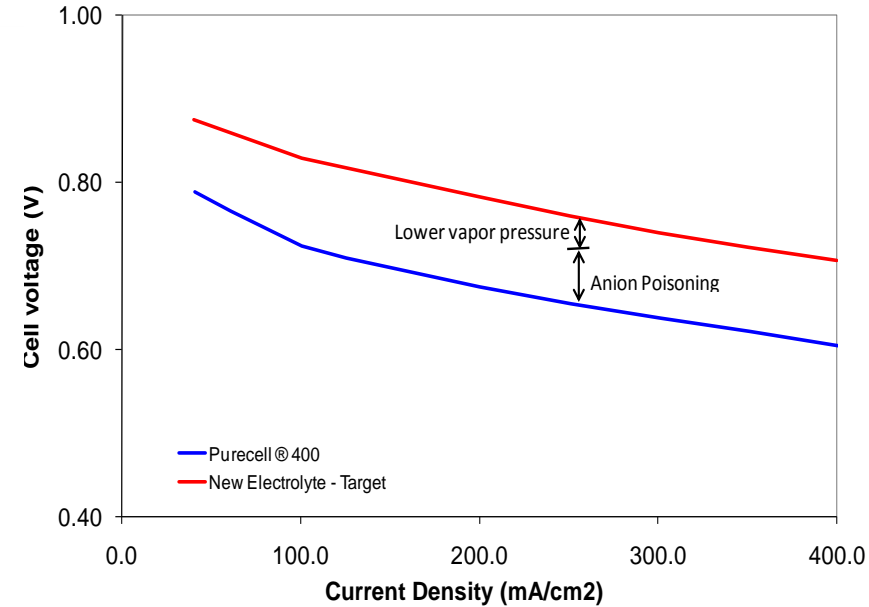
PURECELL[®] FUEL CELL SYSTEM

Alternate electrolyte

RDE of aqueous acids at 1400 RPM



Performance Analysis



Literature shows significant potential for using alternate electrolytes for fuel cells

Eliminating anion poisoning and using electrolytes that have very low vapor pressure result in improving power plant efficiency by ~6 points and/or reducing power plant cost by ~ 15% - 20%.



PURECELL[®] FUEL CELL SYSTEM

Alternate electrolyte – H₃PO₄ additives

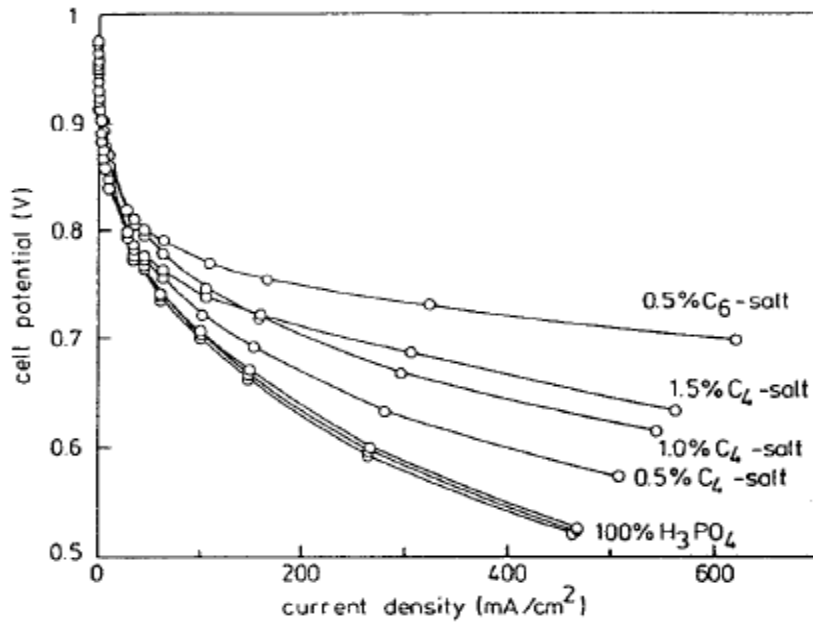


Fig. 8. Polarization curves for electrolyte modified by addition of C₆-salt and C₄-salt (fuel, H₂; oxidant, O₂; electrolyte, 100% H₃PO₄; and temperature, 190°C).

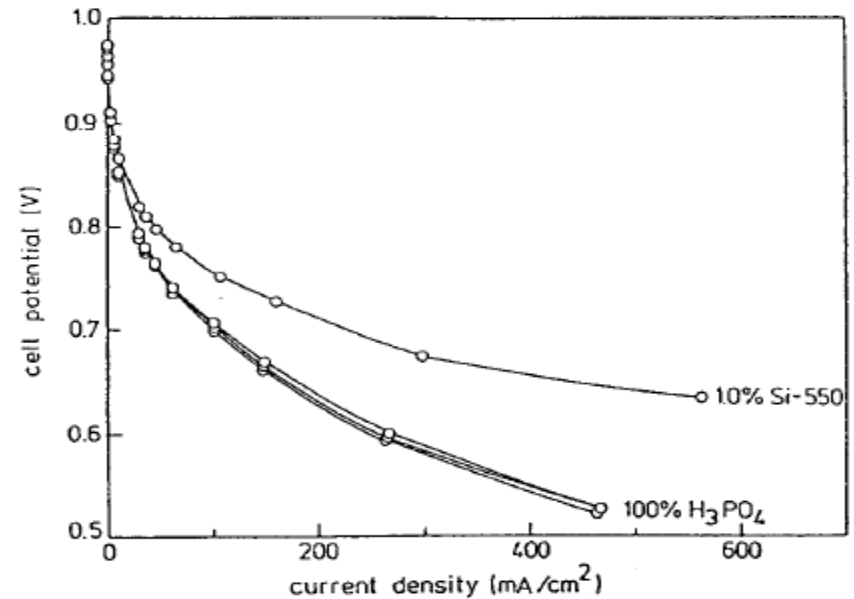


Fig. 10. Polarization curves for electrolyte modified by addition of Si-550 (fuel, H₂; oxidant, O₂; electrolyte, 100% H₃PO₄; temperature, 190°C).

H₃PO₄ modifications using additives have been shown to improve performance

Ref: Xiao Gang et. Al, "Electrolyte additives for phosphoric acid fuel cells, J. Electrochem. Soc., Vol. 140, No. 4, April, 1993



PURECELL[®] FUEL CELL SYSTEM

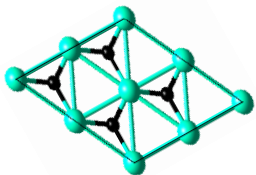
Anode catalysts

Primary requirements for PAFC anode:

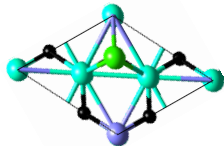
- Stable in operating temperatures between 150 C & 225C
- CO tolerant
- Stable surface area
- Low Pt usage / kW: (PAFC: 2.4 g/kW vs. PEM: 0.03 g/kW)

Opportunities:

- High mass activity catalysts & low Pt loaded anodes
- Research indicates transition metal carbides are significantly active toward HOR and are CO tolerant



● W ● C



● W ● C ● Pt ● Ta

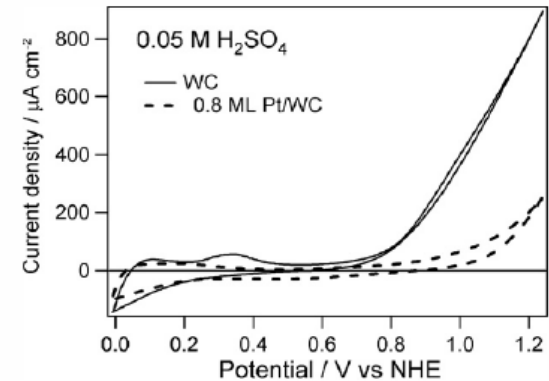
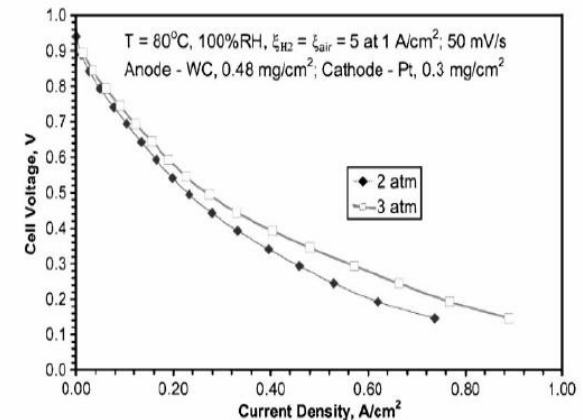


Fig. 4. Cyclic voltammetry curves of WC and 0.8 ML Pt/WC surfaces exposed to 0.05 M H₂SO₄.



H₂ / Air Polarization curves of WC based anode in 5 cm² cell

Ref: D.J.Ham & J.S.Lee, "Transition metal carbides and nitrides as electrode materials for low temperature fuel cells"



PURECELL[®] FUEL CELL SYSTEM

Cathode catalysts

Primary requirements for PAFC cathode:

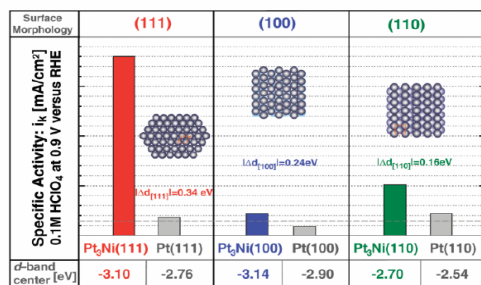
Stable in operating temperatures between 150 C & 225C

Stable surface area

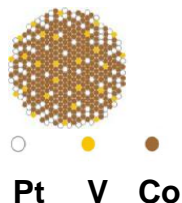
High mass activity

Low Pt usage / kW: (PAFC: 5.2 g/kW vs. PEM: 0.13 g/kW)

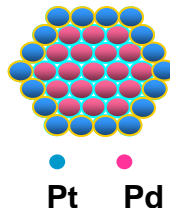
Concepts for Improved mass activity



New synthesis
(3X mass activity)



New structure
(10X mass activity)



Concepts for surface area stabilization

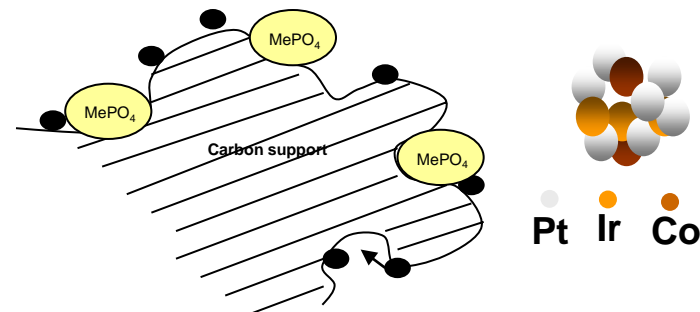


Fig. 3. Influence of the surface morphology and electronic surface properties on the kinetics of ORR. RRDE measurements for ORR in HClO₄ (0.1 M) at 333 K with 1600 revolutions per minute on Pt₃Ni(hk) surfaces as compared to the corresponding Pt(hk) surfaces (a horizontal dashed gray line marks specific activity of polycrystalline Pt) are shown. Specific activity is given as a kinetic current density i_k , measured at 0.9 V versus RHE. Values of d -band center position obtained from UPS spectra are listed for each surface morphology and compared between corresponding Pt₃Ni(hk) and Pt(hk) surfaces.

Ref: Vojislav R. Stamenkovic, et. al, "Improved oxygen reduction activity on Pt₃Ni(111) via increased surface site availability."



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PURECELL® FUEL CELL SYSTEM

Low cost manufacturing – Electrodes

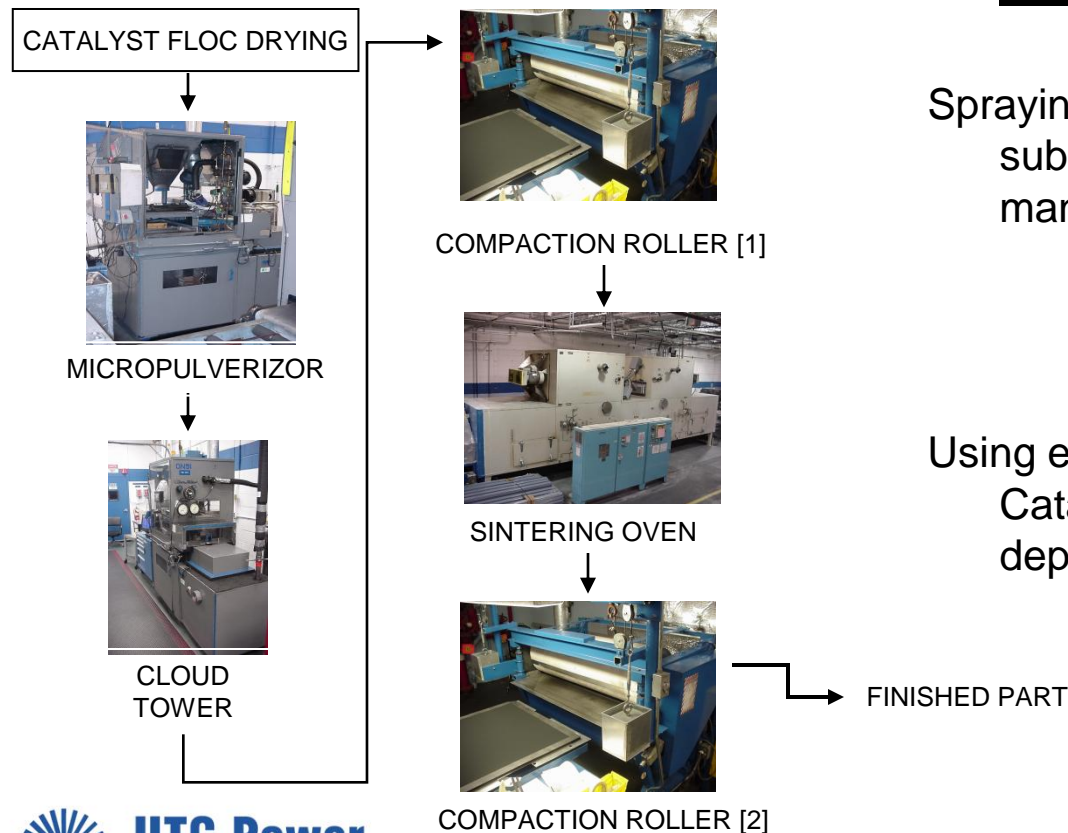
Current process of PAFC electrode manufacture is capital intensive

PAFC electrode manufacturing

Low cost electrode manufacturing concepts

Spraying mix of Catalyst, Teflon® directly onto a substrate with subsequent heat treatment to manufacture electrodes

Using emulsions to obtain a uniform dispersion of Catalyst & Teflon® with subsequent wet deposition of catalyst layer and drying

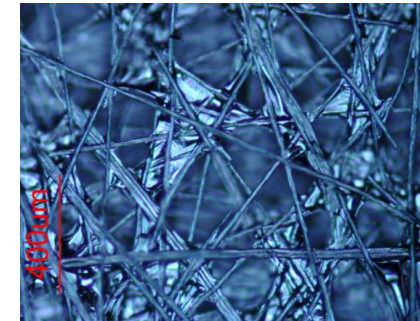




PURECELL[®] FUEL CELL SYSTEM

Low cost materials / manufacturing – GDLs

PAN-based (long)—Today



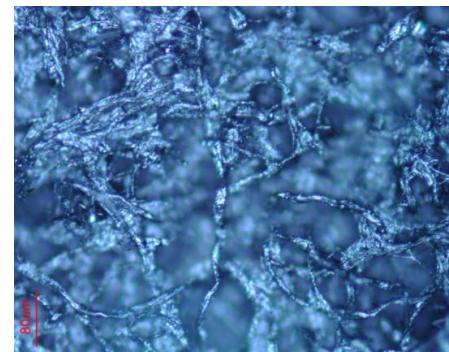
Primary requirements for PAFC GDL

Density	~ 0.6 g/cc
Electrical resistivity:	< 0.08 mV/mil
Thermal conductivity	> 400 BTU/hr-ft ² -°F
Flex strength	> 2200
Corrosion resistance	< 40 mA/g

Opportunities:

Low cost Carbon composite fibers, Carbonized cellulose based fibers & cotton based fibers, low cost manufacturing techniques etc. represent significant cost reduction opportunity for H₃PO₄ fuel cells

Cellulose-based





PURECELL[®] FUEL CELL SYSTEM

Low cost HEXs

Brazed plate HEXs and automotive radiators offer a significant BOP cost reduction opportunity for stationary power plants

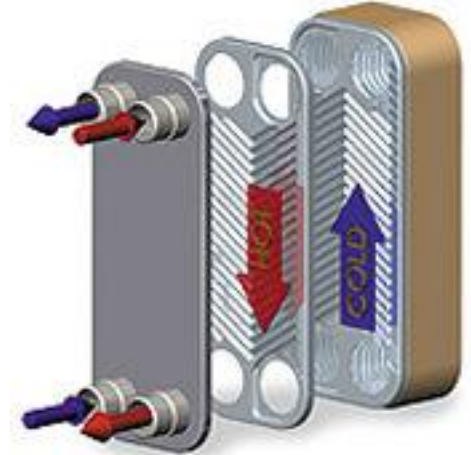
Technology challenges involve thermal cycle stability and coating development to endure high temperature H_3PO_4 environment

Advantages:

Light weight and compact

Low pressure drop for the gas side

Low cost due to volume production and simple structure



Brazed plate HEX



Low cost radiators



PURECELL® FUEL CELL SYSTEM

Non NH₃ producing FPS

Requirement: NH₃ < 250 ppb

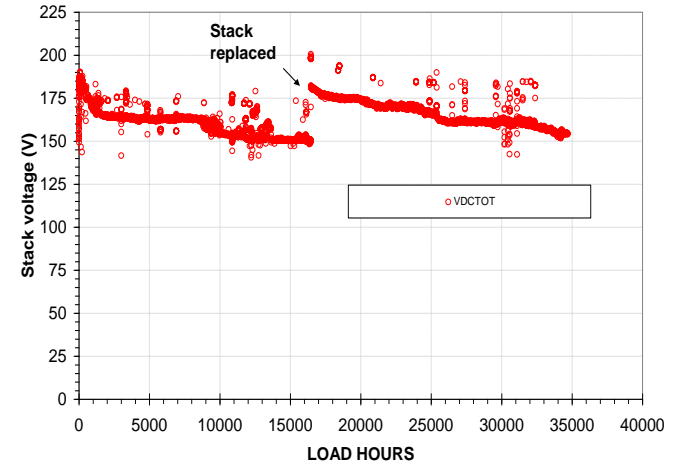
N₂ in natural gas produces NH₃ which poisons cathode catalyst

Purecell® 400 employs a scrubber to remove NH₃ from fuel stream

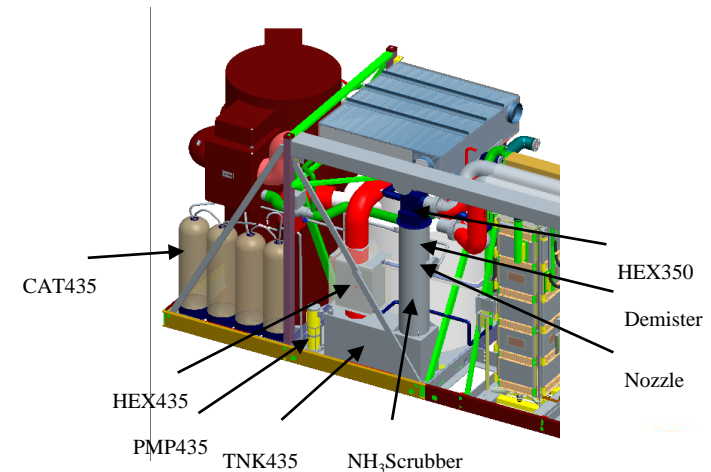
Future concepts:

Investigate non NH₃ producing FPS catalysts

Impact of NH₃ on performance



Purecell® 400 ARD





PURECELL[®] FUEL CELL SYSTEM

Summary

First cost is a significant challenge for all stationary fuel cell power plants

Incremental improvements in technology are currently being worked / implemented by industry

Accelerated commercialization requires increased investment in technology

Appendix F
PBI-Phosphoric Acid Based Membrane Electrode Assemblies: Status Update,
Mr. Emory De Castro, BASF Fuel Cells

PBI-Phosphoric Acid Based Membrane Electrode Assemblies: Status update

PAFC Workshop

16 November 2009

Emory De Castro

BASF Fuel Cell –

Formed from legacy companies with history of catalyst, gas diffusion electrodes, and membrane innovation

2008

Customer application lab in Japan opens April 2008

2007

BASF merges fuel cell activities and forms BASF Fuel Cell

2006

BASF acquires PEMEAS and Engelhard

2005

E-TEK becomes division of PEMEAS

2004

Celanese and investors form PEMEAS

2003

Celanese Ventures introduces Celtec-P MEA to market

2001

Celanese Ventures MEA production plant goes on stream

2000

BASF identifies fuel cell as growth area and launches fuel cell project

1999

Celanese takes over fuel cell project after demerger from Hoechst

BASF develops and manufactures reformer catalysts

1998

Engelhard develops and markets catalysts for fuel cell and reformer

1994

Hoechst develops first high temperature MEA

1990

E-TEK formed to commercialize catalysts and gas diffusion technology

Celtec®-P: MEAs for High Temperature* PEMFC

Membrane:

Based on polybenzimidazole (PBI) and phosphoric acid

Electrodes:

Catalysts and layer structure tailored for high temperature conditions (typically 160 – 180°C) and PBI-PA membrane

Applications:

- Stationary power supply, CHP
- Backup power
- Auxiliary power units
- micro-portable



* 120 – 180 °C

Celtec®-MEAs

Enabling Competitive Fuel Cells

Celtec-P MEA for high temperature PEMFC

- In the market since 2004

Advantages for customers

- Better robustness
- Simplified system
- Higher overall efficiency
- A hybrid of the best advantages of a phosphoric acid system with the manufacturing simplicity of a MEA



Customer Partnerships to Develop Markets from 10W to 10kW

Portable Electronics:



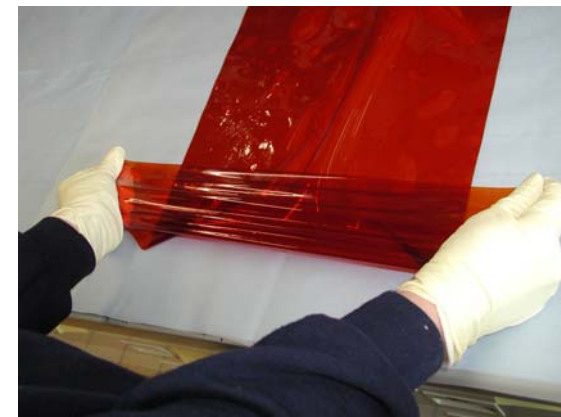
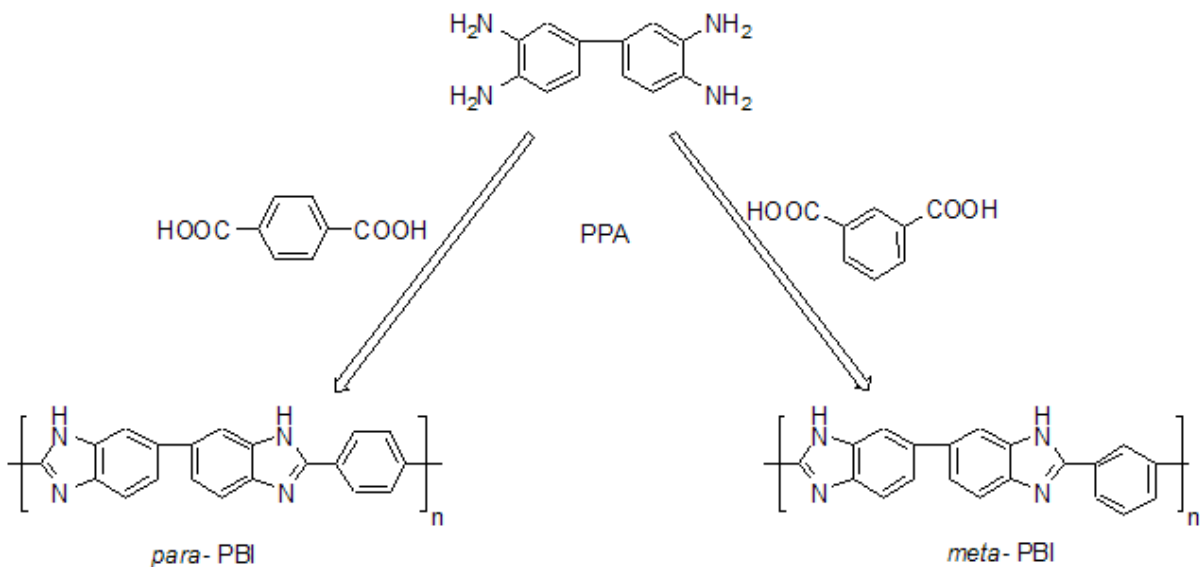
Residential:



Back-up and Premium Power:

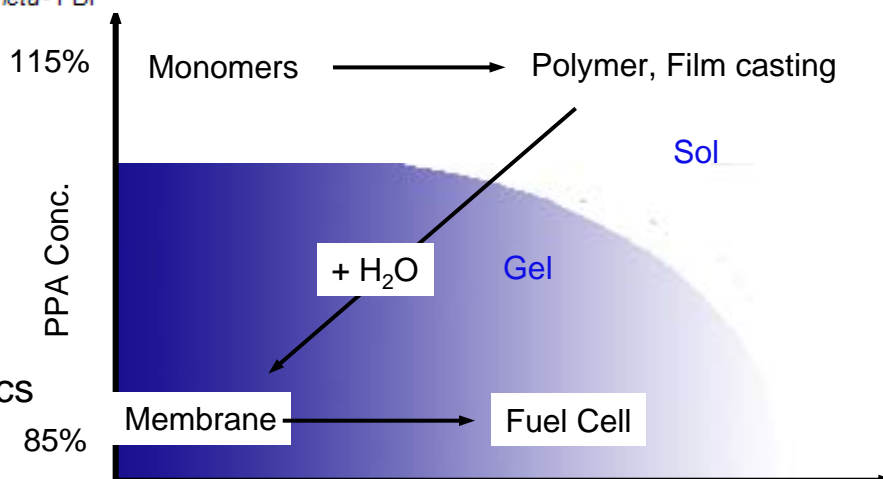


Celtec[®]-P MEAs – BASF Fuel Cell Core MEA Technology



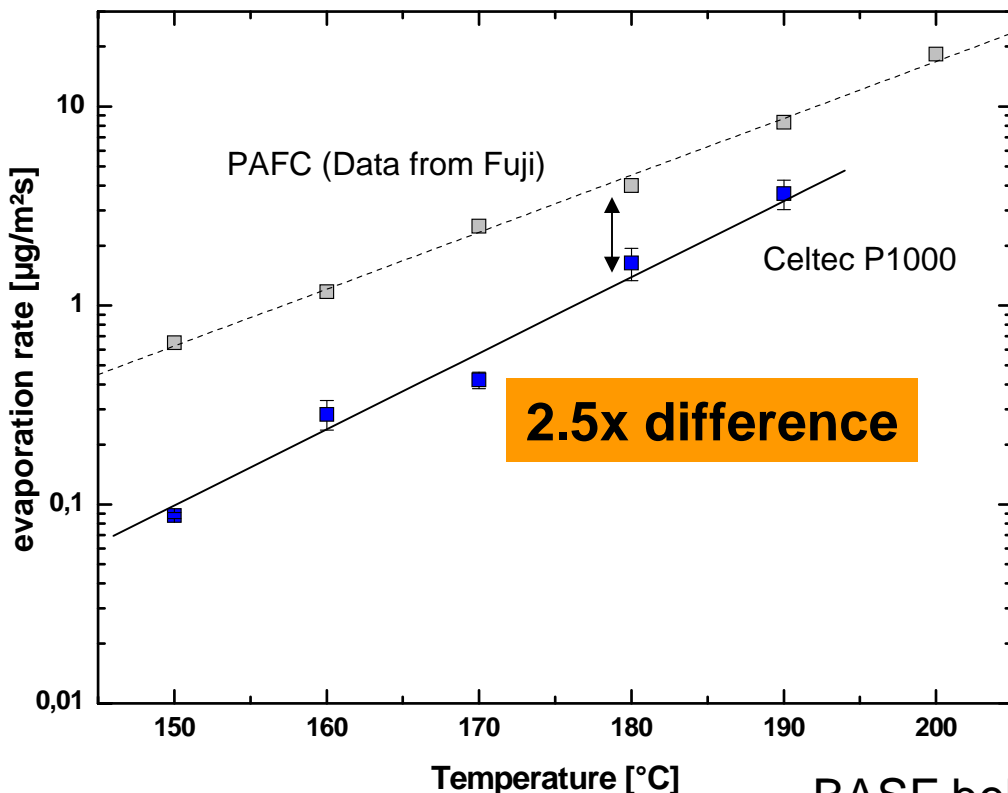
MEA Operation

- T=120°C to 180°C
- High Tolerance to impurities
- Especially suitable for small stationary systems, APUs, small mobile systems for power electronics



Acid evaporation from Celtec MEAs

Hydrogen bonding with PBI may help retain acid



Celtec P 1000: 50cm²,
 $i=0.35\text{A/cm}^2$ 100kPa_a, H₂-Air 1.5-2

PAFC data: 100cm², 100kPa_a
 $i=0.3\text{ A/cm}^2$, H₂-Air 1.25-2

Fuji Electric PAFC data
I. Okae, S. Kato, A. Seya, and
T. Kamoshita, 'Study of the Phosphoric
Acid Management in PAFCs',
The Chemical Society of Japan
67th Spring Meeting, 148 (1990).

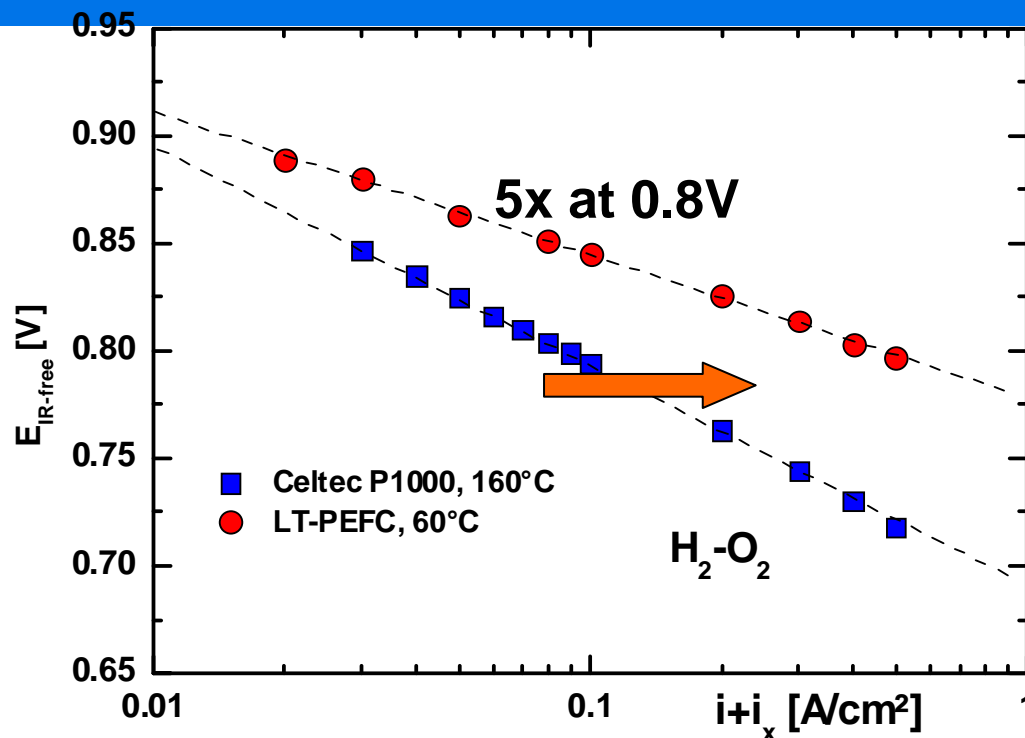
BASF believes this basis may allow either simpler system or longer lifetimes based on acid retention

D.C. Steel. B. Benicewicz. L. Xiao. T.J. Schmidt in

Handbook of Fuel Cells – Fundamentals, Technology and Applications. Edited by Wolf Vielstich, Harumi Yokokawa, Hubert A. Gasteiger.
Volume 5: *Advances in Electrocatalysis, Materials, Diagnostics and Durability*. © 2009 John Wiley & Sons, Ltd. ISBN: 978-0-470-72311-1.

- Celtec-P is a gel type membrane with low solid content
 - We continue to seek out approaches to improve the mechanical properties, e.g. creep or pressure sensitivity
- Benefits of improved mechanical strength
 - Low creep resistance of membrane tightens tolerances for stack manufacturing, i.e., dimensional tolerances of BBP and gaskets become very tight, forcing greater compliance from manufacturers
 - Broadening of these tolerances gives a more robust MEA
 - *Opens up new approaches for higher speed roll-to-product processing for MEA fabrication*

Cathode kinetics in HT-MEAs



Celtec P cathode
(1mg/cm², 160°C, 100kPa_a,
dry H₂/O₂ at s=1.2/9.5)

Low temperature
Nafion type cathode
(0.2mg/cm², 60°C, 101kPa_a
H₂-O₂, 100%RH)

* LT data: Neyerlin et al.,
JECS 153(10) A1955 (2006)

- Overall comparison at 0.8V: 5x better kinetics in Nafion type LT PEFC compared to HT PEF
- What is the reason of the difference?

D.C. Steel, B. Benicewicz, L. Xiao, T.J. Schmidt in
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Challenges for electrocatalysis at the PBI/H₃PO₄ interface

- Activation energy and reaction orders at the PBI/H₃PO₄ interface in high temperature PEFCs are identical than those at the Nafion interface in low temperature PEFCs
 - Identical reaction mechanism

- Major difference is observed in the exchange current density: Roughly 2.5 orders of magnitude lower values at the PBI/H₃PO₄ interface in high temperature PEFCs compared to Nafion interface in low temperature PEFCs (Normalized to 101.325 kPa and 80°C)
 - Strong adsorption of phosphate ions on Pt leads to reduction of surface sites for O₂ adsorption
 - Oxygen solubility in phosphoric acid

Approaches to improve kinetics in HT-cathodes

Modified Cathode Overpotential – current relationship

$$\eta_{ORR} = \frac{2.3RT}{a_c F} \log \left[\frac{i}{10L_c A_{Pt,ec} i_{0,s}^* (1 - \Theta_{anion})^x (c_{O_2}^0)^y} \right]$$

① Increase Pt Loading

② Increase Pt surface area

③ Increase $i_{0,s}^*$

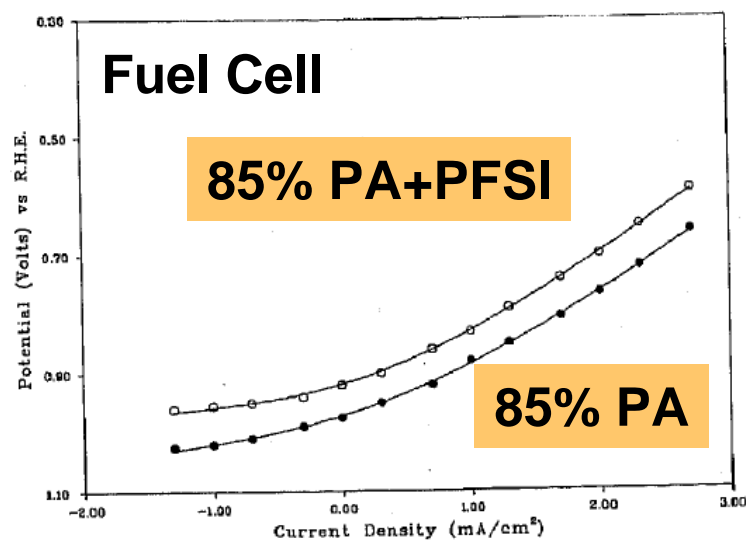
④ Decrease surface coverage of spectator species (anions)

⑤ Increase Solubility of O_2

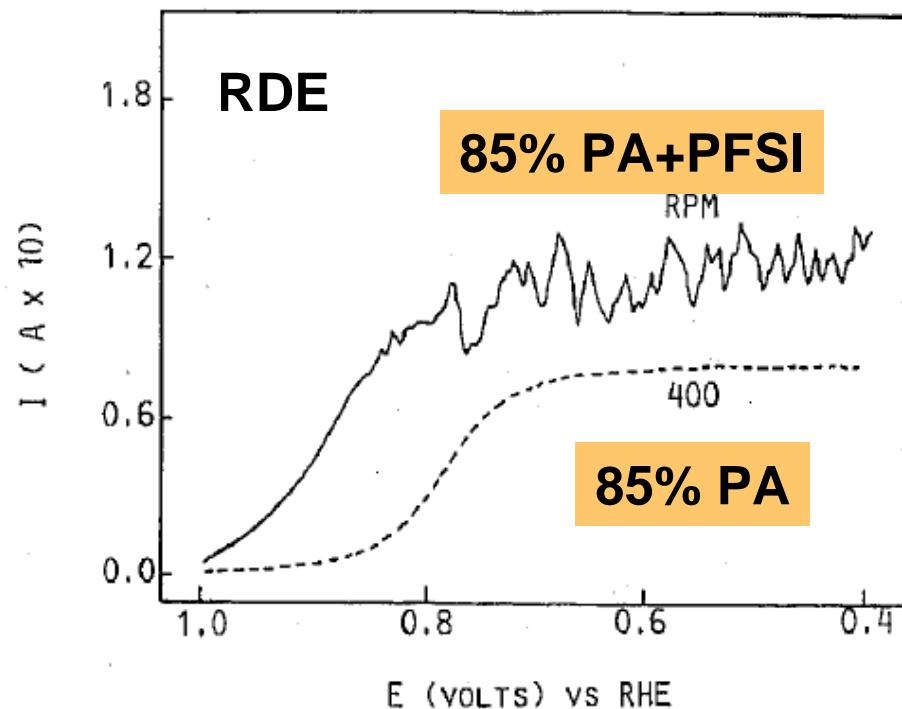
Approaches to improve kinetics in HT-cathodes

Table I. The solubility and the diffusion coefficient of oxygen in phosphoric acid and PFSI

Electrolyte	Solubility $M l^{-1}$	Diffusion coefficient $cm^2 s^{-1}$
85% H_3PO_4	3.3×10^{-4}	1.21×10^{-6}
84% PFSI	4.7×10^{-3}	6.53×10^{-6}



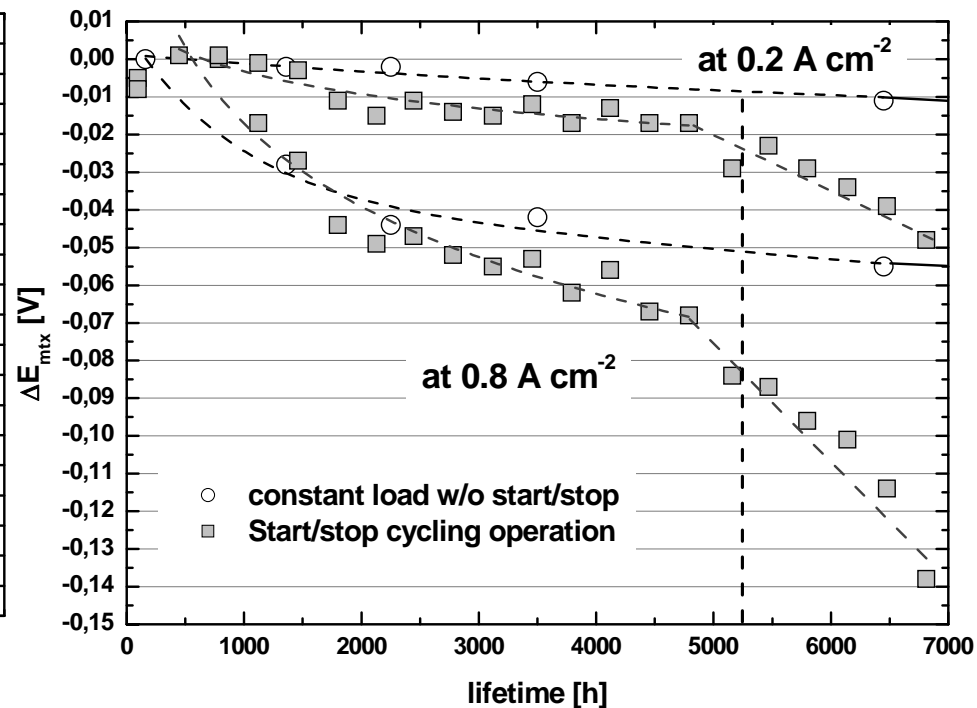
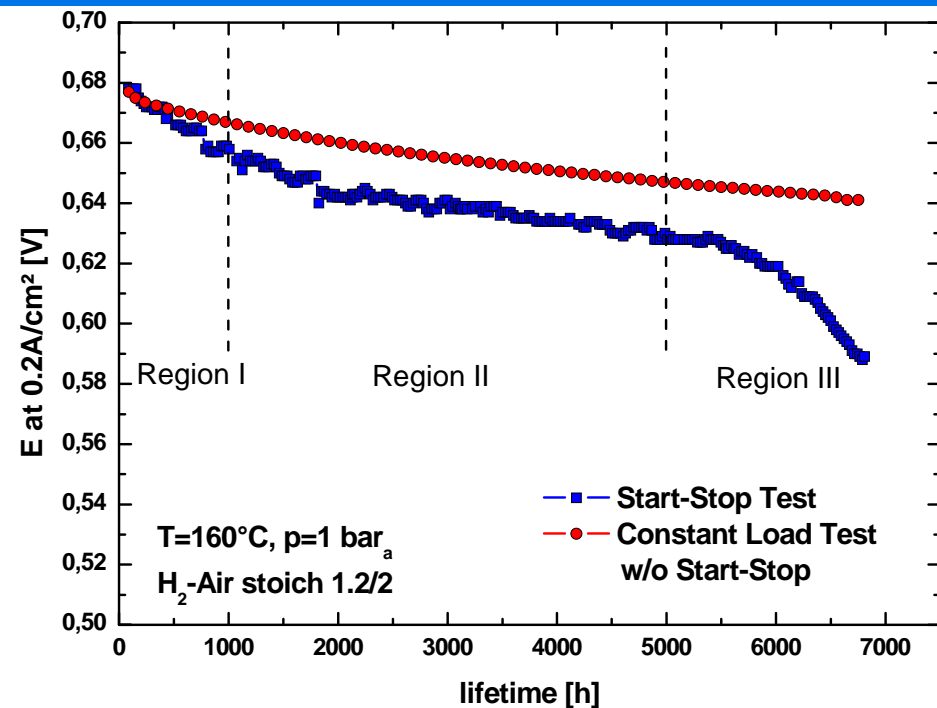
PFSI = perfluorosulfonimide



Razaq et al., JECS 136, 385 (1989)

- Development of alloys more resistant to phosphate anion absorption
 - Tools and techniques for alloy development far more advanced than what existed 20 years ago (for example XAFS, XANES, etc)
 - Synthetic techniques to create more sophisticated alloys have also progressed
- Pursuit of routes to increasing oxygen solubility
 - Significant wealth of new materials relevant to oxygen solubility have been developed

Cathode Stability: Why are improvements necessary?



- Start-Stop operation triggers degradation due to cathode potential excursions to 1.3V or above
- Main effects: increase of mass transport overpotentials
→ carbon corrosion

Comparison HT and LT PEFC

**LT PEFC: Pt/Ketjen Black, 80°C,
66%RH inlet, 0.4mg Pt, 150kPa, 1.3s**

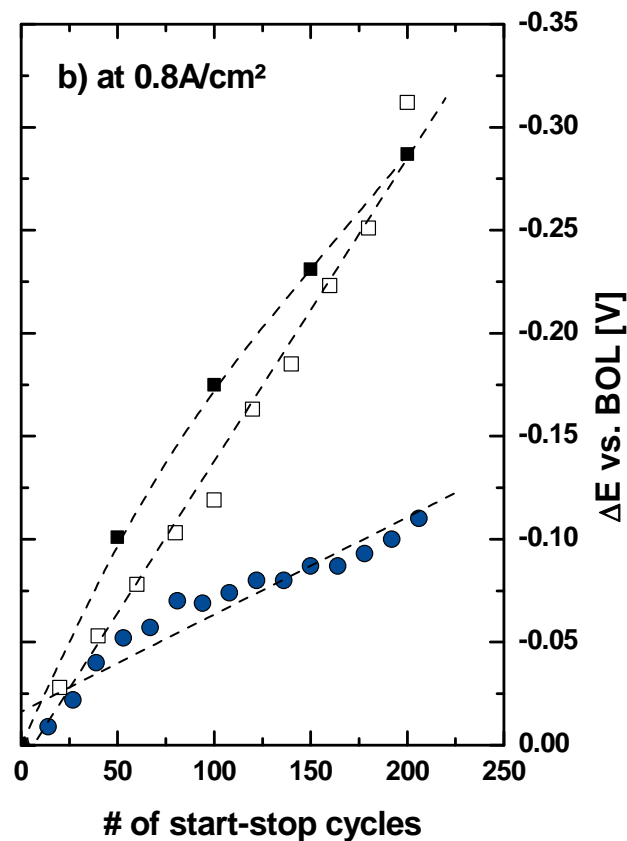
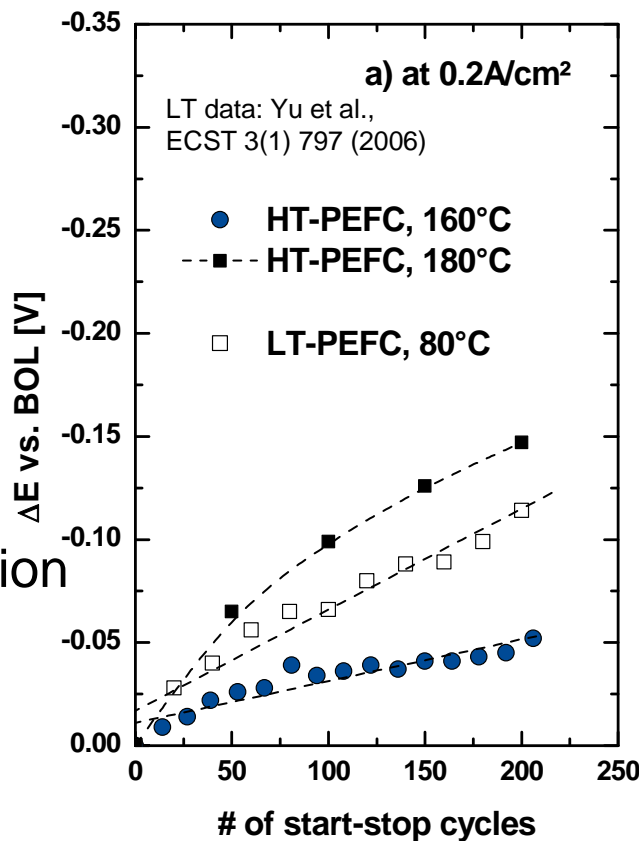
**HT PEFC: Pt-Alloy/Vulcan, 160°C
dry, 0.7mg Pt, 100kPa, 2.5s**

$$i_{\text{corr}} = f(A_c, t_{\text{res}})$$

$$A_c (\text{LT}) \sim 0.45 A_c (\text{HT})$$

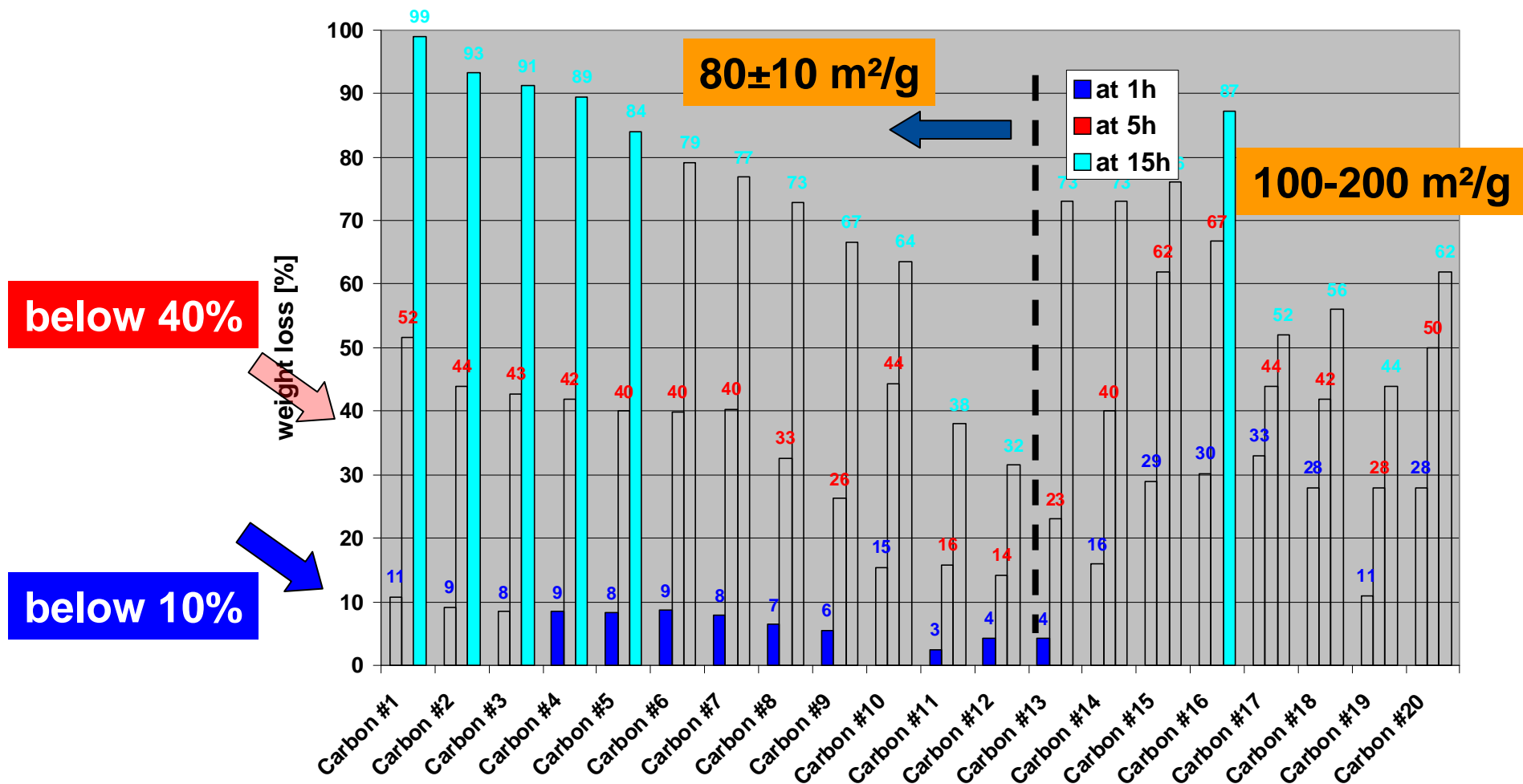
$$t_{\text{res}} (\text{LT}) \sim 0.5 t_{\text{res}} (\text{HT})$$

$p_{\text{H}_2\text{O}}$ drives reaction

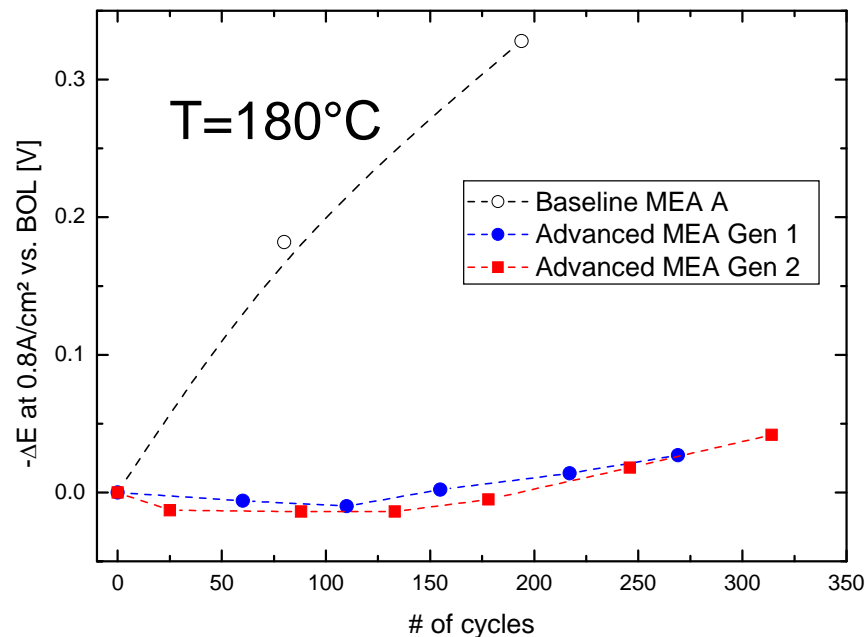
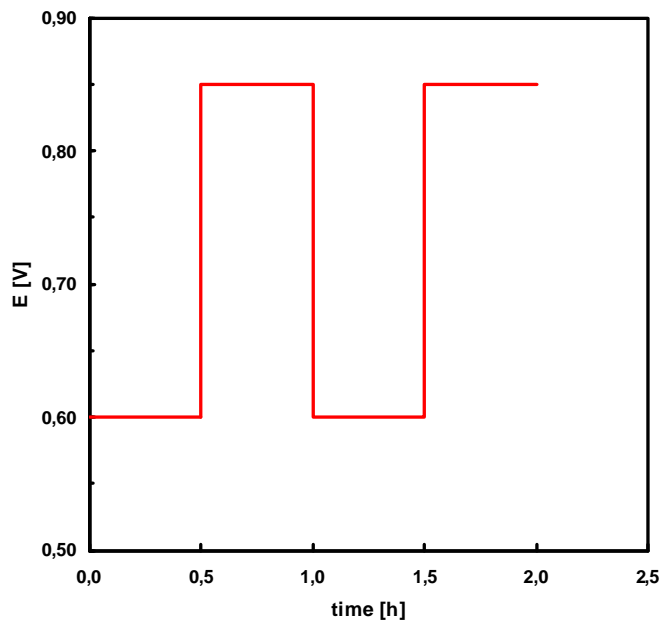


T.J. Schmidt, in *Polymer Electrolyte Fuel Cell Durability*,
 F. Büchi, M. Inaba, T.J.Schmidt (Eds.) Springer, 199-222 (2009)

Stabilized carbons: Carbon Corrosion Results at 1.2V and 180°C



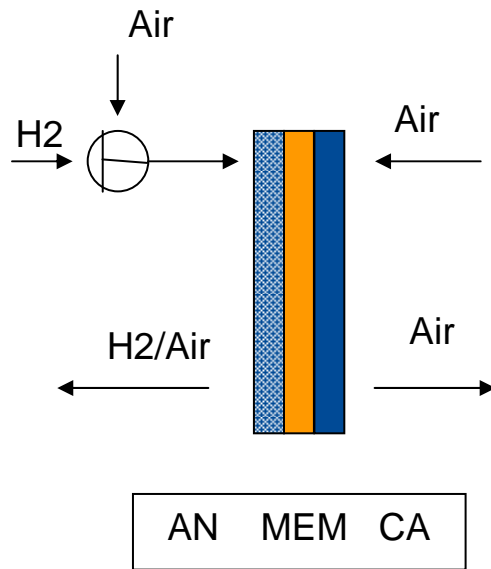
Voltage Cycles/Operation at high cathodic potentials under accelerated conditions



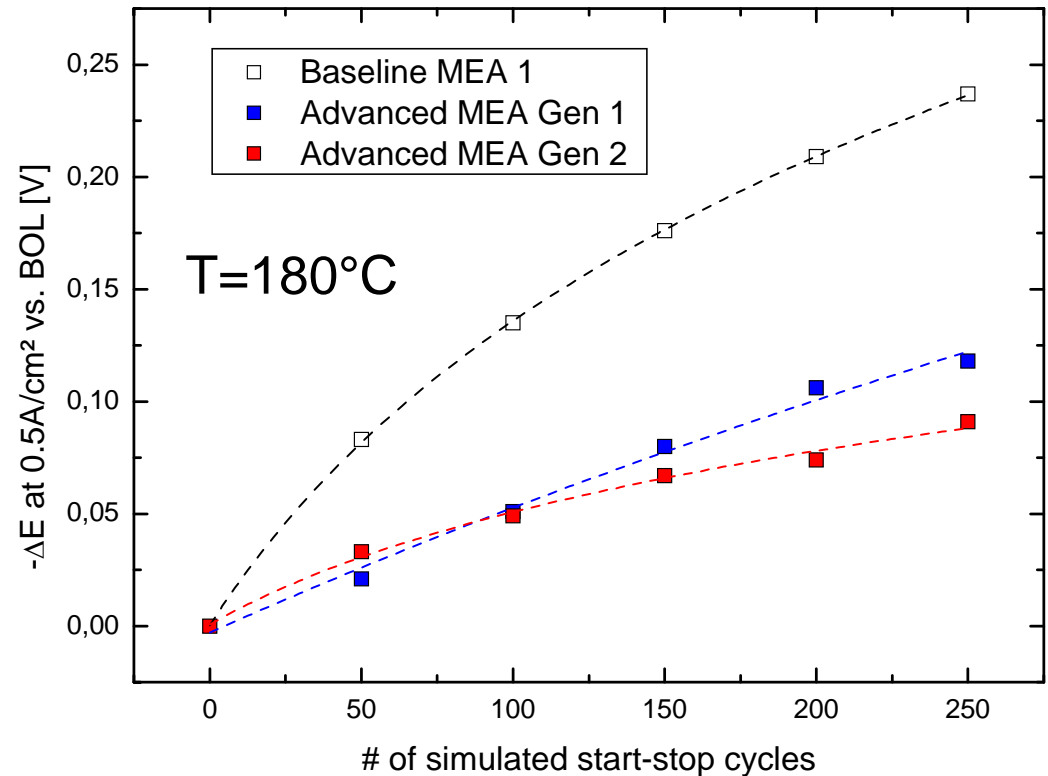
Test: 30 minutes cycles between 0.6V and 0.85V probes catalyst stability

Cycle stability significantly improved with new cathode materials

Start-Stop under accelerated conditions



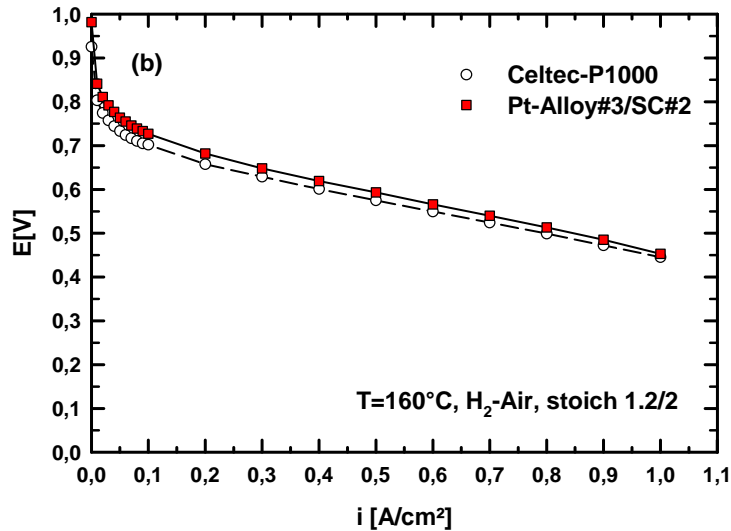
Simulated Start-Stop: Every 30s passing a H₂/Air (Air/H₂) front through anode



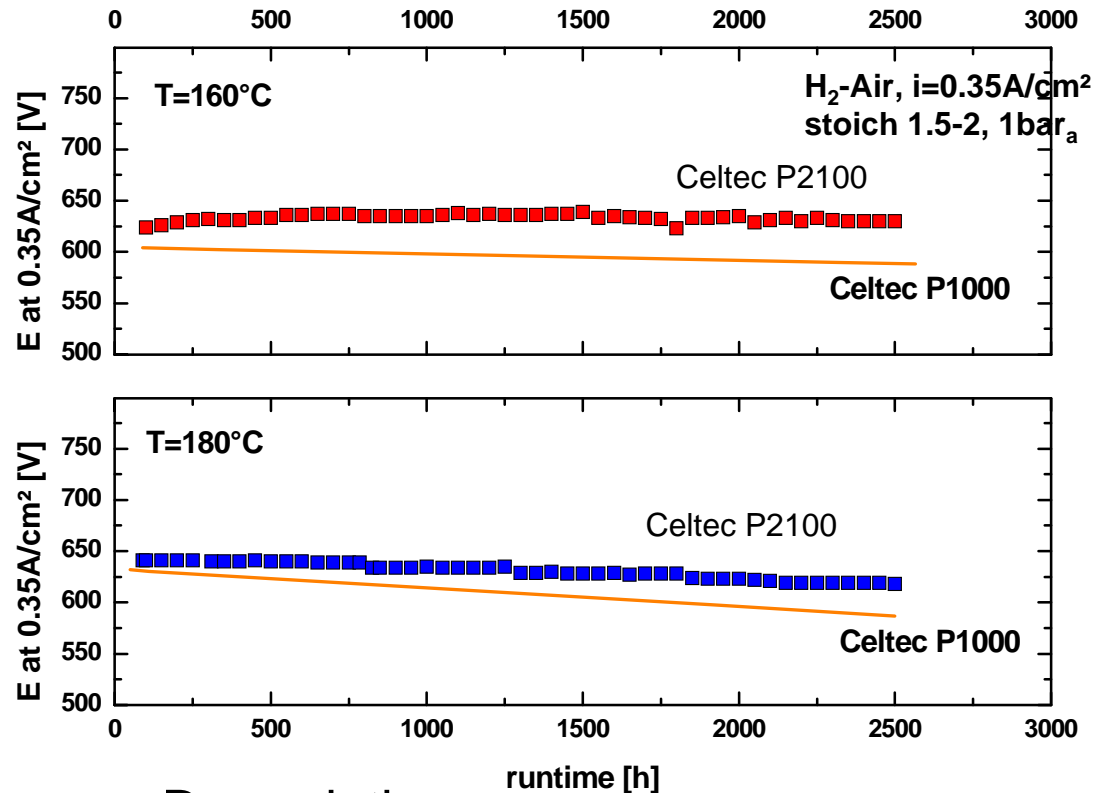
D.C. Steel, B. Benicewicz, L. Xiao, T.J. Schmidt in

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Lifetime tests



New Cathode Generation:
Performance is unaffected



Degradation

160°C : virtually no degradation

180°C : degradation rate in continuous operation improved by factor of 2.4

Summary

R&D Directions in HT-MEA Development

- Increase Membrane Mechanical Strength
 - Simplifies stack building
 - Reduces tolerance requirements
 - Path for next generation manufacturing
- Cathode Alloys
 - Use 21st century tools to design for reduced phosphate anion absorption and realize kinetic potential
 - Exploit new materials with high(er) oxygen solubility
- cathode corrosion
 - stability improvements have be achieved
 - cathode corrosion stability remains focus of development to enter more widespread markets