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TIAX has executed a laboratory-based development program aiming at the improvement of stationary fuel cell systems.

The two-year long development program resulted in an improved understanding of staged fuel cells and inorganic proton conductors through evaluation of results from a number of laboratory tasks:

◆ Development of a fuel cell modeling tool

- Multi-scale model was developed, capable of analyzing the effects of materials and operating conditions
- This model allowed studying various “what-if” conditions for hypothetically staged fuel cells

◆ Study of new high temperature proton conductor

- TIAX discovery of a new class of sulfonated inorganics capable of conducting protons when exposed to water
- study involved synthesis and conductivity measurements of novel compounds up to 140°C

◆ Electrochemical fuel cell measurements

- the feasibility of staged fuel cells was tested in TIAX’s fuel cell laboratories
- experimental design was based on results from modeling

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TIAX* has developed models and materials that address key technologies to improve the efficiency of stationary fuel cell systems.

Results of one of our previous DOE study for a 50 kW PEM fuel cell system produced at introductory scales

2-year program combining modeling and experiments that addressed

- **Membranes promising higher operating temperature**
- **Advanced, multiscale models of catalysts, cells and stacks**
- **Optimization of catalyst loading**
- **Staging of fuel cell stacks to achieve higher efficiency**

****NOTE: TIAX is a new company and was formerly the Technology and Innovation business of Arthur D. Little, Inc., under which this contract originated***

The program proceeded substantially along its planned trajectory, with variations required to adapt to normal uncertainties of advanced research.

INITIAL TASKS and ADDED TASKS	Oct. 2000	April 2001	Oct 2001	April 2002	Aug. 2002
1. Build Test Setup for Stack Testing	■				
2. Verification of Staged Concept using Single Cells		■			
3. Optimize 2-stage Stack for Nafion (voltage)		■			
↳ Catalyst Staging Single Cells			■		
4. Conceptual Design of Staged Stack for Advanced Membranes	■	Task Stopped			
5. Optimization of High Temperature Catalyst		} Tasks canceled due to redirection of program			
6. Screen Optimization Parameters					
7. Statistical Optimization of High Temperature Membranes					
↳ Search Literature for Proton Conductor Candidates		■			
↳ Scan Selected MEA Candidates (Exp. Test of SPEI, sulfonated MeOx)			■		
↳ Focused research of sulfonated TiO₂			■		
↳ Sub-optimize S-TiO₂				■	
↳ Acquire Stacks				■	
◆ Measure Stacks for Staging					■
◆ Incorporate Results in 50kW Model					■

All three major tasks were accomplished and have resulted in improved models, correlations and insights for guiding future research.

Sub-objectives	Results
HT-MEA Development	
Characterize new membranes that promise high temperature operation	<ul style="list-style-type: none">• Correlation of the properties of novel solid acids and binders with conductivity.• Understanding of structures and water dependence needed to achieve and improve performance
Modeling	
Improve model from Phase 1 to model catalyst layers	<ul style="list-style-type: none">• Ability to simulate high temperature performance• Use of simulations to guide and accelerate experiments• Guidance for future protocols to measure fuel cell performance
Staging	
Test feasibility of staging	<ul style="list-style-type: none">• Demonstration of the range of utility of staging• Model incorporating the staging results

Our development of a new class of proton conductor and a new binder confirms the temperature limitations of materials that rely on water.

- **A new class of inorganic proton conductors, based on sulfonated metal oxides, has been identified, the best being nanocrystalline, sulfonated TiO_2**
 - Proton conductivities approach 10^{-2} S/cm
 - Chemically stable against water, in contrast to other “solid acids” recently measured by several R&D groups
 - High conductivity is achieved by increasing the hydrogen ion exchange capacity of the base compound
- **The proton conductivity is yet not as good as Nafion® and, like Nafion, is highly dependent on the presence of water to facilitate proton transfer**

We have created a multi-scale model and analyzed the effects of materials and operating conditions on the performance of a fuel cell.

Model spans microkinetics of surface catalyzed reactions, through transport of molecules and ions to simulate stack performance

Fuel cell staging offers only a small boost in efficiency at peak power but can improve significantly the engineering and cost of an overall system.

CellStage™ Description

Approach for Studying CellStage™

- At peak power, maximum efficiency increases are in the range of 1%
- Validated against fuel cell data in high voltage range, typically not available in literature
- Staged stacks can yield a cost improvement over single stacks of up to 10% through optimal catalyst distribution
- Our analysis suggests that staging also benefits small SOFC systems

Overall costs should decrease by using a staged fuel cell and a HT-MEA but available technology still does not allow a practical system.

- **All available proton electrolyte membranes are highly sensitive to water**
 - 100% humidity needed for our materials for maximum conductivity, which presents system-level difficulties ($P > 1$ atm)
 - Other materials have are degraded by water
- **There is considerable confusion in the literature regarding the essential characteristics of a practical electrolyte and the effective routes forward.**
 - Need for water-insoluble components
 - Absence of structure/activity relations
 - Little information about interactions between binder and inorganic conductor
- **Our model is capable of representing detailed reaction mechanisms and transport**
 - High temperature operation can be simulated using temperature-dependent reaction kinetics and conductivities
 - Paucity of reliable information for calibration and validation
- **Voltage staging affects maximal fuel-cell efficiency weakly but can improve overall operation and costs once the underlying components have been optimized**
 - Flexibility (turndown)
 - Overall efficiency and costs (fewer parasitics, better mixing, catalyst loading, BOP)

It appears that improved analysis and testing methods and consideration of system-level benefits of staging would provide fruitful insights for DOE.

- To gain understanding of potential stack performance improvements the DOE could support:
 - Fundamental analysis and comparison of HT MEA materials (e.g, structure/property relations based on quantum mechanics and molecular dynamics)
 - Development and dissemination of appropriate test protocols for the development of engineering design parameters for fuel cell stacks
- System-level benefits of staging have been extensively studied for large-scale high-temperature fuel cells, but:
 - System-level implications of staging for small-scale fuel cells are not as well understood
 - Benefits of staging in turn-down performance of small high-temperature fuel cell systems could be better characterized (Residential SOFC Analysis)
 - Physical implementation of staging on stack, hot-box, and power electronics should be better characterized
- Some of the (sub-)models developed in this project could be useful modules for other modeling efforts

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Our efforts to develop a HT MEA, since one was not available commercially, have produced new materials and hypotheses for their limits.

Our Approach

- ◆ Search literature and vendors for high acidity compounds and hydrolytically stable compounds
- ◆ Devise novel acid materials
 - Utilize surface groups that tend to bond water (for ion transport)
 - Utilize nanocrystals for enhanced surface area
 - Try to achieve high IEC through targeted synthesis
 - Combine characterization with material synthesis to ensure identity of target compounds and optimize syntheses
- ◆ Investigate binder materials (Nafion, Teflon, SPEI)
- ◆ Use AC impedance methods to quickly scan through candidates

We searched for inorganic compounds with reasonable conductivity at room temperature and high activation energy.

Kinetic parameters for proton transfer in a variety of compounds

- Compounds that have pre-exponential factors and activation energies in the shaded region of the graph are projected to have proton conductivities between 0.01 - 0.1 S cm⁻¹ at 150°C
- Compounds that fall in this shaded region were likely candidates but all were water soluble

A number of efforts at creating high temperature membranes have been reported, but with little success so far.

◆ **Ion conducting polymers without additives**

- ▼ Perfluorinated sulfonic acids. e.g., Nafion: (DuPont, DOW, Asahi Glass, Asahi Chemicals)
- ▼ Sulfonated polyether ether ketone (SPEEK)
- ▼ Sulfonated polyimides: e.g., BAM3G (Ballard)
- ▼ Phenyl sulfone
- ▼ Perfluorosulfonyl imide

◆ **Ion conducting polymers + non-conducting polymer backbone:**

- ▼ Nafion reinforced with teflon (e.g., Gore-Select from W. L. Gore)
- ▼ PBO with sulfonated poly phenyl sulfone (Foster Miller)

◆ **Ion conducting polymer + inorganic proton conductor**

- ▼ Nafion + heteropolyacid such as phosphotungstic acid, silicotungstic acid, phosphomolybdic acid, phosphoric acid, or Silica (DuPont, U. Conn.)
- ▼ Nafion + Butyl Methyl imidazolium triflate (DuPont)
- ▼ S-PEEK + amorphous silica, zirconium phosphate sulfophenylphosphate, zirconium phosphate (DeNora, Julich)

◆ **Non-conducting polymer back bone + inorganic proton conductor**

- ▼ Polybenzimidazole (PBI) + H_3PO_4 (Axiva, Plug-Power)
- ▼ PVDF + CsHSO_4 (Cal. Tech.)
- ▼ PVDF + zeolites (Japanese groups)

Most electrolytes disclosed in the literature have one of two problems: they either require a high degree of hydration, or they leach out in water.

◆ **Ion conducting polymers without additives**

- ▼ It is unlikely that polymeric materials without additives will be viable as high temperature electrolytes as they tend to dry out
- ▼ All the ion conducting polymers are sulfonated forms, which require high degree of hydration to enable proton conduction

◆ **Ion conducting polymers + non-conducting polymer backbone:**

- ▼ Although the non-conducting polymer backbone provides the strength for extremely thin films (e.g., Gore-Select is available as a 12 μm membrane), the fundamental requirement of high degree of hydration remains

◆ **Non-conducting polymer back bone + inorganic proton conductor**

- ▼ Many of the inorganic conductors are extremely soluble in water causing them to leach out when the cell cools down.

◆ **Ion conducting polymer + inorganic proton conductor**

- ▼ As with the previous case, the inorganic component may leach out into water
- ▼ In addition, the sulfonated polymer will have to be somewhat hydrated.

The challenge is to identify inorganic compounds that have adequate proton conductivity at low humidity, and are stable in the presence of liquid water.

A new class of proton conductors discovered at TIAX laboratories shows promise as HT-MEA material, but additional work is needed before commercialization can take place.

- A new class of inorganic proton conductors, based on sulfonated metal oxides has been identified
- Among these sulfonated oxides, nanocrystalline sulfonated TiO_2 demonstrates the highest proton conductivity
 - Best proton conductivities are above 10^{-3} S/cm, and approaching 10^{-2} S/cm
 - The new proton conductor appears more chemically stable against water, in contrast to other “solid acids” recently measured by several R&D groups
 - High conductivity is achieved by increasing the hydrogen ion exchange capacity
 - Some evidence for surface H-diffusion mechanism exists, which opens possibility for enhanced conductivity by bulk modifications besides surface optimization
- Like Nafion, proton conductivity in the materials is highly dependent on water.
- The proton conductivity is not as good as Nafion®
 - The new proton conductor is yet not a practical alternative to Nafion, although it has much lower cost

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Nanocrystalline proton conductors were typically synthesized via a sol-gel process, using alkoxide precursors, here exemplified for TiO_2 .

Synthesis Procedure

Metal
alkoxide
in Isopropanol

Addition of
acid

Hydrolysis
(water addition)

Condensation
(90C vacuum)

Hydrolysis: $\text{Ti}(\text{isopropoxide})_4 + 4\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{Ti}(\text{OH})_4 \cdot \text{H}_2\text{SO}_4 + \text{Isopropanol}$

Condensation: $\text{Ti}(\text{OH})_4 \cdot \text{H}_2\text{SO}_4 \rightarrow \text{TiO}_2 \cdot \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$

The sulfated powder was calcined to produce a nanocrystalline product, which is then pelletized into a membrane using Teflon fibrils.

Calcination

Pelletization

Teflon-bonded
Pellet with Titania

5 μm

Pellet used for
conductivity
measurements

Calcination: $\text{TiO}_2 \cdot \text{H}_2\text{SO}_4$ (amorphous) $\rightarrow$ $\text{TiO}_2 \cdot \text{H}_2\text{SO}_4$ (anatase)

Sulfonated Polyetherimide was investigated as a potential low cost alternative to Nafion as well as a binder for inorganic proton conductors.

Rationale

- Low cost, commercial precursor
- Easy to process into film by phase inversion
- High degree of sulfonation possible
- High temperature stability
- Hydrolytic stability

Results

Polymer	IEC	σ_{ion} S/cm (30°C)
S-PEI	0.95	3.5×10^{-4}
Nafion	0.7	1×10^{-2}

Approach

- Sulfonate Ultem polymer using chlorosulfonic acid in dichloromethane solution at 60°C
- Isolate and wash sulfonated polymer until acid free
- Cast films for AC Impedance Study and IEC

Conclusion

- Conductivity lower than Nafion
- Poor mechanical strength
- Material abandoned

Proton conductivity was measured at various temperatures and humidity levels using AC Impedance spectroscopy.

AC Impedance Technique

- ◆ AC impedance measured between 1Hz to 200kHz, with a 5mV applied signal
- ◆ Ion conductivity extracted from low frequency region of spectra
- ◆ Temperature range: 20°C to 140°C
- ◆ Controlled humidity: 0-100% RH
- ◆ 100% RH measurements under saturated conditions (wet) or steam
- ◆ Quick technique compared to assembly of full MEA and fuel cell measurements

AC Impedance Spectra - Typical Ion Conductor

AC Impedance Spectrometry

Test Cells in Oven

Sample in Test Cell

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DSC Analysis of $\text{Ti}(\text{OH})_4 \cdot \text{H}_2\text{SO}_4$ xerogel indicates a condensation peak around 230°C and a TiO_2 crystallization peak around 520°C .

TGA analysis indicates sulfate decomposition around 520°C, the weight loss is absent in samples prepared with acetic acid or no acid.

XRD of calcined $\text{TiO}_2 \cdot \text{H}_2\text{SO}_4$ shows phase pure anatase TiO_2 . No Titanium sulfate or oxysulfate crystallites are detected.

FTIR of calcined $\text{TiO}_2 \cdot \text{H}_2\text{SO}_4$ shows anatase TiO_2 with absorbed sulfate that appears to be bonded, and not only absorbed, to the titania surface.

Monodentate or bidentate sulfate bridging to the Ti-O backbone affects the ion exchange capacity and proton conductivity.

Bidentate sulfate bridging

Monodentate sulfate bridging

Ion exchange capacity can be modified by variation of calcination temperature.

Calcination illustrates the balance between thermally induced sulfate bonding and sulfate decomposition.

Ionic conductivity is proportional to ion exchange capacity.

Calcination temperature has a significant effect on conductivity as ion exchange capacity is changed.

Ionic Conductivity of S-TiO₂ at Various Calcination Temperatures

100% RH

Increasing Nafion concentration in a S-TiO₂/Nafion composite improves conductivity, with a percolation threshold between 40 to 60%.

Ionic Conductivity of S-TiO₂ with varying Nafion ratio

A 10% Nafion blend enhances conductivity also above 100°C at fully humidified conditions, here for a S-TiO₂-batch having higher conductivity.

**Conductivity is not improved by increasing %sulfuric acid in precursor.
Sulfation appears limited to a maximum of 1.8 meq/gram.**

Conductivity of directly sulfated P25 (commercial product) anatase particles is lower than solgel prepared S-TiO_2 .

Other metal oxides can be sulfated and show high ion exchange capacity, but none as yet has as high conductivity as sulfated TiO_2 .

TIAX needs to improve conductivity in order to have a commercially attractive product, before assessing hydrolytic stability and other key properties.

Next Steps

- **Consider dopants that might improve bond strength of sulfate group.**
 - Quantum chemical modeling and molecular dynamics for identification of potent candidates
 - Increased bond strength may increase conductivity (if IEC also increase)
 - Bond strength should also affect hydrolytic stability for HT operation
- **Explore sulfonation in bulk material**
 - may introduce bulk hydrogen conductivity
 - explore fibrous and layered hydrous TiO_2 , other non-anatase structures, and their sulfated variants.
- **Further assess hydrolytic stability in view of improved conductivity**
- **Further assess fluorination (as water binding agent)**
- **Use other binder than Nafion and explore stability against methanol crossover (enable new more attractive fuel - portable power aspect?)**

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We have created a multiscale model, Grove™, and analyzed the effects of materials and operating conditions on the performance of a fuel cell.

Model spans microkinetics of surface catalyzed reactions, through transport of molecules and ions to simulate stack performance

Elementary reactions
(~nm, ~10⁻¹³ s)

Diffusion, mass transport
(~ μm, ~ 10⁻³ s)

Fluid mixing in channels
(~ cm, 10⁻² s)

1-d and 2-d GROVE™ models were used to assess the benefits of high temperature membranes and the optimum configuration of CellStage™

Model	Configuration of fuel cell simulated	Characteristics	Primary uses
1-D Grove	Small area cell operating under negligible fuel utilization	<ul style="list-style-type: none"> • Cathode kinetics model that is applicable over a wide range of conditions • Anode kinetics: either detailed model for assessing cell performance in the presence of CO or lumped kinetics for modeling measured MEA performance • Species diffusion in GDLs, ionic and water diffusion in membrane • Flow channels assumed well-mixed 	<ul style="list-style-type: none"> • To simulate low-utilization PEMFC performance <ul style="list-style-type: none"> • High temperatures • CO tolerance • Estimate unknown catalyst parameters by fitting Measured MEA performance
2-D Grove	2-D cell with flow channels operating under high fuel utilization.	<ul style="list-style-type: none"> • Cathode kinetics model that is applicable over a wide range of conditions • Anode kinetics: lumped model calibrated by fitting measured performance • Species diffusion in GDLs, ionic and water diffusion in membrane • Flow channels assumed as plug-flow 	<ul style="list-style-type: none"> • Simulate how the cell performance depends on the active area, fuel utilization, etc. • Determine the optimum configuration for CellStage™.

The overpotential bears directly on the performance of the fuel cell.

•Operating conditions for simulations

- ▲ 10 cm^2 cell, Nafion 117 MEA, 80 C, 3 atm, 100 % inlet RH

•Key phenomena described

- ▲ Cathode reactions
- ▲ Membrane resistance
- ▲ Anode reactions

$$V_{\text{cell}} = V_{\text{oc}} - \eta_a - \eta_c - JR_m$$

V_{cell} = cell voltage (V)

V_{oc} = open circuit voltage (V)

η_a = anode overpotential (V)

η_c = cathode overpotential (V)

J = current density (A cm^{-2})

R_m = membrane resistance (W cm^{-2})

Microkinetic models have no inherent assumptions about the kinetics that limit their applicability.

Microkinetics network for PEMFC anode reactions

Microkinetic Models:

- Comprise a sequence of elementary steps, which proceed molecularly as written.
- No assumptions concerning rate determining reactions, reactions in equilibrium, most abundant surface intermediates, etc.
- No assumptions about irreversibility. Hence automatic satisfaction of the de Donder relationships.
- Rate constants are expressed in Arrhenius form, $k = A \exp(-E_a/RT)$, with parameters derived from transition state theory or fundamental measurements
- The reactions listed here are based on current understanding of the mechanism of the anode reactions in the literature
- The highlighted reactions are responsible for electron transfer
- The current is of course directly proportional to the net rate of electron transfer

Generality leads to a large number of coupled stiff differential equations, which must be solved to determine the reaction rates.

CO poisoning at the anode of low temperature PEMFCs leads to poor cell performance.

Effect of CO concentration on Pt cost*

Proposed Strategies

- CO poisons the anode in low temperature fuel cells, leading to poor cell performance and hence high catalyst costs as shown
- Strategies have been proposed in the literature to mitigate the poisoning effects of CO
 - High temperature membranes
 - Oxygen bleed
 - Pulsing of the anode potential
- Time and cost effective optimization among these strategies requires an accurate model for the anode
 - For example, what strategy or combination of strategies will lead to the dashed curve on the figure?

The following section describes the construction and use of an accurate model for the anode kinetics.

Microkinetic models can accurately simulate the performance of fuel cells over a wide range of operating conditions.

- Conventional, global catalyst models represent the data over limited ranges and afford no cross-system learning.
- Microkinetic models, on the other hand, have no inherent assumptions about the kinetics that limit applicability.
- The parameters in a microkinetic model have chemical and physical meaning, affording reusability and broad applicability.
- Advanced microkinetics models provide insight into catalyst performance, including degradation, that bears directly on cost, reliability and control.

The following section describes the construction and use of an accurate model for the anode kinetics.

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We use absolute rate theory to estimate the effect of overpotential on the rate constants of elementary reactions involving charge transfer.

Schematic depiction of the absolute rate theory

- Rate constant modification by electrode potential

$$k_f = A_f \exp\left[-\frac{E_a^f}{RT}\right] \exp\left[\beta \frac{\eta F}{RT}\right]$$

$$k_r = A_r \exp\left[-\frac{E_a^r}{RT}\right] \exp\left[-(1-\beta) \frac{\eta F}{RT}\right]$$

- where β is the symmetry factor (describes the position of the transition state), typically taken as 0.5, ϕ is the electrode potential and ϕ^0 is the electrode potential at which the reaction is in equilibrium
- The current is, of course, directly proportional to the net rate of reaction.
- Note that the overpotential $\eta = \phi - \phi^0$ is a measure of the deviation from equilibrium.

The experimental test station is capable of testing cells or stacks with total area < 200 cm², up to 200°C, 5 bar.

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ElectroBistro shows that a higher average current results from periodic pulsing of the anode overpotential.

Current response to pulsing the anode overpotential

- At the higher cell voltage, CO can be electrochemically oxidized, which leads to a higher current before CO re-adsorbs.
- In estimating the power requirement for pulsing, the following must be taken into account:
 - energy dissipation in charging the double layer
 - impact on the cathode overpotential
 - hence impact on overall cell voltage

Operating conditions

80 C, 3 atm

Overpotential = 0.2 - 0.3 V_{RHE}

Gas: H₂ + 250 ppm CO

High flow rate of gas

0.2 mg Pt /cm², with 10 nm catalyst particles

In agreement with experiment*, ElectroBistro shows that a CO spike causes significant loss of anode activity and that an O₂ pulse accelerates recovery.

Transient performance of PEMFC anode at 0.2 V_{RHE} overpotential

Operating conditions

80 C, 3 atm

Overpotential = 0.2 V_{RHE}

Gas: H₂ + CO + O₂

High flow rate of gas

0.2 mg Pt /cm², with 10 nm catalyst particles

We predict that for Pt electrodes without air bleed, temperatures must exceed 120°C to achieve ‘tolerance’ to 250 ppm CO in PEMFCs.

ElectroBistro prediction of effect of temperature on CO tolerance

- With increasing fuel cell temperature, the sticking probability of CO on Pt decreases. With the result that the surface CO coverage decreases, allowing for a lower anode overpotential.

Operating conditions:

80 C, 3 atm, 0.2 mg/cm² Pt on anode and cathode, w/ 10 nm catalyst particles

Anode: H₂ + CO, Cathode : air

ElectroBistro™ model for PEMFC anode combined with our 1-d GROVE fuel cell model effectively captures the impact of trace levels of CO.

An accurate model for the cathode is required to quantify the potential for power density improvement with high temperature membranes.

- With improved CO tolerance at the anode, the cell performance is dictated by the kinetics of the cathode reactions.
- At high cell voltage (also high fuel cell efficiency), the cathode overpotential limits the cell performance.
- It is expected that operation at high temperatures will reduce the cathode overpotential and hence improve the cell power density.
- However, currently there are no tools to quantify the benefit of operating at higher temperatures.

We estimated the 'best-case' polarization curves by accounting for ohmic losses and the effect of operating conditions on the cathode overpotential.

The projected performance corresponds to a 'best case':

- Mass transfer effects in the GDL and catalyst layers are assumed negligible
- The total ohmic resistance is assumed constant, independent of current density

*Experimental Data From: U. Paulus, T. J. Schmidt, H. A. Gasteiger, R. J. Behm, J. Electroanal. Chem., 495 (2000) 134.

The cell resistance (ionic + electronic) is important in determining the power density for given platinum loading and electrode kinetics.

- Power density curve flattens due to ohmic voltage loss, which reduces the overpotential available for the cathode reaction at the given cell voltage of 0.8 V.

Operating Conditions: 0.8 V, 3 atm, 160 C, 3.5 nm Particles, 2x Pt activity

The cell resistance (ionic + electronic) is important in determining the cost-effectiveness of platinum usage in the stack.

Assumptions: Anode Pt loading = 50 % of that of the cathode, Platinum cost = 18,000 \$/kg, Membrane cost = 50 \$/m², Bipolar + coolant plate = 22 \$/m², GDL = 31 \$/m²

Operating Conditions: 0.8 V, 3 atm, 160 C, 3.5 nm Particles, 2x Pt activity

A factor of 4 reduction in Pt loading is possible if a HTM (having the same ionic resistance as Nafion) allows operation at 140°C instead of 80°C.

- Cell voltage = 0.8 V
- 3 atm, 3.5 nm dia. Pt Particle
- 2x Pt Activity
- $R_{\text{membrane}} = 0.05 \Omega \text{ cm}^{-2}$ (similar to fully humidified 25 μm Nafion film)

However, a factor of 2 increase in catalyst loading is necessary if the HTM operating at 140°C has a factor of four higher resistance than Nafion.

- Cell voltage = 0.8 V
- 3 atm, 3.5 nm dia. Pt Particle
- 2x Pt Activity
- $R_{\text{membrane}} = 0.05 \Omega \text{ cm}^{-2}$ (similar to fully humidified 25 μm Nafion film) or 0.2 W cm^{-2} .

Model results show that HTMs will enhance CO tolerance, but reduction in catalyst loading will depend on the HTM resistivity.

- The general consensus is that, in addition to the benefit of smaller radiators, use of high temperature membranes will result in:
 - simpler fuel processors due to higher CO tolerance at the anode
 - higher power densities due to improved cathode kinetics.
- Until now, there were no tools to quantify the effect of temperature on cell performance, e.g.,
 - what operating temperature will allow complete tolerance to 250 PPM CO?
 - how much will the power density increase by operating at 140°C instead of 80°C?
- To answer such what-if questions, we developed fundamental kinetic models of the anode and cathode that are accurate over a wide range of operating conditions:
 - The model results show that operating at 120°C can provide complete tolerance to 250 ppm CO.
 - However, the potential for improved power density at the higher temperatures can be realized only if the membrane resistance is low.

The 2-D model mimics a fuel cell with flow channels. Essentially, the 1-D model for the GDL and MEAs is propagated along the flow channel.

For given fuel flow, the active area (fuel cell cost) required to achieve a given power density decreases with decreasing cell voltage...

- The energy conversion efficiency is defined as the ratio of output electrical power to the input power in the form of chemical energy of the fuel.
- The operating conditions were: 80 C, 3 atm, 100 % RH, 40 % H₂ (diluted with N₂) and air.
- The flow rates were chosen to give 50 % utilization of H₂ and O₂ at 0.3 A/cm² in a 10 cm² cell.

... however, the maximum efficiency increases with the cell voltage. For example, the maximum efficiency is 53 % at 0.65 V and 60 % at 0.75 V.

Polarization curves were obtained at high reactant flow rates to study the effect of pressure, inlet RH, and H₂ concentration on performance.

Variable	Values used
Pressure	3 atm, 2.2 atm, and 1.2 atm
Inlet RH	100 % and 65 %
H ₂ Concentration	50 %, 30 %, 20 %, 10 %, 5%
O ₂ Concentration	100 %, 30 %

1-D GROVE™ gives a good fit to measured polarization curve and is able to predict the effect of oxygen concentration.

Without further parameter adjustment, 1-d GROVE™ is also able to predict the dependence of cell power density on H₂ concentration.

Calibration of 1-d GROVE Model

Details

- Experimental conditions:
 - 10 cm² single cell, Nafion112 MEA (E-Tek) with 1 mg/cm² Pt loading on both anode and cathode
 - 70 C, 3 atm, 100 % RH anode and cathode
 - Cathode: air, Anode: H₂ in N₂
 - Negligible utilization of fuel and air
- This shows that the model can predict reasonably well cell performance under conditions of high fuel utilization

Polarization curves at different fuel concentrations showed significant mass transport effects at moderate H_2 concentrations.

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Optimization of CellStage™ gave ~ 1.5 % improvement in efficiency for a given stack cost, or a ~ 13 % reduction in cost relative to a single stage.

- Experimental data was first fit by 1-d GROVE model so as to calibrate and validate the model parameters. 2-d GROVE was then used to determine the optimum staging configuration
- Optimization of provides insight into the
 - Model results show that the benefits of CellStage are greater for high efficiency operation
 - The optimum configuration itself changes with operating conditions and cell performance.
 - For a given total area (or cost), CellStage can improve stack efficiency by ~ 1.5 %.
 - Voltage staging by itself reduces cost (power density) by 8 - 13 % relative to single stage stacks.
 - In addition, staging of the catalyst loading also reduces the cost relative to single stacks that have uniform catalyst loading.

The optimum configuration changes with changes in operating conditions, and fuel cell performance.

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We used the 2-d GROVE model to determine the optimum configuration of CellStage™.

◆ 2-d GROVE™ was used to find the optimum configuration for CellStage by studying the effect of the following:

- ▲ Choice of voltages of the two stages
- ▲ Utilization in the first stage, with a fixed overall utilization
- ▲ Different Pt-loading for each stage
- ▲ Total efficiency

F_H = Molar flow rate of hydrogen [moles s⁻¹]

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Model results showed that the efficiency and power density of the staged stack depends on the choice of voltages and ratio of the active area.

2-d Grove Model Results

Details of the Simulations

- Data for the conventional stacks was generated after the kinetic parameters in 2d_GROVE model were revised based on the fit to experimental data
- For all data, only the efficiency corresponding to fuel utilization between 70 and 90 % is shown.
- For the CellStage data, the total active area was varied and the ratio of the active areas (A_1/A_2) was also varied
- Clearly, further optimization is possible for the data shown here

CellStage™ can reduce the area required to achieve a given efficiency depending on the choice of V_1 , V_2 and A_1/A_2 .

The results also show that for a given efficiency, the utilization in the first stage determines the power density that can be obtained.

Measured performance for total area of 60 cm²

Details of the Simulations

- The results show that the power density can be maximized by reducing the utilization in the first stack (U_1) and cell voltage of the second stack (V_2).
- However, the reducing both U_1 and V_2 will reduce the total efficiency.
- Therefore, an optimum choice for U_1 and V_2 exists, for which the cell power density can be maximized.
- The simulations corresponded to 0.8 V for the first stack, 70 C, 3 atm total pressure, air feed on cathode, 50 % hydrogen diluted with nitrogen on the anode.

A single stage was first optimized for 0.75 V and 90% utilization by choosing the anode catalyst loading that minimized stack costs.

The anode catalyst for the Cellstage was chosen so as to minimize stack costs at 90 % utilization

Details

- Operating voltage = 0.75 V
- Total fuel utilization = 90 %.
- Operating conditions: 80 C, 3 atm, 25 μm Nafion membrane, 0.4 mg Pt/cm² on cathode
- Flows: 50 % H₂ in N₂ for the anode, air at 3 stoichs for the cathode
- Costs: Platinum = 19 \$/g, Nafion = 100 \$/m², Bipolar plates + GDL = 50 \$/m².
- At low catalyst loading, the costs of non-catalytic materials dominate, whereas the higher costs of the platinum are offset by higher power density

With respect to the optimized single stage, CellStage improves power density by ~ 5% and efficiency by ~ 0.3%.

Efficiency change was calculated for identical power densities of CellStage and the single stage stack

Power density comparisons are made for the same efficiency of CellStage and single stage

Operating Conditions: 3 atm, 80°C, catalyst loadings: 0.2 mg Pt /cm² anode and 0.4 mg Pt/cm² cathode, Flows: 50 % H₂ in N₂ anode and Air at 3 times stoichiometry cathode, total fuel utilization at 90 % for all cases.

Note that an ‘apples to apples’ comparison requires efficiencies to be compared at identical power densities and *vice versa*.

Experimental results with two single cells showed that staging can improve efficiency by 2-3% over non-optimized single stage.

Operating conditions:

- Fixed total area
- Varied V_2 with V_1 held constant
- Fixed fuel flow
- 70 C, 30 atm, 60 cm² cell, 100 % RH
- Anode: 6.8 A equivalent of H₂ of 50 % H₂ in N₂,
Cathode: 24 A equivalent of O₂

However, at lower efficiencies, the efficiency improvement afforded by CellStage could also be obtained by lowering voltage of the single stage.

- In the conventional stack, the entire 60 cm² active area operated at the same voltage.
- In CellStage, cell 1 was operated at voltages of 0.757, 0.737, 0.721, 0.707, and 0.689 V. For each voltage of cell 1, cell 2 was operated at 0.8 V, 0.75, 0.7, 0.65, and 0.6 V.
- In these experiments, the flow rate was held constant.

For fixed area, the efficiency can be increased by decreasing the cell voltage or by decreasing the flow rate.

Measured performance of a 60 cm² single cell

Staging could significantly improve turn-down performance, and possibly cost of residential SOFC systems.

- Voltage staging offers significant benefits in system efficiency, especially at turn-down:
 - Modest efficiency gains at peak power (~1%)
 - Over 10% efficiency improvement at turn-down
 - Further turn-down possible by allowing some stack to “idle” (thermal management)
- Balance of plant benefits could accrue from staged air and fuel supply:
 - Increased internal reforming possible
 - Reduced need for anode recycle
 - Reduced air preheat requirements

Annual Fuel Consumption and Operating Cost for Stand-Alone Residential SOFC + BES Systems

For assumptions see main report

We believe that with our staged-stack concept, overall system efficiency can be increased from 42% to 44% cost-effectively.

- ◆ The highest efficiency conventional systems are projected to achieve 42% LHV efficiency
- ◆ CellStage™ could increase this level to 44% by:
 - Increasing average cell voltage operation from 0.77 to 0.79 V
 - Decreasing cathode humidity requirements from 90% to 80%
- ◆ Catalyst staging does not significantly increase energy efficiency, but will significantly affect cost due to lower overall catalyst loading

Overall system efficiencies for 50 kW fuel cell power generators has been evaluated using a thermodynamic model.

We modeled the staged concept assuming the cell voltage and humidity requirements would be more favorable than a conventional system.

- Model based on steady state operation (no transients)
- PEM fuel cell stack with cooling and humidification
 - Conventional high efficiency system assumes 0.77 V single cell voltage and 90% cathode inlet relative humidity (RH)
 - Staged concept assumes 0.79 V and 80% RH

Fuel Cell Stack Assumptions	Conventional	Staged
Operating Temperature	70 °C	70 °C
Operating Pressure	1.5 atm ¹	1.5 atm ¹
Hydrogen Utilization	90%	90%
Single Cell Voltage	0.77 V	0.79 V
Cathode Excess Air	100%	100%
Cathode Humidification Requirements	90% RH	80% RH

¹ 3 atm is often targeted in automotive applications, but 1.5 atm is more practical for stationary applications.

The lower humidification requirements for the staged concept allow us to recuperate more heat from the steam reformer burner (or TGB).

- Steam reformer (SR) with high and low temperature shift beds and CO cleanup (PrOX)
- Integrated SR burner with recuperation
- Fueled by methane and anode off-gas
 - Supplies heat for the steam reforming reaction, preheats fuel, generates steam, and provides heat required for cathode humidification
- Balance of Plant components include: pumps, compressors, fans, heat exchangers, and power electronics

BOP Assumptions	Conventional	Staged
Fuel for Fuel Processor	Methane ¹	Methane ¹
Steam Reforming Temperature	750 °C	750 °C
Burner Air Recuperation Temperature	550 °C	700 °C
Compressor Efficiency	70% ²	70% ²
Power Electronics Efficiency ³	95%	95%

¹ Main component in natural gas.

² These efficiencies represent targets that are necessary for obtaining high overall system efficiency.

³ Power electronics are necessary on a stationary system to convert the fuel cell generated DC power to usable AC power.

More burner recuperation and higher voltage increase the fuel processor and stack efficiencies, increasing overall efficiency from 42 to 44%.

System Performance Parameters (LHV basis)		Conventional		Staged	
		Eff, %	Power, kW	Eff, %	Power, kW
1	Net AC power output (design specification)		50.0		50.0
2	Total AC parasitic loads (compressor, fans, pumps)		3.7		3.5
3	Power electronics efficiency (aggressive assumption)	95		95	
4	Gross DC power		56.4		56.1
5	Stack Efficiency ¹ (includes voltage, utilization, and loss from air-bleed)	55		57	
6	Hydrogen required at anode		101.9		98.9
7	Fuel processor efficiency ¹ (reformer, water-gas-shift, and PROX)	85 ²		87 ²	
8	Fuel (methane) required		119.7		113.5
9	Overall system efficiency	42		44	

¹ The fuel processor uses the un-utilized hydrogen of the fuel cell to generate heat for the reforming reaction, but the un-utilized hydrogen is not included as a fuel input for the fuel processor efficiency calculation. The un-utilized hydrogen is taken into account in the fuel cell efficiency calculation instead.

² SR-based fuel processor efficiency assumes a high level of heat integration that has not been verified experimentally, but could be possible based on thermodynamic analysis assuming reasonable approach temperatures. Note: This efficiency could be >100%, since it does not include the un-utilized hydrogen from the fuel cell as an input (see footnote 1).

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Conclusions

Overall costs should be decreased by using a staged fuel cell and a HT-MEA but available technology still does not allow a practical system.

- **All available proton electrolyte membranes are highly sensitive to humidification**
 - 100% humidity needed for our materials for maximum conductivity, which presents system-level difficulties ($P > 1$ atm)
 - Other materials have similar need for water and/or are degraded by water
- **There is considerable confusion in the literature regarding the essential characteristics of a practical electrolyte and routes forward.**
 - Need for water-insoluble components
 - Absence of structure/activity relations
 - Little information about interactions between binder and inorganic conductor
- **Our model is capable of representing detailed reaction mechanisms and transport**
 - High temperature operation can be simulated using temperature-dependent reaction kinetics and conductivities
 - Paucity of reliable information for calibration and validation
- **Voltage staging affects maximal fuel-cell efficiency weakly but can improve overall operation and costs**
 - Flexibility (turndown)
 - Overall efficiency and costs (fewer parasitics, better mixing, catalyst loading, BOP)

Next Steps

It appears that improved analysis and testing methods and consideration of system-level benefits of staging would provide fruitful insights for DOE.

- To gain understanding of potential stack performance improvements the DOE could support:
 - Fundamental analysis and comparison of HT MEA materials (e.g, structure/property relations based on quantum mechanics and molecular dynamics)
 - Development and dissemination of appropriate test protocols for the development of engineering design parameters for fuel cell stacks
- System-level benefits of staging have been extensively studied for large-scale high-temperature fuel cells, but:
 - System-level implications of staging for small-scale fuel cells are not as well understood
 - Benefits of staging in turn-down performance of small high-temperature fuel cell systems could be better characterized (Residential SOFC Analysis)
 - Physical implementation of staging on stack, hot-box, and power electronics should be better characterized
- Some of the (sub-)models developed in this project could be useful modules for other modeling efforts

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References PEMFC Modeling & Calibration

- T. E. Springer, T. Rockward, T. A. Zawodzinski, and S. Gottesfeld, *J. Electrochem. Soc.* **148**:A11 (2001)
- U. Paulus, T. J. Schmidt, H. A. Gasteiger, R. J. Behm, *J. Electroanal. Chem.*, 495 (2000) 134.
- E. J. Carlson, J. H. Thijssen, S. Lasher, S. Sriramulu, G. C. Stevens, and N. Garland, in 2002 Future Car Congress Proceedings, *SAE International*, Arlington, Virginia, 2002, p. 8 pp.
- J. Dumesic, D. Rudd, L. Aparicio, J. Rekoske, and A. Trevino, The Microkinetics of Heterogeneous Catalysis, American Chemical Society, Washington, D. C., 1993.
- E. Shustorovich and H. Sellers, *Surface Science Reports* **31**:1 (1998).
- Haile, *Solid State Ionics* **77** (1995) 128
- Gong, *Mater. Res. Soc. Symp. Proc.* **135**,377 (1989)
- Casciola, *Solid State Ionics*, **22** (1986) 127
- Lal, *Solid State Ionics*, **5** (1981) 451
- Howe, *Mat. Res. Bull.* **12** (1977) 701
- Nakamura, *Chem. Letters* (1979) 17
- Savinell, US5525436, US6025085
- Kreuer, *Solid State Ionics*, **28-30** (1988) 589
- Adrian, *Green Chemistry*, February (1999) p. 17-20
- Parvulescu, *Applied Catalysts A: General* **176** (1999) 27-43
- Yadav, *Microporous and Mesoporous Materials*, **33** (1999) 1-48
- Song, *Catal. Rev. Sci. Eng.* **38** (3), 329-412 (1996)
- Hino, Arata, *J. Chem. Soc. Chem. Commun.*, (1980) 851
- Hino, Kobayashi, *J. Am. Chem. Soc.*, **101**, (1979) 6431
- Arata, *Applied Catalysis A: General* **146** (1996) 3-32

References PEMFC Modeling & Calibration

- Slade, Solid State Ionics 35 (1989) 29-33
- Slade, Solid State Ionics 38 (1990) 207
- Dalai, Inc. Eng. Chem. Res. 37 (10) (1998), 3869-3878
- Peak, Journal of Colloidal and Interfacial Science 218, 289-299 (1999)
- Hug, Journal of Colloidal and Interfacial Science 188, 415-422 (1997)
- Kurosaki, Nippon Kagaku Kaishi, (1976), p. 1816
- David, Catal. Today 20 (1994) 219-256
- Song, Catal. Rev.-Sci. Eng. (1996), 38, 329-411
- Yamazaki, Applied Catalysis A: General 210 (2001) 97-102
- Huang, Applied Catalysis A: General 171 (1998) 65-73
- Zhen, Journal of Molecular Catalysis A, Chemical 178, (2002) 97-104
- Proton Conductors, Colomban, Cambridge Univ. Press (1992)
- TIAX Laboratory Notebook 28544: pages 22, 23, 24, 27, 28, 29, 30, 31, 32, 33, 34
- TIAX Laboratory Notebook 28626: pages 25, 26

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Using polarization curves at different H_2 concentrations, we can visualize how the current density in a large area cell will depend on fuel utilization.

Note, we obtained the data under conditions of negligible utilization.

For hydrogen concentrations less than 30 %, the cell performance depends strongly on the hydrogen concentration.

The fuel cell performance decreases with a decrease in operating pressure and inlet humidity.

At 1.2 atm, the effect of inlet RH on cell performance is not as significant as at 3 atm.

For hydrogen concentrations less than 30 %, the cell performance depends strongly on the hydrogen concentration.

Cell performance decreases with decreasing pressure for given hydrogen concentration.