R&D Plan for the
High Temperature Membrane Working Group

Introduction/Background

The High Temperature Membrane Working Group was established to provide a forum for greater interaction in the effort to develop high temperature membranes for PEM fuel cells. The goal of this effort is particularly challenging and requires significant fundamental research and development. The Working Group meets twice a year (immediately before or after the Electrochemical Society meeting) and includes universities, national labs, small business and industry and is open to any interested individual/organization. The first meeting was in October, 2000. Working Group members are listed in Appendix A.

This plan was developed to guide the R&D activities of the Working Group. The Roadmap contains four primary topic elements:

1. **Status of Membrane Technology for PEM Fuel Cells for Automotive and Stationary Applications.**
   This section is a review of the desired characteristics for membranes and provides the rationale for developing new membranes for elevated temperature operation. The inability of membranes that satisfactorily operate at 80^oC to perform at 120^oC is documented.

2. **Development Challenges & Potential Solutions**
   The technical challenges in developing high temperature membranes that must be resolved are listed and the current approaches to resolve those challenges described. The weaknesses of these approaches are also summarized.

3. **New Approaches to develop Elevated Temperature Membranes and Catalyst-Coated Membranes (CCMs) Are Needed.**
   A near-term phased approach is proposed that would explore proton conductors at higher temperatures in the near-term. Longer-term approaches are also proposed and preparation of CCMs and supporting research are considered as well.

4. **Technical Targets and Schedule**
   Technical performance targets for both membranes and CCMs and for both automotive and stationary applications have been developed and reviewed by the Working Group. A preliminary schedule for implementing approaches is also presented.

1. Status of Membrane Technology for PEM Fuel Cells

A. Reasons to Develop Membranes for Elevated Temperature Operation

- Rejection of heat from fuel cell stacks operating at 80°C is difficult, requiring radiators with large surface area.
- Tolerance to impurities, most notably CO, increases substantially at $T \geq 120°C$. For stationary applications, the largest system enhancements are obtained for temperatures $\geq 150^{o}C$.
- Electrode kinetic rates generally increase with increasing temperature resulting in improved cell performance.

B. Desired Characteristics of Membranes for Fuel Cells for Automotive and Stationary Applications

- Operation at a temperature of $120^{o}C$ for automotive applications.
- Operation at temperatures > $150^{o}C$ for stationary applications.
- Low resistance under cell operating conditions.
- Long-term chemical and mechanical stability at elevated temperatures in oxidizing and reducing environments.
- Good mechanical strength, preferably with resistance to swelling.
- Low gas cross-over--pinhole free!
- Interfacial compatibility with catalyst layers.
- Low cost.
- Minimal or zero dependence on external hydration.

C. State of Development of Fuel Cell Membranes

- Present-day, state-of-the-art membranes used in PEMFCs operating at 80°C do not possess long-term stability when operating at 120°C.
- Various approaches underway to develop new membranes (see 2.B. below) are of uncertain value for operation at $T \geq 120°C$.

2. Development Challenges & Potential Solutions

A. Development Challenge

- More thermally stable membranes needed, **<u>BUT</u>** membranes also must maintain conductivity.
- Two approaches proposed to address this challenge:
  - o for automotive applications, develop membranes for operation at $T \approx 120°C$ (would reduce radiator size by 50% and allow use of conventional coolants {ethylene glycol}; but would have limited impact on CO tolerance)
  - o for stationary applications, develop membranes for operation at $T \geq 150^{o}C$ (would allow a dramatic decrease in radiator size and have excellent CO tolerance, eliminating some fuel processor clean-up components for operation on reformate)

- Critical technical requirements depend on application
  - o $T \approx 120°C$: need to maintain or enhance water content to

achieve proton conductivity

- o T ≥ 150°C: need to replace water function to achieve proton conductivity

B. Present-day Approaches to Elevated Temperature Membranes

- New Polymeric Materials
  - o Typically sulfonated aromatics
- Conductivity-enhancing additives to new or existing polymers
  - o Dispersed solid acids
  - o Water 'traps'
  - o Sol-gel phase
- Solid-state Materials
  - o Oxides
  - o Proton-conducting glasses
- Water 'replacements' in Polymers
  - o Imidazole (Kreuer)
  - o Inorganic phases
  - o Phosphoric Acid and other acids

C. Weaknesses of Present-day Approaches to develop Elevated Temperature Membranes

- Difficult to make catalyst-coated membranes (CCMs) that function well
  - o Difficulty in fabricating CCMs
    - Polymers with improved thermal stability typically have less favorable mechanical and interfacial properties
  - o Difficulty in maintaining cathode function with low hydration levels
    - Polymers with solid additives ultimately fail to meet the requirement for intimate interaction between acid moieties and Pt sites
    - New polymers are most typically (though not always) sulfonated aromatics with lower acidity; this lower acidity has substantial negative implications for catalyst layer performance for low water content systems
    - Liquid additives (phosphoric acid, imidazole) tend to adsorb on Pt
- Polymers with longevity uncertainities, even at 120^{o}C, are used in some approaches
- In some approaches, materials are used that water can wash away (imbibed liquid acids, solid inorganic acids)
- Thermally stable polymers often have mediocre conductivity, especially under decreased humidification conditions
- Start-up, life-cycle issues: Materials must conduct at low temperatures to allow fuel cell 'bootstrapping'. Additives must not wash out in the presence of condensed water as cell is cooled.

3. New Approaches to develop Elevated Temperature Membranes and CCMs Are Needed

A. Phased approach to new membrane development is suggested

B. Proton conductors for operation at high temperatures should be explored in the near term (present through FY 2005)

- Identification of additional thermally stable proton conductors that would allow higher temperature applications should be targeted
- Given the difficulty of the higher temperature goal, this approach could provide a 'fall-back' position
- Most approaches have clear flaws and thus some development should focus on overcoming these flaws
- Proton conductors which operate at T > 150°C represent a difficult challenge requiring sustained long-term effort (present through FY '08)

C. Near-term Approaches:

- New polymers with improved thermal stability
- Polymers with hydrophilic additives or improved hydrophilicity
- Polymers with added acids
- Water-dependent inorganic conductors
- Phosphoric acid-based systems
- Emphasis should be on non-Nafion systems

D. Longer-term Approaches:

- New polymers with improved thermal stability form a basis for conduction
- Non-aqueous proton conductors and additives
- Inorganic conductors

E. An additional, essential problem for all approaches: Preparation of CCMs/MEAs

- New approaches needed to achieve good adhesion between polymer membrane and catalyst layer
- Detailed understanding of nature of local structure in catalyst layers, linked to function, must be pursued
- Non-adsorbing ionic conducting phases should be looked at

F. Fundamental Supporting Research

- Improved understanding of proton dissociation, conduction in non-aqueous systems needed
- Research focusing on materials properties of catalyst layers needed

4. Technical Targets and Schedule

A. Necessary Attributes and Technical Targets for High-temperature Membranes and CCMs. Suggested schedule for Implementing Approaches that were detailed in Section 3.

- Membrane Attributes:
    - low cost
    - high ionic conductivity
    - electrically insulating
    - gas impermeable
    - conduction independent of water content
    - physical properties independent of water content
    - high temperature performance (including improved CO tolerance)
    - maintain conduction in face of repeated exposure to condensed water
    - able to conduct sufficiently at low temperature to allow bootstrapping of stack
    - durable
    - good interfacial properties
    - mechanical strength
    - recyclable
- CCM Attributes:
    - resistant to CO poisoning in the presence of percent levels of CO
    - ultra low loading of precious metals
    - good performance with minimal hydration
    - low cost
- Technical Targets for Membranes: Automotive Applications
    - See Table I
- Technical Targets for CCMs: Automotive Applications
    - See Table II
- Technical Targets for Membranes: Stationary Applications
    - See Table III
- Technical Targets for CCMs: Stationary Applications
    - See Table IV
- Proposed Schedule
    - See Figure I

Table I: Technical Targets for Membranes: Automotive

All targets must be achieved simultaneously

Characteristics	Units	Calendar year		
		2003 status[a]	2005[b]	2010[b]
Membrane conductivity @ 25% RH @ Operating Temperature	Ω-cm^{-1}	0.02	0.05	0.1
@ Room Temperature	Ω-cm^{-1}	0.05	0.07	0.07
@ -20^{o}C	Ω-cm^{-1}	0.01	0.01	0.01
Oxygen cross-over[c]	mA/cm^2	5	5	2
Hydrogen cross-over[c]	mA/cm^2	5	5	2
Cost[d]	$/kW		50	5
Operating Temperature	^{o}C	80	120	120
Durability[e]	hours	1000	>4000[f]	>5000[g]
Survivability[h]	^{o}C	–20	–30	–40
Thermal Cyclability in Presence of Condensed Water		YES	YES	YES

Notes:

a) Status is present day @ 80^{o}C unless otherwise noted
b) Targets are for new membranes/CCMs
c) Tested in CCM
d) Projected to mass manufacturing, 500,000 stacks
e) Performance targets must be achieved at the end of the durability time period
f) Includes thermal cycling
g) Includes thermal and realistic drive cycles
h) Indicates temperature from which bootstrapping stack must be achieved

Table II: Technical Targets for CCMs: Automotive

All targets must be achieved simultaneously

Characteristics	Units	Calendar year		
		2003 status[a]	2005[b]	2010[b]
Membrane Areal Resistance in cell, 25% Relative humidity @ operating temperature	Ω-cm^2	0.03	0.05	0.1
@ Room Temperature	Ω-cm^2	0.15	0.15	0.1
@ -20^{o}C	Ω-cm^2	0.7	0.5	0.3
Cost[c]	$/kW	200	100	10
Operating Temperature	^{o}C	80	120	120
Durability[d]	hours	1000	>2000[e]	>5000[f]
Survivability[g] temperature - lower Upper	^{o}C ^{o}C	–20 ?	–30 175	–40 200
Total Catalyst Loading (both electrodes)	mg/cm^2 g/kW(peak)	0.8 2	0.4 0.5	0.1 0.08
Performance @ 0.25 power (0.8V)	mA/cm^2 mW/cm^2	125 100	250 200	400 320
Performance @ full power	mW/cm^2	400	800	1280
Extent of Performance Degradation Over Lifetime	%	-10	-10	-10
CO Tolerance (steady state—w/o air bleed)	ppm	100	2000	5000
Recoverability CO (transient)	ppm	500	10000	10000
Thermal Cyclability in Presence of Condensed Water		YES	YES	YES

Notes:

a) Status is present day @ 80^{o}C unless otherwise noted
b) Targets are for new membranes/CCMs
c) Projected to mass manufacturing, 500,000 stacks
d) Performance targets must be achieved at the end of the durability time period
e) Includes thermal cycling
f) Includes thermal and realistic drive cycles
g) Indicates temperature from which bootstrapping stack must be achieved

Table III: Technical Targets for Membranes: Stationary
All targets must be achieved simultaneously

Characteristics	Units	Calendar year		
		2003 status[a]	2005[b]	2010[b]
Membrane Conductivity @ Operating Temperature	Ω-cm^2	0.1	0.1	0.1
Oxygen Cross-over[c]	mA/cm^2	5	5	2
Hydrogen Cross-over[c]	mA/cm^2	5	5	2
Cost[d]	$/kW		100	50
Operating Temperature	^{o}C	160	175	180
Durability[e]	hours	5000	>15000[f]	>40000[f]
Survivability[g]	^{o}C	–20	–30	–40

Notes:

a) Status is present day 80^{o}C unless otherwise noted
b) Targets are for new membranes/CCMs
c) Tested in CCM
d) Projected to mass manufactured 1,000 stacks
e) Performance targets must be achieved at the end of the durability time period
f) Includes thermal cycling
g) Indicates temperature from which bootstrapping stack must be achieved
h) All conductivity numbers must be achieved without humidification and with proton transference number >0.95

Table IV: Technical Targets for CCMs : Stationary

All targets must be achieved simultaneously

Characteristics	Units	Calendar year		
		2003 status[a]	2005[b]	2010[b]
Membrane Areal Resistance in Cell, @ Operating Temperature	Ω-cm^2	0.1	0.1	0.1
Cost[c]	$/kW	TBD	250	100
Operating Temperature	^oC	160	175	180
Durability[d]	hours	5000	>15000[e]	>40000[e]
Survivability[f]	^oC	–20	–30	–40
Catalyst Loading	mg/cm^2 g/kW(0.7 V)	2	1	0.25
Performance (@0.7 V) --EOL	A/cm^2	0.15	0.25	0.35
CO tolerance (steady state—w/o air bleed)	ppm	8000	30000	50000
Recoverability CO (transient, <30 min)	ppm	20000	50000	100000

Notes:

a) Status is present day @ 80^{o}C unless otherwise noted
b) Targets are for new membranes/CCMs
c) Projected to mass manufactured 500,000 stacks
d) Performance targets must be achieved at the end of the durability time period
e) Includes thermal cycling
f) Indicates temperature from which bootstrapping stack must be achieved

Figure 1. Gantt chart to be inserted later.

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