JOURNAL OF
POWER
SOURCES

Short communication

The United States Department of Energy's high temperature, low relative humidity membrane program

Nancy L. Garland [a,*], John P. Kopasz [b]

[a] U.S. Department of Energy, 1000 Independence Avenue, SW, Washington, DC 20375-0121, USA
[b] Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

Abstract

The U.S. Department of Energy (USDOE) Hydrogen Program works with industry, academia, and National Laboratories through research and development to overcome technical barriers of fuel cell and hydrogen production, delivery, and storage technologies. Two of the major challenges in the advancement of fuel cell technology are cost and durability of the polymer electrolyte membranes used for proton conduction in the fuel cell. To address these challenges, DOE initiated new membrane research and development projects to design membranes that meet its 2010 technical targets and will lead to membranes that operate in a fuel cell system that performs as well and costs as little as internal combustion engines. Three strategies are employed in the program: implementation of phase segregation in the membrane to create proton conduction pathways, use of non-aqueous proton conductors for operation under dry conditions, and hydrophilic additives to retain water at low relative humidity.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Polymer electrolyte fuel cells; Membrane; Hydrogen fuel cell

1. Introduction

The goal of the Fuel Cell Program at the U.S. Department of Energy is to develop and demonstrate fuel cell power system technologies for transportation, stationary, and portable applications. For light-duty vehicle applications, R&D efforts are focused on polymer electrolyte membrane (PEM) fuel cells that typically operate at low temperature ($\sim$80 °C) and have minimal start-up and transient response times compared to other types of fuel cells. Current polymer electrolyte membranes used in fuel cells depend on the presence of water to conduct the protons thus they are limited to operating temperatures of 60–80 °C and require external humidification to maintain optimum performance. The conductivity of membranes decreases as the relative humidity (RH) decreases because typically the membrane relies on water to "ferry" the protons from the anode to the cathode [1]. Conductivity of the membrane increases slightly as the temperature increases [2], and then decreases at higher temperature as the water content decreases.

PEM fuel cell systems require thermal and water management systems to maintain temperature and keep the membrane humidified. The thermal and water management requirements increase the weight and volume of the system and add system complexity. These issues could be minimized if the fuel cell could be operated at higher temperatures (up to 120 °C) and at lower relative humidity. If no humidification is used, then flooding issues are reduced at operating temperatures below 100 °C and eliminated at operating temperatures above 100 °C. When on-board reforming of gasoline or natural gas was considered as an interim pathway to introduce fuel cell vehicles into the marketplace, poisoning of fuel cells by carbon monoxide in the reformate fuel was a concern; operation of fuel cells running on reformate but at higher temperature would mitigate CO poisoning. CO poisoning is of less concern now that direct hydrogen is the fuel for transportation fuel cells; however, increasing the CO tolerance would reduce the cost of hydrogen from hydrocarbon sources.

To determine the benefits of PEM fuel cell operation at higher temperatures, Ahluwalia examined the effect of pressure, temperature, and relative humidity on radiator heat load Q of an 80 kW$_e$ fuel cell system [3]. Heat load is the amount of heat that a radiator needs to reject from the system. Ahluwalia showed

* Corresponding author. Tel.: +1 202 586 5673; fax: +1 202 586 9811.
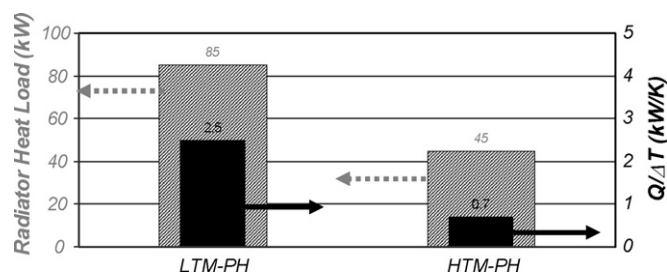*E-mail address:* nancy.garland@ee.doe.gov (N.L. Garland).

Fig. 1. Radiator heat load for 80 kW fuel cells systems. LTM-PH, low temperature pressurized (2.5 atm) and humidified; HTM-PH, high temperature pressurized (2.5 atm) and humidified.

that the radiator could be reduced to one-third the size if the operating temperature is increased from 80 to 120 °C as illustrated in Fig. 1. $Q/\Delta T$, a measure of the ease with which heat can be rejected from a system, decreases from 2.5 kW K^{-1} for an 80 °C humidified system to 0.7 kW K^{-1} for a 120 °C system. Since other components such as humidifiers and condensers get larger as the temperature is raised from 80 to 120 °C, balance-of-plant advantages would be lost if the fuel cell system needs to maintain a high relative humidity. A membrane whose proton conductivity does not depend on humidification level would allow the fuel cell developer to eliminate air and fuel humidifiers, reduce the sizes of air and fuel pre-heaters, and maintain the stack at 120 °C at all loads [3]. In 2006, the DOE initiated 12 new R&D projects by industry and academic researchers to develop polymer electrolyte membranes that operate at high temperature and low relative humidity and that approach the 2010 DOE technical targets for membranes. These membranes must operate under all conditions specified in the technical targets table, including start-up from sub-freezing conditions. The status of

polymer electrolyte membrane properties and the DOE 2010 and 2015 technical targets for these membranes and found in Table 1. The target for membrane conductivity in 2010 is 0.1 S cm^{-1} at 120 °C and 1.5 kPa inlet water vapor partial pressure to the fuel cell stack (50% relative humidity at room temperature). In the rest of this manuscript, lessons learned from several previous DOE membrane projects will be described and then strategies for the new DOE high temperature membrane program and the new R&D projects that incorporate those strategies will be discussed.

2. Previous DOE R&D efforts on membranes

Several important lessons have been learned from previous DOE-funded membrane research projects. Membrane development can be challenging because properties such as conductivity, chemical stability, mechanical strength, and durability as well as cost must be achieved simultaneously. Often an improvement of one property of a material is accompanied by a change for the worse of another property. For example, decreasing the equivalent weight of a polymer can increase proton conductivity but it can lead to problems with mechanical integrity due to increased swelling and durability problems. Fig. 2 illustrates the decreased performance with increased swelling. DuPont has shown that for Nafion$^{\circledR}$-type membranes, increased water uptake improves conductivity but leads to increased swelling and an increase in the decay rate of the open circuit voltage. MEA performance drops due to stresses (swelling and shrinking) on the membrane during cycling [4]. Increases in conductivity must be achieved while minimizing water uptake and swelling. Recent work has increased membrane durability while maintaining high conductivity [5,6]. Membranes for automotive PEMFC systems

Table 1
DOE technical targets for membranes

Characteristic	Units	2005 status	2010 target	2015 target
Operating temperature	°C	≤80	≤120	≤120
Inlet water vapor partial pressure	kPa	50	≤1.5	≤1.5
Membrane conductivity at inlet water vapor partial pressure				
Operating temperature	S cm^{-1}	0.10	0.10	0.10
Room temperature	S cm^{-1}	0.07	0.07	0.07
−20 °C	S cm^{-1}	0.01	0.01	0.01
Oxygen crossover[a]	mA cm^{-2}	5	2	2
Hydrogen crossover[a]	mA cm^{-2}	5	2	2
Area specific resistance	Ω cm^2	0.03	0.02	0.02
Cost[b]	$ m^{-2}	25[c]	20	20
Durability with cycling				
At operating temperature ≤80 °C	h	~2000[d]	5000[e]	5000[e]
At operating temperature >80 °C	h	Not available[f]	2000	5000[e]
Unassisted start from	°C	−20	−40	−40
Thermal cyclability in presence of condensed water		Yes	Yes	Yes

[a] Tested in MEA at 1 atm O$_2$ or H$_2$ at nominal stack operating temperature.
[b] Based on 2002 dollars and costs projected to high volume production (500,000 stacks per year).
[c] Based on 2005 TIAX study and will be periodically updated.
[d] Steady state single cell durability is 25,000 h.
[e] Based on appropriate test protocol (to be developed).
[f] High temperature membranes are still in a development stage and durability data is not available.
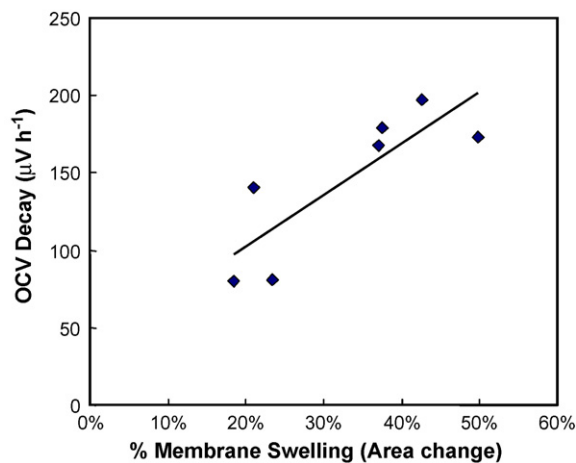
Fig. 2. Open circuit voltage decay rate as a function of change in membrane swelling.

3. New DOE R&D efforts for high temperature membrane development

To address the thermal and water management issues in fuel cells described above, DOE recently initiated new R&D efforts emphasizing fuel cell membrane materials that can operate at temperatures up to $120\,°C$ with an inlet water partial pressure of 1.5 kPa and at <2.5 atm total pressure. Operation under low water partial pressure conditions is a challenge since current materials rely on the presence of water for proton conduction. The goal of these efforts is to prepare and evaluate new polymeric electrolytes, develop methodology to predict durability of new materials, and define new approaches to achieve conduction in low RH, high temperature ($T > 100\,°C$) environments. The proton conductivity of the electrolytes, as well as mechanical, mass transport, and surface properties will be characterized. Catalyst-coated membranes and membrane electrode assemblies based on promising new electrolyte materials will be evaluated against the DOE targets.

In the DOE program, as many different types of membrane materials as possible will be explored. Both fluorinated and hydrocarbon membranes will be investigated. Three strategies to improve conductivity at high temperatures and low RH were adopted. The first strategy is to control the phase segregation between the proton-conducting hydrophilic part of the membrane and the hydrophobic part that provides mechanical strength. The second strategy is to employ proton conductors that do not rely on water for conduction. The third strategy is to use hydrophilic additives to attract and hold water under low RH conditions so that the water can be used for proton conduction. Table 2 illustrates the individual projects and their strategies. These strategies and the new DOE projects that employ them will now be described in more detail.

3.1. Phase segregation

Two different approaches to phase segregation are being pursued in the DOE program. First is phase segregation within a single molecule using blocks of hydrophilic and hydrophobic phases; the hydrophobic portion provides the mechanical

must operate over the complete range of automotive operating conditions. While PBI-phosphoric acid systems operate at high temperature and low RH, those systems suffer from leaching of phosphoric acid under automotive conditions, especially at lower temperatures where water will condense. Hydrocarbon membranes can be a viable alternative to fluorinated membranes. Lower cost and an increased operating temperature range are some advantages that hydrocarbon membranes offer. UTC Power has shown that hydrocarbon membranes such as the BPSH (Bi-Phenol Sulfone H-form) membrane from Virginia Tech can withstand fuel cell conditions for extended time periods, even though they perform poorly in tests such as the Fenton's test which are meant to be a gauge of chemical durability of membranes in fuel cell environments [7]. The high chemical stability is related to the low oxygen permeability [8]. Hydrocarbon membranes for the most part have lower water uptake at a given equivalent weight and lower conductivity relative to perfluorosulfonic acid membranes particularly at low RH [9]. Recent work, though, has suggested that block copolymers with better phase segregation can demonstrate higher conductivities [9]. Block copolymers can have conductivities up to an order of magnitude higher than random copolymers at 50% RH [10].

Table 2
DOE high temperature membrane projects and approaches

	Strategy 1 (polymer)	Strategy 1 (membrane)	Strategy 2 (non-aqueous)	Strategy 3 (hydrophilic additive)
Principal investigators				
Arizona State			X	
Case Western I	X			
Case Western II		X		X
Clemson	X			
Colorado School of Mines			X	
Fuel Cell Energy		X		X
GE Global Research	X			X
Giner		X		
Penn State	X		X	
University of Tennessee	X			
Virginia Polytechnic	X			
University of Central Florida	X			X

stability of the membrane. Second, composite membranes are prepared in which the physical form (geometry) of one of the materials causes the phase separation (i.e., one polymer acts as a porous support while a second, ion-conducting polymer is constrained in the pores).

With block copolymers, the local acid density should increase providing an easier pathway for proton conduction. Under high temperature, low RH conditions, the acid groups would still have sufficient water for proton conduction, or, in the extreme case, the local density of acid groups could become high enough that proton hopping could occur between the acidic groups. By controlling phase segregation, swelling should be minimized and mechanical integrity maintained, unlike the situation with low EW Nafion®-type materials.

These different approaches to achieve phase segregation are being investigated in the current DOE program. GE Global Research and Virginia Tech plan to alter the architecture of a single polymer to obtain phase separation while Case Western and Giner plan to use composite membranes in which the physical form of one of the materials causes the phase separation.

Virginia Tech is developing random and block (hydrophilic–hydrophobic multiblock) copolymers using a hydrophilic aromatic oligomer with reactive phenoxide end groups. A perfluorinated- or hydrocarbon-functional hydrophobic material provides mechanical strength.

GE Global Research is exploring the effect of variations in polymer architecture on membrane performance. GE Global is developing aromatic hydrocarbon polymer structures containing grafted chains with acidic groups. The unique structures include polymers with long graft chains, random graft copolymers, or "blocky" graft copolymers in which several side chains are co-located on the backbone. Bunching the side chains together should increase proton conductivity by providing conducting paths. The hydrophobic polymer backbones should bunch together to provide better mechanical support. By controlling the size of the domains, a balance between water uptake and swelling in the hydrophilic portion can be obtained. Several of the new GE polymers possess conductivity similar to Nafion® at 80 °C from 25 to 100% RH [9].

Case Western Reserve University is taking two different approaches to prepare membrane materials with frozen-in free volume for proton conduction. The frozen-in free volume creates nanoscale free channels that can hold water and enhance proton conductivity. Liquid crystalline, rigid rod materials show good dimensional stability. First, bulky, hydrophobic co-monomers will be synthesized and then block copolymers will be prepared. The block copolymers should operate better than random copolymers at low RH. In addition to engineering the polymer structure, efforts will be made to engineer the membrane structure. The second approach is preparation of completely rigid, two-dimensional structures with high free volume. These structures should be able to hold a significant number of waters per acid group [11].

In a separate project, Case Western is developing a high density, three-dimensional network of nanocapillary proton-conducting polymer fibers embedded in an inert polymer matrix that provides mechanical strength. The high density of fibers

in the mat and the high ion-exchange capacity of the sulfonic acid polymers should ensure high proton conductivity. The hydrophobic polymer matrix minimizes water swelling of the nanocapillaries and provides toughness to the membrane. Crosslinking of the fibers should prevent water dissolution of the polymer and help maintain the integrity of the fiber network. Condensation of water within the nanocapillaries should promote water retention and increase proton conductivity under low relative humidity conditions [12].

Giner is incorporating low EW perfluorosulfonic acid ionomers within the pores of a two-dimensional polymeric matrix. As noted previously, low EW ionomers will increase conductivity but increase water uptake. A mechanically and chemically stable membrane material will be used for a porous support structure. The polymer matrix should inhibit swelling in the *x* and *y* planes of the membrane as well as improve the freeze–thaw and wet–dry cycling durability. A three-dimensional matrix could eliminate swelling in the *z*-direction as well and provide stability over a wide humidity range leading to more durable membrane electrode assemblies [13].

Fuel Cell Energy will, like others, use a polymer support for mechanical stability and a low EW ionomer for proton conductivity. The unique feature of this project is the formation of ionomer clusters that are immobilized in the support. Fuel Cell Energy will also use stabilized nanoadditives to expand the operating temperature range to lower temperature (sub-freezing) and reduce hydrogen and oxygen crossover. The ratio of additive to polymer will be optimized. Experimental data will be fed into a model to predict conductivity in composite structures [14].

3.2. Non-aqueous proton conductors

The second strategy to increase conductivity at high temperature and low RH is the use of inorganic materials that conduct protons without water. The Colorado School of Mines (CSM) is using heteropolyacids (HPAs) for proton conduction. HPAs are inorganic compounds with high conductivity at room temperature but they are water-soluble and will wash out of a PEM unless they are immobilized [15]. CSM plans to immobilize the HPA by covalently attaching the HPA to a polymer. Currently, robust HPA immobilization strategies using phenyl-HPA derivatives are being examined. Hybrid HPA-polymers will be optimized for higher temperature and drier fuel cell operation by controlling the morphology and structure of the polymers. The mechanical properties and oxidative stability of the films will also be optimized.

Pennsylvania State University is developing composites of inorganic proton conductors with an end-chain functionalized Teflon®-based polymer [16]. The proton conductors will be hydrophilic inorganic particulate materials with structural or surface proton conductivity. The proposed inorganic proton conductors include layered and three-dimensional hydrogen phosphates, mesoporous oxides, and porous titanosilicates and they will compose up to 80 wt.% of the composite. Mechanical strength is provided by a low molecular weight, Teflon®-based polymer with vinylidene fluoride and inorganic functionalized end groups. The end groups will contribute to the

hydrophilicity of the material and link the polymer and inorganic phases.

Arizona State University's approach is based on protic salt electrolytes; protic salts are formed from transfer of a proton between molecular Brönsted acids and Brönsted bases [17]. Arizona State is preparing membranes consisting of porous matrices filled with water-immiscible ionic liquids immobilized by capillary forces and with ionic liquids absorbed in polymers. In addition, non-leachable membranes of novel polymers and polymer blends with no plasticizers that allow all acid and base moieties to be immobilized by covalent and electrostatic binding will be prepared. Acid and base moieties as well as polymer properties will be varied to optimize membrane properties. ASU has shown that protic salts such as ethylammonium nitrate can be used as a fuel cell electrolyte at temperatures up to 140 °C.

Clemson is concentrating on a family of fluoroalkylphosphonic acid as proton conductors. Fluoroalkylphosphonic acids are strong acids that can dissociate allowing for both vehicular (hydronium ion) and hopping (Grotthus-like) proton transport mechanisms [18]. The acids are robust, adsorb to Pt relatively weakly, and exhibit higher oxygen solubility than other phosphorous-based electrolytes. The target ionomers will contain no water-soluble component, an advantage in a fuel cell environment. Fluoroalkylphosphonic acid electrolytes will be synthesized in the form of small molecules, trifluorovinylether monomers, and ionomer membranes. Proton transport in fluoroalkylphosphonic acid-based small molecules and polymeric electrolytes via the Grotthus mechanism will be predicted using multi-state empirical valence bond models.

3.3. Additives

Hydrophilic additives in membranes can be used to retain water for proton conduction at higher temperatures. Additives may also help constrain the hydrophobic phase in the polymer network. Additives such as hydrophilic inorganic fillers (e.g., silica or zirconium phosphate/phosphonate) or heteropolyacids (e.g., phosphotungstic acid) will be pursued. Some inorganic additives can increase conductivity under low RH conditions.

GE Global Research is exploring hydrophilic organic additives to improve water retention and to improve proton conductivity at low relative humidity [10]. The additives should also be water-insoluble and thermally stable. The University of Central Florida is working on composites of inorganic additives such as phosphotungstic acid (PTA) with various polymers [19]. Work has been initiated to stabilize and reduce the particle size of PTA. New membranes containing particles of PTA will be fabricated from non-Nafion®-based poly(perfluorosulfonic acids) with EW < 1100, sulfonated poly(ether ether ketone)s with various sulfonation degrees, or sulfonated poly(ether ketone ketone) (SPEKK) as the proton-conducting component in a blend with either poly(ether sulfone) or SPEKK with different sulfonation levels. A Nafion®–Teflon®–PTA membrane demonstrates conductivity superior to a Nafion®-112 membrane at 120 °C and 20–100% RH [20].

The University of Tennessee is optimizing fuel cell membranes based on poly(cyclohexadiene) (PCHD) [21]. The ring-like structure of PCHD can contribute mechanical strength and thermal stability and PCHD can be incorporated into a variety of polymer structures. PCHD can be functionalized to optimize performance properties such as conductivity, hydrophilicity, permeability, and thermal stability. Metal oxide nanoparticle additives can improve proton conductivity and thermal properties of the membrane. Preliminary results show that a membrane of crosslinked, aromatized (90 mol%), and sulfonated (13 mol%) PCHD has a water uptake of 5.3 wt.% and a proton conductivity of 1.2×10^{-2} S cm^{-1} at room temperature and 2.8×10^{-2} S cm^{-1} at 80 °C. A membrane of crosslinked, non-aromatized, and sulfonated (47 mol%) PCHD has a water uptake of 4 wt.% and a proton conductivity of 1.6×10^{-2} S cm^{-1} at room temperature and 3.6×10^{-2} S cm^{-1} at 80 °C.

Virginia Tech is considering proton-conducting zirconium additives to optimize the performance of its polymers [8]. Zirconium compounds could be added to multiblock copolymers and random copolymers could be reinforced with zirconium phenyl phosphonate layered structures. The filler will contain sulfonic acid groups to enhance conductivity.

4. Concluding remarks

This document has provided an overview of the DOE High Temperature Membrane Program. Most R&D efforts are built upon fluorinated polymers such as Nafion® however the hydrocarbon membrane materials prepared by GE Global Research and the University of Tennessee, for example, will provide a good comparison between the two types of polymers. About half of the membranes will incorporate some type of inorganic filler such as phosphotungstic acid or a zirconium component. A comparison between these materials and membranes without fillers will be instructive.

References

[1] M.F. Mathias, R. Makharia, H.A. Gasteiger, J.J. Conley, T.J. Fuller, C.J. Gittleman, S.S. Kocha, D.P. Miller, C.K. Mittelsteadt, T. Xie, S.G. Yan, P.T. Yu, Electrochem. Soc. Interf. (2005) 25–35.
[2] D. Myers, S. Niyogi, Proceedings of Hydrogen Fuel Cells and Infrastructure Technologies Program Review, Crystal City, VA, 2006, http://www.hydrogen.energy.gov/pdfs/review06/fc_1_myers.pdf.
[3] R.K. Ahluwalia, Presentation to the USDOE High Temperature Membrane Working Group Meeting, Philadelphia, PA, 2004.
[4] G. Escobedo, Proceedings of Hydrogen Fuel Cells and Infrastructure Technologies Program Review, Crystal City, VA, 2005.
[5] G. Escobedo, Hydrogen, Fuel Cells and Infrastructure Technologies Annual Progress Report, 2006.
[6] M. Hicks, Hydrogen, Fuel Cells and Infrastructure Technologies Annual Progress Report, 2006.
[7] L. Protsailo, Proceedings of Hydrogen, Fuel Cells and Infrastructure Technologies Program Review, Crystal City, VA, 2005.
[8] J.E. McGrath, D.G. Baird, Hydrogen, Fuel Cells and Infrastructure Technologies Annual Progress Report, 2006.

[9] J.E. McGrath, Proceedings of Hydrogen, Fuel Cells and Infrastructure Technologies Program Review, Crystal City, VA, 2006.

[10] J. Hung, J. Stone, J. Suriano, H. Zhou, Proceedings of Hydrogen Fuel Cells and Infrastructure Technologies Program Review, Crystal City, VA, 2006.

[11] M. Litt, Hydrogen, Fuel Cells and Infrastructure Technologies Annual Progress Report, 2006.

[12] P. Pintauro, Hydrogen, Fuel Cells and Infrastructure Technologies Annual Progress Report, 2006.

[13] H. Liu, Hydrogen, Fuel Cells and Infrastructure Technologies Annual Progress Report, 2006.

[14] L. Lipp, Proceedings of Hydrogen Fuel Cells and Infrastructure Technologies Program Review, Crystal City, VA, 2006.

[15] A. Herring, Proceedings of Hydrogen Fuel Cells and Infrastructure Technologies Program Review, Crystal City, VA, 2006.

[16] S. Lvov, M. Chung, S. Komarneni, Hydrogen, Fuel Cells and Infrastructure Technologies Annual Progress Report, 2006.

[17] D. Gervasio, C.A. Angell, J. Kinder, R. Marzke, J. Yarger, Hydrogen, Fuel Cells and Infrastructure Technologies Annual Progress Report, 2006.

[18] S. Creager, D. DesMarteau, Hydrogen, Fuel Cells and Infrastructure Technologies Annual Progress Report, 2006.

[19] D.K. Slattery, J. Fenton, Hydrogen, Fuel Cells and Infrastructure Technologies Annual Progress Report, 2006.

[20] J.M. Fenton, Hydrogen, Fuel Cells and Infrastructure Technologies Annual Progress Report, 2006.

[21] J.W. Mays, Hydrogen, Fuel Cells and Infrastructure Technologies Annual Progress Report, 2006.