Program Director:  David Keffer
Program Co-Director Claudia Rawn

Open House
October 23, 2008
Funding: $3 million (NSF) plus $1M (UTK) over five years;
Traineeship: support 16 PhD Students, curriculum open to all UTK CAS and CoE graduate students
Highly interdisciplinary program
- 20 UTK faculty
- 5 departments
  - Biochemistry, Cellular and Molecular Biology
  - Chemical and Biomolecular Engineering
  - Chemistry
  - Civil and Environmental Engineering
  - Materials Science and Engineering
- 6 ORNL staff members from six different groups
Our world faces an impending global energy/climate crisis that will be the defining challenge for your generation of engineers. The search for alternative fuels that will power the future and mitigate human effects on the environment is an extraordinarily complicated task, requiring an interdisciplinary training in which an engineer has expertise in biomolecular engineering to modify algae to produce hydrogen from sunlight or expertise in chemical engineering in order to design nanostructured materials to store and convert hydrogen to electricity. However, expertise in one field is not enough. To solve the problem, you must be conversant in all of the fields relevant to sustainable energy production. To educate this engineer is the goal of the STAIR program at UT.
Sustainable Energy Research

- train scientists/engineers in bio and materials
- conduct research within the arena of sustainability
Integrated Discovery Program with Sustainable Context

**H₂ production**

H₂O Photolysis in Algae and Cyanobacteria

**H₂ storage**

Materials discovery of novel nanoporous adsorbents with high capacity and fast charging

- metal-porphyrin frameworks
- decorated carbon fullerenes

**H₂ conversion**

Understanding structure-property relationships in proton exchange membrane fuel cells to aid design of next generation devices

Each task has experimental and computational elements.
New Curriculum

**Novel Multidisciplinary Educational Program:**

- Promote expertise in biomolecular engineering and materials science
- Emphasis on sustainability science: Life cycle, economics and policy
  
  - Two Core STAIR master courses: Team taught and modular; Develop breadth in all three research areas.
  
  - Two Core STAIR case courses: Case studies to promote integration of concepts & create depth of knowledge in at least two of the research areas.
  
  - Industrial/National laboratory research component

Open to all CoE and CAS students
Participants at the University of Tennessee
5 departments in 2 colleges

**Arts and Sciences**

- Biochemistry, Cellular and Molecular Biology
  - Barry Bruce
  - David Joy
- Chemistry
  - Jimmy Mays
  - Bob Compton

**Engineering**

- Chemical and Biomolecular Engineering
  - Eric Boder
  - Brian Edwards
  - Paul Frymier
  - David Keffer
  - Bamin Khomami
  - Stephen Paddison

- Civil and Environmental Engineering
  - Sandeep Agnihotri
  - Randy Gentry
  - Dayakar Penumadu

- Materials Science and Engineering
  - Claudia Rawn
Collaboration with Oak Ridge National Laboratory

Spallation Neutron Source
With the world's highest flux reactor-based neutron source (the High Flux Isotope Reactor) and the world's most intense pulsed accelerator-based neutron source (the Spallation Neutron Source), ORNL provides neutron scattering capabilities unavailable anywhere else in the world.

National Center for Computational Science
Today the computing resources of the NCCS are among the fastest in the world, able to perform more than 119 trillion calculations per second.
Institute for a Secure and Sustainable Environment

Development of a Sustainability Science Agenda

ISSE Centers
- Center for Clean Products and Clean Technologies
- Community Partnership Center
- East Tennessee Clean Fuels Coalition
- Southern Appalachian Information Node
- Southern Appalachian Man and the Biosphere Program
- Tennessee Solid Waste Education Project
- Water Resources Research Center
- Southeastern Water Resources Institute
- Center for Climate Change and Environment

ISSE is a state funded Center of Excellence with an annual research budget of ~$3M.

Use-inspired fundamental research.

Director Randy Gentry
**Mission:** To educate the next generation of world leaders in sustainable energy. The mission of the center will be achieved by synergetic activities in research, education, outreach, and facilities and operation.

- **SEERC** is growing out of a strong, existing institutions represented by the green “sepals”.
- The pink and blue “petals” denote the thriving Institutes, Centers, and Colleges that are strongly interacting/supporting SEERC.
Outreach

Students will participate in providing workshops/exhibits for the K-12 audience at AMSE and at local schools.

IGERT Fellow, Michelle Minton, at Northwest Middle school in October, 2008.
Recruiting

New Opportunities
across the Mathematical and Biological Sciences
at the University of Tennessee

NIMBioS — National Institute for Mathematical and Biological Synthesis
SCALE-IT — Scalable Computing and Leading Edge Innovative Technologies
STAIR — Sustainable Technology through Advanced Interdisciplinary Research

NIMBioS is a major initiative to foster interdisciplinary research at the interface between the mathematical and biological sciences. The institute will address fundamental science and applied problems and will develop a cadre of diverse researchers capable of conceiving and engaging in research at this interface. NIMBioS is sponsored by the National Science Foundation, the US Department of Homeland Security and the US Department of Agriculture. Industry partners are IBM and EARN, and the Great Smoky Mountains National Park is a collaborative partner. In addition to existing graduate programs across the mathematical and biological sciences and engineering, the University of Tennessee, Knoxville will provide interdisciplinary graduate education opportunities through SCALE-IT and STAIR, two new NSF-funded Integrative Graduate Education and Research Traineeship (IGERT) programs.

NIMBioS Opportunities

NIMBioS is sponsoring an array of activities starting January 2009 to foster research and education at the interface between mathematics and biology. The initial round of proposals are due November 30, 2008, for activities to be held starting January 2009. Details about the application process for activities are posted at http://nimbios.org and include:

- Proposals for Working Groups to investigate novel, focused research questions requiring an interdisciplinary perspective. These involve 10-15 researchers who visit NIMBioS for up to a week at a time over one to two years.

- Proposals for Investigative Workshops to foster a broader perspective of an area of fundamental or applied interest at the mathematics/biology interface. These involve 30-40 researchers and students visiting NIMBioS for 3-4 days and are expected to identify areas for possible future Working Groups.

- Proposals for post-doctoral fellowships based at NIMBioS for periods of one to two years. Applications are particularly encouraged from those who already have some experience in research at the mathematics/biology interface, but applications are welcome from all individuals who wish to expand their interdisciplinary background through opportunities at NIMBioS.

- Proposals for visiting positions of variable length for short-term visits of less than a month for students and researchers or longer-term sabbatical visits.

NIMBioS will host a Research Experience for Undergraduate program during Summer 2009, with applications due February 15, 2009.

Graduate Student Opportunities through SCALE-IT and STAIR IGERT Programs

The University of Tennessee, Knoxville has outstanding opportunities for highly motivated students with interest in interdisciplinary science and engineering Ph.D. programs.

SCALE-IT is an NSF-funded IGERT program at UT and Oak Ridge National Lab. Students can address biological problems at all scales, ranging from atomic level molecular dynamics simulations of proteins to large bioinformatics and statistical problems related to populations and ecosystems. Unique resources are available for research in these areas, with UT as a leading contributor to Terra-Grid, a collaboration of the National Institute of Computational Science at UT leading the way with the TeraGrid Supercomputer, and the opening of new facilities in biology with the Spallation Neutron Source at Oak Ridge National Lab. Interested students should contact Dr. Cynthia Peterson (CYPETSON@utk.edu), or visit http://web.ece.utk.edu/~cpetson.

STAIR is also an NSF-funded IGERT program at UTI. The STAIR program provides an opportunity to earn a Ph.D. in one of three areas in sustainable energy, production of hydrogen through biological pathways, discovery of nanomaterials for hydrogen storage, and identification of structure/property relationships in hydrogen-based fuel cells. Through an integrated curriculum, participants become knowledgeable in the broad range of biotechnology and materials research challenges, as well as social constraints, surrounding sustainable energy. Interested students should contact Dr. David Kiefert (davek@utk.edu), or visit http://classics.engr.utk.edu/stair.

For information on Tennessee’s Environment and Energy Institute, contact Dr. Paul G. Delfino at (865) 974-1200. NIMBioS is a major initiative to foster interdisciplinary research at the interface between the mathematical and biological sciences.
Task 1: Production of H<sub>2</sub> via Biological Pathways
Production of Hydrogen via Water Photolysis in Algae and Cyanobacteria

- Hydrogen can store energy and be used without affecting the CO<sub>2</sub> balance, bio-photolysis has potential to be 40% efficient.
- Phototrophic organisms split water, producing O<sub>2</sub>, e<sup>-</sup>, and H<sup>+</sup>

- Can perform either formation of NADPH or H<sub>2</sub>
- Live algal systems produce H<sub>2</sub> when anaerobic, no sulfur present, light on

- Extracted Photosystem I (PSI), plastocyanin, and either Pt or Hydrogenase will evolve hydrogen in vitro
- Next step: Hydrogenase-PSI and PSI-cyt<sub>c<sub>553</sub></sub> fusion complexes
Creation of New Biomaterials for Fuels Production

Protein characterization and modeling

Barry Bruce
BCMB

Bamin
Khomami
CBE

Paul
Frymier
CBE

Characterization of new materials

Evolution, cloning and expression of new proteins, complexes

Eric Boder
CBE

Hugh O’Neill
ORNL

Barry Bruce
BCMB

Characterization of new materials

In-vitro formation of new materials

Time after induction (h)

- ALA

+ ALA

0 2 4 6 8 12
Creation of New Proteins and Complexes

- Genomic sequencing enables site directed mutagenesis, cloning, and expression in a production host.
- Protein characterization (structure and sequence) and modeling direct evolution of new proteins.

Models of algal cytochrome (left) and mutagenized bacterial cytochrome (right)

Crystal structures and molecular models of PSI, cyt c$_{553}$, and PSI-hydrogenase fusion proteins.
Characterization and Synthesis

- New proteins and complexes are characterized by TEM, x-ray diffraction and neutron scattering.
  
  **Stromal end of PSI from a thermophilic cyanobacterium**

  TEM of PSI deposited on a gold surface, overlayed with PSI crystal structure.

- The new biomaterials are used in *in-vitro* coupling strategies to form hybrids of biological and non-biological materials.

  **Platinized water-splitting conjugate of PSI and PSI**

Assay for New Function

- Hydrogen production can be measured directly in custom fabricated equipment.

- Binding and electron transport kinetics are measured with laser spectroscopy and oxygen uptake.

Hydrogen evolution as a function of time from platinized PSI nano-particles.

Oxygen uptake data (top) and time-resolved laser absorption spectroscopy data (right).
Task 2: Materials Discovery for H₂ Storage:

A successful system for the onboard vehicular storage of hydrogen must meet a set of technical specifications defining gravimetric capacity, volumetric capacity, charging/discharging rates, economic feasibility and consumer safety. No existing material satisfies all criteria.

- Materials that chemisorb H₂ (metal hydrides) have high capacity but slow discharge rates. Materials that physisorb H₂ (metal organic frameworks) have higher discharge rates but low capacity at ambient temperature and pressure.

- Practical onboard vehicular H₂ storage systems require a novel nanoporous adsorbent that both binds H₂ strongly, yielding high capacity, and is reversible, yielding fast charging and discharging.
Task 2: Integrated Discovery Program

**synthesis**
- metal-porphyrin frameworks (MPF) replace organic part of MOFs with a porphyrin
- decorated carbon fullerenes (DCF) insert metal atoms in fullerenes

**characterization**
- x-ray diffraction
- neutron diffraction
- pore size distribution
- H₂ adsorption isotherms
- crystal structure
- H₂ capacity
- controllability by electric field

**modeling**
- quantum mechanical calculations
- molecular dynamics simulation
- Monte Carlo simulation

Theory guides functionalization of next iteration of materials.
Synthesis of Hydrogen Storage Materials

Metal Porphyrin Frameworks (Rawn)


Decorated Carbon Fullerenes (Compton)

Fullerenes can be decorated with organic and organometallic compounds.

Laser ablation of metals in vacuo (e.g., Mg above) is used to dope or decorate the fullerenes with endohedral or exohedral metal atoms.

crystalline nanoporous frameworks with exposed metal centers

porphyrin crystals from UT
Characterization of Hydrogen Storage Materials

Determinations of Structure (Rawn)

- X-ray and neutron scattering

Use single crystal and/or powder diffraction to determine atomic positions.

Exploit isotopic substitution.

Adsorption Capacity (Agnihotri)

Pore size distribution for initial MPFs synthesized at UT. The peak at 23 Å is the nanoporous space. The broader peak at larger pores is either crystal defects or interstitial space.
Modeling of Hydrogen Storage Materials

Modeling Nanoporous Materials at UT
- separation of hydrocarbons in zeolite-Y
- detection of explosives (RDX) in IRMOF-5
- high density storage of hydrogen in MPF (Keffer)

Simulations predict adsorption capacity and adsorbate mobility before synthesis
- MOF-5
- MIPF
- experiment for MOF-5 (Rovessi et al.)
- simulation for MOF-5 (Garberoglio et al.)
- experiment for MOF-5 (Poirier et al.)

hydrogen adsorption isotherms

diffusivities
Task 3: Hydrogen Conversion to Energy

Polymer Electrolyte Membrane (PEM) H₂ Fuel Cells:

Hydrogen is utilized as an energy carrier through oxidation over a noble metal catalyst (Pt or Pt/Ru) to produce a current of electrons and protons which are combined with the reduction of oxygen resulting in only water vapor as a product.

Current PEM fuel cells use an ionomer (typically a perfluorosulfonic acid polymer such as Nafion) that is limited to operating conditions of high humidity and T < 90 °C.

Under operation, a problematic water concentration gradient occurs in electrolyte causing: increased membrane resistance and need to add and remove H₂O.
Task 3: Understanding Structure/Property Relationships

**synthesis**
- novel fluorinated, sulfonated block copolymers

**characterization**
- neutron tomography
- SEM/TEM
- small angle x-ray scattering
- dielectric spectroscopy
- proton conductivity

**modeling**
- quantum mechanical calculations
- classical molecular dynamics simulation
- mesoscale modeling
- mean field modeling

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Theory guides functionalization of next iteration of materials.

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Jimmy Mays
Chem

Dayakar Penumadu
CEE

David Joy
BCMB

Stephen Paddison
CBE

Brian Edwards
CBE

David Keffer
CBE
Synthesis of Novel Fuel Cell Membranes

novel fluorinated, sulfonated block co-polymers (Mays)

Sulfonated portions provide carrier for charge. Fluorinated portions provide membrane durability.

Synthesis procedure allows precise control over block size, degrees of fluorination and sulfonation.

Block co-polymers phase segregate on the tens of nm or larger scale.

Backbone of sulfonated block segregates from aqueous phase on nanoscale.
Characterization of Fuel Cell Membranes

Properties of Fuel Cell PEMs

Small Angle X-ray Scattering of PEMs at various degrees of hydration.

Proton conductivity of PEMs as a function of water content.

Elastic Moduli (above) & dielectric spectra (below) of PEMs.
Modeling of Fuel Cell Membranes

**Multiscale Materials Modeling**

Classical MD simulations of electrolyte-electrode interface

Proton Transfer Energetics

**Coarse grain simulations of hydrated PFSA membranes**

*Energy & Environmental Science*

*COVER ARTICLE: Proton transfer and energetics of hydrated PFSA membranes with molecular simulations*
Questions?
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