



# Cluster E: Polymers in Energy

**An Industry / University Collaborative Program**

at the

**Center for UMass / Industry Research on Polymers**

UNIVERSITY OF MASSACHUSETTS AMHERST



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## **Center for UMass / Industry Research on Polymers - University of Massachusetts Amherst**

### **Cluster E: Polymers in Energy**

The Center for UMass / Industry Research on Polymers (CUMIRP) is pleased to announce the formation of a new research cluster within its 'Part I' consortium program. The new cluster, "Cluster E: Polymers in Energy", will focus on polymers used in the energy field. The initial research areas will be in polymers in fuel cells and solar energy.

There is significant research on-going in these areas at UMass Amherst that will provide a leverage platform for the new cluster. The NSF-Materials Research Science and Engineering Center (MRSEC) has programs to study the basic and fundamental science in polymer directed self-assemblies for well defined nano-architectures and also in polymer based assemblies for photovoltaics. The University is home to the NSF-Chemical Bonding Center (CBC) 'Center for Fueling the Future' with a significant effort in the fundamental understanding of proton transport and molecular level mobility. These NSF Centers are complimented by the Massachusetts Center for Renewable Energy Science and Technology (MassCREST), a state supported institution aimed at the development of efficient fuel and solar cells and alternative fuels and support systems. These centers provide a strong foundation for the basic and fundamental science that will provide the platform for the more-applied research conducted within CUMIRP Cluster E. The resultant research is further enhanced by the NSF-Nanotechnology Science and Engineering Center (NSEC) 'The Center for Hierarchical Manufacturing' with the capabilities for research and translation to the manufacturing environment.

To support the on-going research in these centers, there has been a significant investment in facilities and infrastructure. The MRSEC has supported a photovoltaic fabrication lab used in the preparation and testing of new solar energy harvesting devices. The CBC and the MassCREST have invested in a charge mobility measurement set-up and is in the process of setting up a state-of-the-art proton mobility measurements unit, with additional investments planned. The NSEC has a significant operational infrastructure to assist with research development and prototyping including 2,000 sq.ft. of clean room facilities.

The intent of the CUMIRP program is to bring together the polymer research at UMass with our industrial partners. A more comprehensive description of the overall CUMIRP program is included at the end of this document. The research Cluster E will officially launch September 1, 2008. Members joining the program will be sent details for eight proposed projects, four in fuel cells and four in photovoltaics. Below are summaries of the initial research thrust areas for the Cluster.

### **Overview: Fuel Cells Research at UMass Amherst**

The increasing demand for cleaner, more efficient and environmentally-friendly power generation has stimulated the development of *hydrogen* as an alternative to fossil fuels. Proton exchange membrane fuel cells (PEM-FCs) offer one of the most promising technologies for the utilization of hydrogen as a fuel for the future. Nafion<sup>®</sup>, a sulfonated perfluoro-ethylene copolymer discovered in the late 1960s, remains the most widely used polymer electrolyte membrane for this purpose today, but not without serious problems. The most notable problem is that Nafion requires hydration for proton conduction, limiting its operation to temperatures below 80°C. Operating at higher temperatures may allow better efficiencies and less sensitivity to catalyst poisoning. To identify superior PEMs, it is imperative that we perform a systematic *structure-property relationship* study, to understand connections between chemical and morphological changes in PEMs, and how these influence proton conduction properties.

The University of Massachusetts Amherst (UMass-Amherst) provides an ideal setting for this multi-disciplinary research program. UMass-Amherst has tremendous, well-established strength in materials science and nanotechnology. The campus's well-earned reputation for research excellence derives from extensive faculty expertise in designing novel soft materials (i.e. polymers), organizing these soft materials on hard surfaces (e.g. metals and ceramics), and characterizing these materials at soft-hard interfaces.

The commercialization of polymer electrolyte membrane fuel cells (PEM-FCs) is becoming an increasingly important goal as the demand for clean, efficient, and portable energy rises. The polymeric membrane in PEM-FCs serves the dual purpose of electrical barrier and proton transport medium. Presently, state-of-the-art membranes are perfluorosulfonic acid polymers (PFSA) such as Nafion® from DuPont, however, there are several technical challenges associated with PFSAs. The membranes require a minimum hydration level to function as proton conductors. Therefore, operating temperature is limited, and complex hydration control systems must be implemented to assure even water distribution across the membrane. Operating PEM-FCs at temperatures above 100°C is desirable in order to increase the electrode catalyst efficiency and reduce catalyst poisoning by residual CO in reformed hydrogen feed gases. To achieve widespread market adoption, fuel cell membranes need to be more versatile. Current limitations on temperature and relative humidity (RH) hinder their tremendous energy production potential. We are employing our interdisciplinary expertise in polymer science, chemistry, polymer mechanics and engineering along with theoretical modeling to develop polymer electrolyte membranes (PEMs) capable of operating under a broad range of conditions; extremes of temperature both hot and cold as well as the full range of relative humidities. All the while remaining thermally, mechanically, and chemically stable.

The need for novel, or improved membranes is widely recognized in the research community. In the search for new polymers for proton conducting membranes the usual approach has been to sulfonate a wide range of thermally and chemically robust aromatic based engineering polymers: poly(aryl ethers), poly(aryl sulfones), poly(aryl ketones), or polyphenylenes, for example. While these materials have demonstrated some improvements in thermal stability, conductivity at low RH shows no improvement, and in some cases decreases dramatically. An alternate approach to increase conductivity at low humidity involves incorporating inorganic additives such as heteropoly-acids, ceramic oxides or zirconium phosphates into polymer electrolyte membranes; however these systems have shown, at best, modest improvements in performance to date and it seems unlikely that such systems will be able to reach the level of performance required for widespread application. We believe that the conductivity in current systems is limited by the fact that the engineering polymers themselves are initially prepared by step-growth polymerization mechanisms. This "condensation" route to polymeric materials, so-called by virtue of the polymerization mechanism, results in random copolymers that have a broad molecular weight distribution (polydisperse samples). This factor makes it very difficult for the material to assume the well-defined nanoscale morphologies necessary for good ionic conductivity, owing to the inherent heterogeneity of chain composition and dimensions. Although requisite conductivity values in polydisperse materials can be reached by high levels of sulfonic acid group incorporation along the polymer backbone, either by aggressive sulfonation or by the use of a pre-sulfonated co-monomer, the result is the added complication that the membranes absorb sufficient quantities of water to become either soft gels or to completely dissolve. Either way the membrane fails. We believe a fundamentally different research approach is needed to develop successful membrane materials.

New technologies for membranes and seals utilize more controlled morphological structures than those being commercially used today in order to improve membrane efficiency and seal life. These controlled morphological structures will inevitably undergo differential swelling where one phase will swell relative to the other(s). This combined with other boundary constraints imposed by design and part performance requirements will impose significant hygrothermal stresses to these materials. Moreover,

these stresses will be cyclic in nature throughout the service life of these systems, thereby inducing cyclic fatigue damage.

Research at UMass is ideally suited to identifying optimized morphologies that minimize fatigue damage (thereby enhancing membrane and seal service life) while maintaining high performance and efficiency. This group has published numerous articles associated with the physics and mechanics of environmental stress cracking in polymeric materials as well as in the development of constitutive models for describing the mechanical response of numerous thermoplastic elastomeric materials. In concert with this, are a number of unique facilities that allow for the development of constitutive models based on structure-property relationships that take into account the complex morphological transitions that can occur as stress is applied to the materials. Some of these facilities include, a deformation calorimeter that allows for direct assessment of what part of the work of deformation is enthalpic vs entropic in nature. In addition, simultaneous wide angle and small angle X-Ray diffraction can be done on samples as a function of deformation allowing for characterization of membrane and seal micro and nano structure during deformation. These facilities along with others specialized equipment and expertise will provide guidance for the development, selection, and implementation of materials used in membranes and seals for optimum lifetimes and superior performance.

The development of next generation membranes will require that new approaches to membrane electrode assemblies (MEA) fabrication be discovered. Chemical, electrical, and mechanical durability will all need to be optimized in order to produce fuel cell MEA with sufficient lifetimes to find practical applications. A critical component will be the development of new gaskets and sealants that are mechanically robust enough to last the entire lifetime of the fuel cell.

### **Overview: Solar Energy Research at UMass Amherst**

In organic-based photovoltaic devices, it is a challenge to assemble electron and hole conductors into nanoscale structures that have a heterojunction between the charge-carrier conductors for efficient charge separation *and* continuous phases of charge-carrier conductors for efficient charge mobility. A molecular heterojunction can be created by tethering an electron conductor to a hole conductor; donor-acceptor dyads and diblock co-polymers containing electron and hole conducting blocks are examples of molecular heterojunctions. Electron conductors (*n*-type semiconductors) are electron deficient and hole conductors (*p*-type semiconductors) are electron-rich; there is a natural tendency for electron-deficient compounds to mix with electron-rich compounds. Therefore, although excitons can dissociate efficiently at a molecular heterojunction, the mixed packing of charge-carrier conductors results in charge recombination and poor charge mobility. Thus, for efficient harvest of solar energy in photovoltaics, investigators at UMass Amherst work in the following areas:

- Strategy for long-lived charge separated state at a molecular level
- Macromolecular design for broad light absorption & charge separation
- Ability to tune band-gaps and the redox potentials of the chromophores and charge transporters
- Achieve nanoscale bulk heterojunctions with these molecules
- Develop novel design principles for enhancing the exciton lifetime of fluorogenic polymers
- Develop strategies for anti-reflective surfaces for enhanced light trapping in the PV device architectures

*Charge-separation at the molecular level:* In order to achieve efficient conversion of sunlight into the electrical energy, the primary event in the photoinduced process is the charge separation within a molecule. It is important that this charge separated state lives long enough to be transported through the appropriate charge carriers, eventually to the respective electrodes. We have and will design, synthesize,

and investigate novel molecules that exhibit faster charge separation rates than the charge recombination rates. These molecules will not only be characterized simply for efficiencies in solution and solid-state, but will be incorporated at bulk heterojunction interfaces (see below for our bulk heterojunction strategies) and measure the effect of such incorporations upon solar cell efficiency.

*Broad light absorption and charge separation:* Another factor that is often ignored in organic PV architectures involves the strategy to capture the rather broad spectral range of solar energy. We are interested in developing dendrimer- and polymer-based strategies that will minimize loss due to transmittance. When the light absorption is broad, it is a challenging prospect to be able to consistently funnel all the energy to a location where charge separation occurs. We have developed fundamentally new strategies that could simultaneously achieve this.

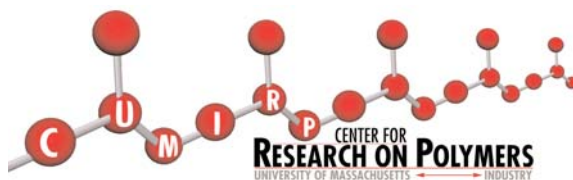
*Band-gap and redox potential tuning:* Two of the parameters that are big parts of the Figures of Merit for an organic PV involve the short circuit current, open circuit voltage, and the shape of the I-V curve. The parameters that control these properties will involve the excited state energies of the chromophores, redox potentials of the charge transporters, and the charge carrier mobility in the bulk for these charge transport materials. The molecular design that we pursue allow for significant tuning in the first two factors. Controlling charge carrier mobilities in polymers is not trivial, since the structure-property relationships are not clearly understood with respect to mobility. We believe that a significant departure from the traditional conjugated polymer approach might be warranted to be able to identify promising polymers with high charge carrier mobilities. Such strategies will be developed in this research cluster in CUMIRP.

*Nanoscale bulk heterojunctions:* Harvesting the exciton, the electron-hole pair generated by photon absorption in the photoactive material, is central to realizing high efficiencies – achieving a 10% overall efficiency with a low-cost all-organic format would represent an enormous breakthrough. One of the fundamental issue is the small diffusion length of an optically prepared exciton (typically <10 nm), thus mandating device features on the nanoscopic level. Here, we propose *a new architecture* based on a nanoscale interdigitated assembly of a hole-transporting (HT) polymer with an electron-transporting (ET) polymer. The ~10 nm distances between interdigitated polymer domains provide maximum surface contact between the two charge transporting (CT) layers and, therefore, enhance the probability of charge separation within the exciton lifetime. We will approach this with both all-organic and organic-inorganic composite nanomaterials.

*Increasing the exciton lifetime:* While capturing the essence of an excitation within nanoscale distances is one approach, a complementary approach would be to enhance the lifetime of the excitation using nanoscale confinement. Since the exciton lifetime is proportional to  $t^{1/2}$ , where  $t$  is the fluorescence lifetime, any means by which  $t$  can be extended directly affects the charge-harvesting efficiency. One particularly intriguing means of extending the fluorescence lifetime is based on tuning the local density of photon (emission) modes accessible to the light-harvesting molecule. In the case of a high dielectric constant cylinder, simulations indicate that by tuning the cylinder diameter – combined with high dielectric constant – we can expect significant inhibition of radiative recombination, which may translate directly into higher efficiency photovoltaic devices.

*Anti-reflective surfaces:* Ideally one wants all incident light to enter a solar cell. None should be reflected. This project involves research to make an "ideal" antireflective layer by appropriately structuring the solar cell material itself. For such an approach, an ideal antireflective layer must meet two conditions -- the layer must be the correct thickness and it must have an index of refraction that is the geometric mean of air and the solar cell material. Current approaches by the investigators within this Cluster will address this possibility.

In summary, the broad range of complementary strengths within the Cluster E of CUMIRP will be brought to bear for developing novel strategies for increasing the efficiency of polymer-based solar cells.



## A National Science Foundation established Industry / University Cooperative Research Center since 1980

**Mission Statement:** To act as a cross-roads where University research and education meet with Industrial and Government partners in Polymer Science and Engineering at the University of Massachusetts Amherst.

**The Center:** The oldest National Science Foundation established Industry / University Cooperative Research Center (NSF-I/UCRC), established in 1980, has evolved into a dynamic Center program. Its multi-part structure offers flexibility to participating members in tailoring their research programs. The customized approach allows Sponsors to meet the challenges of cutting-edge science in a fast-paced business world.

### CUMIRP Part I

**Part I** of CUMIRP retains the NSF-I/UCRC format in which the research cost and results are shared with other members in a focused, team-oriented approach. Research Clusters, targeted toward specific research areas, allow small team dynamics between Industry Sponsors and University Faculty, Staff and Students. Members of CUMIRP Part I can choose which cooperative research areas (Clusters) they wish to support with their membership dues. Part I members can obtain a non-exclusive, royalty-free license to a University patent resulting from the research done in their specific Research Cluster. Other benefits include invitations to: the member-specific Cluster meetings, the bi-annual meeting featuring hot topics in science, the annual UMass Polymer Poster Symposium and the various Materials Research Science & Engineering Center (MRSEC) meetings and workshops. CUMIRP also assists sponsors of all Parts in recruiting future employees.

CUMIRP Part I has structured its fee schedule to be accessible to all sized companies, and encourages small and mid-sized companies to participate. Membership dues for the CUMIRP Part I Clusters are \$6,000, \$18,000 and \$30,000 for small (<\$100 M sales), medium (\$100 M - \$1 B sales) and large companies (>\$1 B sales), respectively. This dues schedule, along with a 40% discount for a second research cluster membership and additional discounts for the *Membership-at-Large* option, makes Industrial participation an affordable and attractive investment. The sharing of research and patent costs by Cluster members allows for a tremendous leveraging of a sponsor's dues. Industrial Sponsors from all sized companies find the cooperative Research Cluster concept a great value for their research dollar.

### CUMIRP Part II

**Part II** of CUMIRP is structured so that a single company can support research with a faculty member (or team of faculty) and a post-doctoral employee or graduate student. CUMIRP Part II can be viewed by industrial sponsors as the University extension of their research and development program, as sponsors and University researchers collaboratively design the program to meet the Sponsor's unique needs. Sponsors of Part II research pay the associated costs of the project and have a first option to obtain an exclusive license to any resulting University patent. Part II members are invited to attend CUMIRP and MRSEC lectures, meetings and symposiums, and memberships can accommodate visiting industrial researchers. CUMIRP Part II is the preferred format for Sponsors to achieve directed results, while allowing them the option to join a Part I Cluster at a 40% reduction in dues.

### CUMIRP Part III

**Part III** of CUMIRP is for Unrestricted Research Grants which allow for creative and unrestricted use of funds by the UMass Faculty. Resident Industrial CUMIRP Research Professorships, Internships and funding of Industrial Lectureships are also possible. Part III of CUMIRP has expanded rapidly not only because unrestricted grants carry a lower University overhead rate, but also because of the flexibility Part III memberships offer. As with Part I and Part II, sponsors electing Part III memberships are invited to CUMIRP and MRSEC functions and symposia.

### CUMIRP Part IV

Part IV of CUMIRP provides participants a venue to scope out potential programs through idea development and concept feasibility in short duration, focused research studies. The research projects are conducted under a Memorandum of Understanding, which incorporates the basic framework of a research agreement with a brief statement of work and project objectives.

Part IV is recommended as a means for concept exploration to establish initial feasibility and preliminary results. This information is useful in determining whether a longer term research program (Part II) is warranted and assists in providing research direction. This mechanism provides access to faculty expertise, specialized research services and facilities often necessary in defining a sound research program. Part IV projects carry a lower University overhead rate (comparable to Part III), maximizing your research funds. This program is available on a limited basis with agreement of the individual faculty member and the CUMIRP Director.



**Silvio O. Conte National Center for Polymer Research** on the UMass/Amherst campus. The office wing (above - 39,000 sq.ft.) is connected to a laboratory complex (133,000 sq.ft.) and houses the complete Polymer Science & Engineering Department, the Materials Research Science & Engineering Center (MRSEC), and the Center for the University of Massachusetts Industry Research on Polymers (CUMIRP).

### Management of CUMIRP

CUMIRP is managed by a full-time director and is governed by a Steering Committee composed of five members of the University Faculty. An Industrial Advisory Board (IAB) provides feedback to the Steering Committee on CUMIRP policies and operations. Board members are active sponsors in the CUMIRP program.

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