

SYMPOSIUM W

Electroresponsive Polymers and Their Applications

November 27 - December 1, 2005

Chairs

Vivek Bharti

3M Company
201-1W-28, 3M Center
St. Paul, MN 55144-1000
651-736-8057

Quiming M. Zhang

Dept. of Electrical Engineering
The Pennsylvania State University
University Park, PA 16802
814-863-8994

John Madden

Dept. of Electrical & Computer Engineering
The University of British Columbia
Vancouver, BC, V6T 1Z4 Canada
604-827-5306

Yoseph Bar-Cohen

Jet Propulsion Laboratory
4800 Oak Grove Dr.
Pasadena, CA 91109
818-354-2610

Zhong-Yang Cheng

Dept. of Materials Engineering
Auburn University
210 Ross Hall
Auburn, AL 36849-5321
334-844-4913

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* Invited paper

TUTORIAL

FTT/U/W: Smart Materials – Fundamentals and Applications
Sunday November 27, 2005
9:00 AM - 12:30 PM
Room 200 (Hynes)

This tutorial will focus on the broad range of inorganic and organic functional materials that are being studied for applications as “Smart Materials,” including piezoelectrics, multiferroics, and electroactive polymeric materials. The tutorial aims to give the attendee a broad perspective of the various materials and their fundamental science, and then finish up with a summary discussion of their applications. Each segment will include background information, a description of the method, the current state of the art, new trends, and unique advantages and limitations (e.g., for fabrication of particular materials or devices, scalability, unusual geometries, and integration in multistep hybrid device fabrication schemes). The intention of the tutorial is to give the attendees a fundamental background on each method, the strengths of each technique, the ease/difficulty/cost of setting up, and future directions.

Fundamentals of Piezoelectric Materials – Troler-McKinstry
Multiferroics – Viehland
Electroactive Polymers – Cheng
Applications and Examples – Madden

Instructors:

Z. Y. Cheng
Auburn University

John Madden
University of British Columbia

Susan Troler-McKinstry
The Pennsylvania State University

Dwight Viehland
Virginia Tech

SESSION W1: Polymer Sensors and Their Applications

Chairs: J. Madden and Q. M. Zhang
Monday Morning, November 28, 2005
Gardner (Sheraton)

8:00 AM *W1.1

Lesser-Known Piezoelectric and Pyroelectric Applications of Electroactive Polymers. Sidney Lang¹ and Supasart Muensit²;

¹Chemical Engineering, Ben-Gurion University of the Negev, Beer Sheva, Israel; ²Department of Physics, Prince of Songkla University, Hatyai, Thailand.

The piezoelectric effect was first observed in polyvinylidene fluoride polymer (PVDF) in 1969 and the pyroelectric effect was found several years later. A number of additional ferroelectric polymers have been discovered since that time including the copolymers of PVDF and tri- and tetrafluoroethylene and the odd nylons. A large number of applications of piezoelectricity and pyroelectricity have been developed. The magnitudes of the effects in polymers are much lower than those of ferroelectric ceramics (an exception is the piezoelectric effect in porous polymers). However, other factors make these very desirable materials for applications. The polymers have low permittivities, low acoustic impedances and low thermal conductivities. They are available in large area sheets and they are flexible and relatively low in cost. Among the better-known applications of these materials are: actuators, vibration controllers, medical ultrasound and other medical devices, infrared sensors, strain measurement devices, shape-controlled structures, structural health monitors, hydrophones, acoustic wave devices, electronic components, loudspeakers and microphones, microbalances and automotive devices. However, this lecture will concentrate on some of the lesser-known applications including tactile sensors, astrophysics devices, energy conversion systems, shock sensors and physical property measurement techniques.

8:30 AM *W1.2

Piezoelectric polymers. Siegfried Bauer, Simona Bauer-Gogonea and Reinhard Schwoedauer; Soft Matter Physics, Johannes Kepler University, Linz, Austria.

Piezoelectricity is common to polar polymers. In dipole glasses and

ferroelectric polymers dipole density piezoelectricity is usually observed. In internally charged cellular space charge electrets intrinsic piezoelectricity is observed with huge d_{33} coefficients exceeding those of traditional piezoelectric polymer materials. Internally charged cellular polymers behave like typical ferroelectrics, hence they provide a novel class of ferroic materials. Due to the strong piezoelectric effects in soft ferroelectric foams they can be used in a wide range of applications as transducers for interconverting mechanical and electrical signals. An overview on the preparation of cellular polymers by physical foaming (extrusion, biaxial stretching and controlled inflation by pressure treatments), on the charging by microstorms, on the piezo- and pyroelectric properties and on analogies to ferroelectric materials is given. The huge potential of internally charged cellular space-charge electrets is illustrated with a tour d'horizon through selected applications. Work partially supported by the Austrian Science Funds (FWF).

9:00 AM *W1.3

Piezoelectric Poly(vinylidene fluoride) (PVDF) Thermally Stable to 125C. Mitch Thompson, Measurement Specialties, Inc., Wayne, Pennsylvania.

As a transducer material, PVDF can be found in a wide variety of commercial, industrial, medical, and scientific applications. Despite its popularity, however, PVDF has long been considered unsuitable for use at elevated temperatures, typically above 85C. This limitation precludes a substantial number of applications and there is a market demand for piezoelectric PVDF stable throughout the -40C to 125C operating temperature range of industrial grade electronics. Recent enhancements in the processing of ferroelectric PVDF have made it possible to produce material with reasonable piezoelectric activity that will not suffer an irreversible loss in performance after temperature excursions as high as 125C. These enhancements include control of tension and snap back during post polarization thermal annealing; control of necking during a multi-gap orientation process; complex coordination of draw ratio, draw rate, and draw temperature profiles; and ageing, storage, and surface preparation processes. Details of the enhanced processes will not be discussed. However, measurements of the elastic, dielectric, and piezoelectric properties of this thermally stabilized piezoelectric PVDF will be presented over a temperature range of 25C to 125C and a frequency range of 0.1 to 100 Hz. Mechanical shrinkage and longitudinal/transverse thermal coefficients of expansion and other data will also be presented.

9:30 AM W1.4

Effect of High-Energy Electron Irradiation on Nonisothermal Crystallization Kinetics in P(VDF-TrFE) 65/35 mol% Copolymer. Zhimin Li and Z.-Y. Cheng; Materials Engineering, Auburn University, Auburn, Alabama.

The effect of high-energy electron irradiation on the crystallization process in P(VDF-TrFE) 65/35 mol% copolymers was studied by nonisothermal crystallization using the differential scanning calorimetry (DSC) technique. The experimental data is analyzed using modified Avrami, Ozawa and combined Avrami-Ozawa methods. All these methods fit the experimental data obtained from the irradiated sample well. However, the data obtained from the unirradiated samples does not fit well using Avrami or Ozawa methods. It is found the crystallization in the irradiated samples has one dimension less than in the unirradiated samples, and the crystallization activation energy (350 kJ/mol) in the irradiated sample is smaller than (430 kJ/mol) in the unirradiated samples. The results indicate the crystallization in the irradiated samples is more or less heterogeneous in nature, and the surface energy of the crystals in the irradiated samples is smaller than in the unirradiated samples.

10:15 AM W1.5

Energy Harvesting Using Electrostrictive Poly(vinylidene fluoride-trifluoroethylene) Polymers and Single Crystal PMN-PT/Epoxy 1-3 Composite. Kailiang Ren^{1,2}, Yiming Liu¹, Heath Hofmann¹ and Qiming Zhang^{1,2}; ¹Department of Electrical Engineering, Pennsylvania State University, University Park, Pennsylvania; ²Material Research Institution, Pennsylvania State University, University Park, Pennsylvania.

Recent the research about energy harvesting attracted a great deal of attention due to a lot of application, such as wireless sensor, military application and so on. In this paper, the electrostrictive polymers are used for the energy harvesting because of the giant strain (~5%) and the relatively high energy conversion efficiency, approaching those of natural muscles. This paper presents how to change the mechanical and electric boundary to maximum the energy conversion efficiency and demonstrates experimentally an energy harvesting of 39mJ/cc/cycle and mechanical-to-electrical coupling efficiency of about 10% for irradiated polymer. We also investigated energy harvesting using single crystal PMN-PT/Epoxy 1-3 Composite in a soft epoxy matrix. The resistor circuit was used to measure harvested

energy from it. It is shown that 1-3 composites enable the single crystals operating in the longitudinal mode to achieve high efficiency for energy harvesting while the soft-polymer-matrix-supported single-crystal rods maintain high mechanical integrity under different external loads. The experiment demonstrates that the power density of 96.2 mW/cc can be achieved by using single crystal PMN-PT /Epoxy 1-3 composite. It also indicates that the high coupling factor of single crystal PMN-PT 1-3 composites lead to much higher electric energy output for similar mechanical energy input.

10:30 AM W1.6

Self Assembling Mechanism of Biologically Synthesized Electrospun Electroactive Polymers. A. S. Bishop and P. I. Gouma; Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, New York.

The processing parameters of polyaniline (PANI) dictate the desired morphology and overall structural stability of the deposited polymer for biological and chemical sensor applications. Electrospun composites of biologically synthesized PANI with poly-vinyl-pyrrolidone (PVP) as the base polymer were prepared and have exhibited evidence of self assimilation of the PANI particles into porous tubular microstructures. Moreover, it appears the encapsulation of Urease E.C.3.5.1.5 aids the self-assembling nature of the conducting polymer during exposure to NO_x and NH₃ gases. During the sensing experimentation the self-assembling nature of the bio-composite intensifies and micro-porous structures of PANI are produced. The result is a porous, hybrid, active sensing matrix that amplifies the reactivity of the immobilized enzyme. Investigations of the self assembling mechanism and its effect on the sensory nature of bio-doped PANI will be discussed in this paper.

10:45 AM W1.7

Evolving thin polymer film driven by electrostatic field. Dongchoul Kim and Wei Lu; Mechanical Engineering, University of Michigan, Ann Arbor, Michigan.

Experiments have shown that a thin polymer film subjected to an electrostatic field may lose stability at the polymer-air interface, leading to uniform self-organized pillars emerging out of the film surface. A three dimensional dynamic model for the morphological evolution of thin polymer film under an electrostatic field is developed based on a phase field model to study this behavior. The coupled diffusion, viscous flow, and dielectric effect are incorporated into this model presenting the interplay of the thermodynamic forces and the kinetic processes. The semi-implicit Fourier spectral method and the preconditioned biconjugate-gradient method are applied in the simulations for high efficiency and numerical stability. The regular nano scale pillars, which have been described by the competition between the surface energy and the electrostatic energy, are demonstrated by simulation. Three dimensional simulation results indicate that the kinetic constraint of the substrate plays a critical role in structural uniformity. The pillar size is insensitive to the film thickness, but the distance between pillars and the growth rate are significantly affected. This study provides a possible route to control a structural formation of thin polymer film by a designed electric field.

11:00 AM W1.8

An Ultraviolet Radiation Sensor Using Conducting Polyamine Film. Zhijun Zhang¹, William J. Buttner¹, Joseph R. Stetter¹ and Kurt P. Scott²; ¹Department of Biological, Chemical and Physical Sciences, Illinois Institute of Technology, Chicago, Illinois; ²Atlas Materials Technology LLC, Chicago, Illinois.

Traditional ultraviolet sensors are photovoltaic devices using semiconducting materials or the photoelectric effect of metal combined with the gas multiplication effect. We report on a novel inexpensive ultraviolet sensor using conducting polyaniline nanoparticle chemically doped with various additives. UV radiation intensity (irradiance) determines both the rate and magnitude of the electrical property degradation of the polyaniline. The sensing principle is based on the accumulated UV-induced polymer degradation effect on the conductivity. The sensing device is a microfabricated structure on a SiO₂/Si substrate with an accurately controlled polymer film coupled with an interdigitated electrode structure with a variety of inter-electrode spacing from 15 to 100 micrometer. The materials electrical property degradation where the law of reciprocity is valid was used as the basis for building an inexpensive and fast response UV sensor.

11:15 AM W1.9

Piezopolymer Diaphragm as High Performance Biosensor Platform. Zhimin Li, Suiqiong Li and Z.-Y. Cheng; Materials Eng, Auburn University, Auburn, Alabama.

A new type of biosensor based on a microdiaphragm made of PVDF piezoelectric polymer is induced. The microfabrication process is

reported. The performance of the sensors was characterized in air and liquid. The results show that the diaphragm has a higher sensitivity than the cantilevers. More importantly, the mechanical merit factor (Q value) of the diaphragm is much higher than the cantilevers. The feasibility of employing piezopolymer diaphragm as a biosensor platform is demonstrated by detecting yeast cell in water.

11:30 AM W1.10

Emeraldine Base Thin Film Carbon Dioxide Sensor. Mihai Irimia-Vladu and Jeffrey W. Fergus; Materials Science and Education Center, Auburn University, Auburn, Alabama.

Introduction Respiration, or carbon dioxide evolution, is a universal indicator for biological activity, so determination of carbon dioxide evolution is useful for many biological applications. Among many potential applications, the measurement of carbon dioxide evolution has also been found to be a rapid, nondestructive means for examining microbial contamination of food. Sensor Design The sensor developed in this work consists of a thin emeraldine base-polyaniline (EB-PANI) film. The sensing mechanism is based on intermediate stages of the transformation of the emeraldine base polyaniline to a conductive salt type (ES-PANI). This EB-ES transformation is the consequence of the exposure of EB-PANI to a protonic acid and is accompanied by a change in the conductivity of the polymer film. Carbonic acid, unfortunately, is a very weak acid and is unable to induce a conductivity change, but the intermediate steps that predetermine this transformation are detected by impedance spectroscopy even when the overall conductivity of the film is unchanged. Experimental The polymer film solution was made from a stock solution of 3% EB-PANI of Mw=5000 in N-methyl-2 pyrrolidone (NMP). The polymer solution was cast on interdigitated electrodes and the solvent removed under flowing nitrogen gas at room temperature. The interdigitated microelectrode (15 micrometer interdigitated spacing) containing the thin EB-PANI film was suspended in a beaker containing pure deionized water, through which ultra pure carbon dioxide gas was bubbled. Results and Discussion Typical impedance spectra for the emeraldine thin films contain a single semicircle. The overall conductivity of the film does not change when carbon dioxide is bubbled through the water, but an additional semicircle starts to appear corresponding to a change in pH of the solution from 6.0 to 4.4. The original semicircle diminishes in size but maintains the same peak frequency. The film is very sensitive to pH changes, so an additional semicircle appears in unpurified argon gas due to reduction of the pH of the water solution to 4.65. The impedance spectra are fitted with a series sequence of parallel R-CPE elements and the resistance values are grouped in two equivalent resistances. The formation of the second semicircle at pH values lower than 5 is not a result of gas convection in liquid media as it is formed when carbon dioxide gas is passed above the thin polymer film the surface of which is covered by a water droplet or by wet filter paper. The time necessary for stabilization of the second semicircle is about 30 minutes in the latter two cases, whereas when carbon dioxide is bubbled directly through water the semicircle forms in less than 2 minutes. The sensor output is stable and reproducible after 4 months of testing.

11:45 AM W1.11

Electronic Acoustic Sensor. Vivek Bharti¹ and Fred L. DeRoos²; ¹Corporate Materials Research Laboratory, 3M Center, St. Paul, Minnesota; ²Corporate Research Analytical Laboratory, 3M Center, St. Paul, Minnesota.

The acoustic sensor (stethoscope) is a fundamental tool for the diagnosis of diseases and conditions of the cardiovascular (CV) system. Several studies have shown that there is a significant decline in the accuracy of diagnosing heart sounds following initial training. There is clearly a need for technology that will allow physicians to monitor auscultation with a reduced learning curve using equipment that is low-cost, robust and easy to use. In this paper, we will present some results of our efforts in this area.

SESSION W2: Polymer Sensors and Their Applications II

Chairs: Mitch Thompson and M. Zahn
Monday Afternoon, November 28, 2005
Gardner (Sheraton)

1:30 PM *W2.1

Electroresponsive Polymer and its Sensor Applications. Heikki Raisanen, Emfit Ltd, Vaajakoski, Finland.

Emfit Ltd is manufacturer of electroresponsive ferroelectric sensors. These film-like sensors can be used for various applications, like dementia care, actigraphs, visitor count and keypads. The sensor material is based on a polyolefin material manufactured in a continuous biaxial orientation process that stretches the film in two perpendicular directions (machine direction and the transverse

direction). The structure of Emfit material consists of flat voids separated by thin polyolefin layers. The voids are made by compounding small particles, which function as rupture nuclei and form closed lens like cavities to the film during the biaxial orientation. A permanent electric charge is injected into the material using corona charging process. The voided internal structure makes the film soft and elastic in the thickness direction. This means that the voids expand and contract in relation to the orientation of the film. The excellent sensor and actuator operations of EMFi are based on the fact that reduction in the thickness of the film caused by an external force takes place in the gas voids and these are much softer than the polymer layers.

2:00 PM *W2.2

Kerr Electro-Optic Field and Charge Mapping Measurements in Electron Beam Irradiated Polymethylmethacrylate (PMMA) In Air and In Vacuum. Markus Zahn, Laboratory for Electromagnetic and Electronic Systems, MIT, Cambridge, Massachusetts.

Kerr electro-optic field and charge mapping measurements are reported for energetic electron beam penetration into short circuited polymethylmethacrylate in air and in vacuum. The accumulated trapped charge results in large electric fields up to 3 MV/cm which allows recording by photographic film and videotape of the resulting numerous light maxima and minima. The short circuit imposes the constraint of zero average electric field so that the electric field is oppositely directed on either side of the zero field point. To obtain the Kerr constant of PMMA a photomultiplier tube (PMT) detector was used with aligned and crossed polarizers with He-Ne light for a PMMA sample between parallel plane electrodes stressed by a high voltage pulse $v(t)$. Early in the high voltage pulse, space charge effects are negligible and the electric field is uniform, allowing determination of the Kerr constant to be $B \sim 2 \times 10^{-15}$ m/V². Thus for samples of length L the representative field strength $E_m = 1/\sqrt{2BL}$ necessary for the first light maximum with crossed polarizers or first light minimum with aligned polarizers is $E_m = 0.73$ MV/cm for $L = 4.7$ cm, $E_m = 0.50$ MV/cm for $L = 10.2$ cm, and $E_m = 0.44$ MV/cm for $L = 12.7$ cm. The electron beam is generated by a Van de Graaff generator and for air measurements exits from the accelerator tube through a thin (.003 inch) aluminum window and passes through ~ 50 cm air to the PMMA sample which is short-circuited through current monitors at the top and bottom surfaces. Although the field and charge distributions were similar whether the sample was in vacuum or air, many more electrical breakdowns occurred in vacuum, generally when the total accumulated charge per unit area was $Q \sim 10^{-2}$ C/m². The maximum charge density often accumulated over such a thin region so that within the accuracy of our spatial resolution it appeared as a sheet charge causing a discontinuous electric field, where optical fringes coincide in the central region. For a typical maximum electric field of order 1.5 MV/cm at the top and bottom surfaces, the peak charge density is roughly $q \sim 3.9$ C/m³. The total electric stress on the sample is roughly 7.4×10^5 nt/m². Measurements are reported at electron beam energies of 0.6, 1.6 and 2.6 MeV at low (20 nA/cm²) and high (300 nA/cm²) current densities and for sample thicknesses of 0.635, 0.95, 1.27 and 2.54 cm which cover the range where the electron beam penetration distance is larger, comparable to, or smaller than the sample thickness. A computerized image digitization system allows easy processing of the time dependences of field and charge distributions, the electric field strengths at the boundaries, the total accumulated charge per unit area, the locations of the zero electric field (peak potential), the average position of the charge, and the magnitude and location of the maximum charge density.

3:30 PM W2.3

Novel Resistive Strain Sensors for Large Strain (100%) Sensing. Minren Lin, Kaoliang Ren and Qiming Zhang; Materials Research Institute and Electrical Engineering Department, The Pennsylvania State University, University Park, Pennsylvania.

Strain sensors based on resistive change with strain have been used for many decades. However, these earlier strain sensors are limited to very small strains, typically at below 1% strain level. For biomedical and bioengineering applications, strain sensors which are capable of sensing strains to much higher than 10% and in some cases 100% strain level sensing are highly desirable. Although there were several attempts to develop such a strain sensors in the past, the large drafting of the resistance value after large strain change (>10%) makes them unusable for these applications. In this presentation, we will report our recent work investigating strain sensors based on several approaches. We will discuss the origin of these resistance drifting and approaches to eliminate the drifting. We will present a novel approach which can realize strain sensing to more than 100% (from 0% to 100%) strain without any resistance drafting after the strain change. Based on this approach, micro-sensors and macro-sensors are designed which can sense both the tensile strain and shear strain. These new resistive sensors with strain sensing to

more than 100% without drafting can be used for a broad range of bio- and engineering applications.

3:45 PM W2.4

Chemical and Biological Sensing Using Organic Electrochemical Transistors. Jeff Mabeck¹, John DeFranco¹, Chris Chase³, Nate Cady², Carl Batt² and George Malliaras¹; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Food Science, Cornell University, Ithaca, New York; ³Agave BioSystems, Ithaca, New York.

We report on chemical and biological sensing using organic electrochemical transistors based on the electroresponsive polymer poly(3,4-ethylenedioxythiophene) doped to a highly conducting state with poly(styrene sulfonate) (PEDOT:PSS). The source-drain current through a film of PEDOT:PSS can be modulated by electrochemical doping or de-doping, where the PEDOT conductivity change is mediated by ions from an adjacent electrolyte. A poly(dimethylsiloxane) (PDMS) microfluidic channel is used to confine and direct the flow of liquid electrolyte over the transistor, and we demonstrate a novel technique for controlling the doping or de-doping of the PEDOT by integrating a gate electrode into the "ceiling" of the microfluidic channel. The transistor behavior is shown to depend on the ionic strength of the electrolyte, and the response to a variety of different cations is explored. Ion specificity for K^+ is achieved by incorporating a crown ether (18-crown-6) into the PEDOT:PSS film. Glucose sensing has also been achieved by using the enzyme glucose oxidase and monitoring the enzymatic production of hydrogen peroxide. Our work on cell sensing and DNA detection using PEDOT:PSS transistors will also be discussed.

4:00 PM W2.5

State-of-the-Art Developments in the Field of Electroactive Polymers. Aleksandra Vinogradov¹, Ji Su², Christopher Jenkins³ and Yoseph Bar-Cohen⁴; ¹Mechanical and Industrial Engineering, Montana State University, Bozeman, Montana, Montana; ²NASA Langley Research Center, Hampton, Virginia; ³South Dakota School of Mines and Technology, Rapid City, South Dakota; ⁴Jet Propulsion Laboratory, Pasadena, California.

The paper represents an effort to outline the accomplishments and challenges in the field of electroactive polymers. It provides a summary review of several classes of electroactive polymers, including piezoelectric, ionic and conductive polymers, and soft electroactive foams. The historical background, properties and applications of these materials, and ongoing research efforts to synthesize advanced electroactive polymers with novel or enhanced performance characteristics are described. It has been observed that electroactive polymers and composites represent a diverse and rapidly growing class of intelligent materials distinguished by many useful qualities such as superior strength to weight ratio, high corrosion resistance, low friction coefficients, high compliance, and cost effectiveness. In addition, such polymer systems offer unique opportunities in terms of tailoring their properties to suit specific operational needs. Polymers are easy to shape, thus complicated parts performing several functions can be produced in a single operation. These unique properties of electroactive polymers have stimulated an explosive growth in their use in numerous applications. In the past decades, polymer-based transducers, sensors and actuators have shaped an impressive array of advanced technologies, including acoustic microscopy, active vibration control, damage detection in fibrous composites, optoelectronics, and marine fouling prevention. At present, electroactive polymers have been viewed as primary candidate materials for shape and position control of compliant structures in weight sensitive applications. Medical applications of smart polymers are driven by their biocompatibility and high sensitivity to small changes in physiological conditions. The success in the development, manufacturing and production of electroactive polymer systems is undisputable. It appears, however, that whereas the application range of electroactive polymers has increased dramatically, the respective knowledge base required to sustain further technological progress remains fragmented and incomplete. In this view, the associated challenges and future research directions in the field are discussed in detail.

4:15 PM W2.6

Polarization Dependence of Electrical Properties of PANI - BaTiO₃ Nanofibers. Maxim P. Nikiforov¹, Haiqing Q. Liu², Jun Kameoka³, Harold G. Craighead² and Dawn A. Bonnell¹; ¹Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²School of Engineering and Applied Physics, Cornell University, Ithaca, New York; ³Electrical Engineering, Texas A&M University, College Station, Texas.

The properties of conducting polymers are being exploited in a wide range of functional devices including chemical sensors, electrochromic displays, etc. Recently a scanned-tip electrospinning deposition approach has been developed to produce various kinds of oriented

polymer nanofibers as individuals, and readily integrate them with microfabricated surface structures for nanoscale device applications. In order to increase the functionality of the nanofibers, we dispersed 50 nm-diameter ferroelectric nanoparticles in the polymer. Polyaniline (PANI) - BaTiO₃ nanofibers were patterned on gold microelectrodes to produce circuits which can be subjected to large external fields. The external fields were used to orient the polarization of the nanoparticles. The field dependence and composition dependence of the fiber electrical properties were characterized by two-point resistance measurements. The relative concentration of BaTiO₃ nanoparticles was quantified by energy dispersive spectroscopy. The fiber resistance was observed to increase with the polarization voltage. A simple model of heterogeneous resistive media was used to fit the current dependence at 1 V on the polarization voltage. From this model, the volume polarization was extracted. The volume polarization increased with the increase of BaTiO₃ content. We conclude that the incorporation of ferroelectric nanoparticles into conducting polymers can add a dimension of functionality to the polymer, which may be utilized in future sensor or information storage applications.

4:30 PM **W2.7**

Ion Beam Modified Conducting Polymer Composites: Material for Gas Sensing. Virendra Singh¹, Chetna Dhand¹, Kaur Manindar¹, Tejvir Singh¹ and Alok Srivastava^{1,2}; ¹Department of Chemistry, Panjab University, Chandigarh, India; ²Applied Science and Technology Division, University of Applied Sciences, Julich, Germany.

A polyaniline based conducting composite was prepared by oxidative polymerisation of aniline in presence of polyvinylchloride (PVC) matrix. The coherent free standing thin films of the composite were prepared by solution casting method. The PVC-polyaniline composite (90:10) of thickness 40 μm was irradiated with 90 MeV C⁵⁺ ions at different ion fluence ranging 10¹¹-10¹³ ions/cm². The changes in resistance of pristine and irradiated composite in presence of ammonia gas were studied. A general decrease in surface resistance is observed upon irradiation. The sensitivity, response time and recovery time were studied as a function of ion fluence on exposing the sensor material to ammonia gas at ambient condition. It is observed that irradiated composite films are more sensitive and fast in response to ammonia gas. The preliminary results observed are encouraging.

SESSION W3: Polymer Actuator I
Chairs: Vivek Bharti and Z-Y Cheng
Tuesday Morning, November 29, 2005
Gardner (Sheraton)

8:00 AM ***W3.1**

Improving the Dispersion of Polymer Nanocomposites for Electro-responsive Materials. Mark D. Dadmun^{1,2}, Asif Rasheed¹, Phillip Britt² and Dave Geohegan²; ¹Chemistry, University of Tennessee, Knoxville, Tennessee; ²Oak Ridge National Laboratory, Oak Ridge, TN, Tennessee.

The addition of a small amount of carbon nanotubes is known to dramatically improve the electro-responsive activity of a conjugated polymer. However, there is very little correlation of this activity to the dispersion of the nanotube in the polymer matrix. In this talk, work in our lab that has shown that optimized hydrogen bonding between a copolymer and an anisotropic filler enhances miscibility of the mixture will be discussed. Controlling the extent of hydrogen bonding between a copolymer and carbon nanotube gives a well-dispersed nanocomposite for both single and multi-wall carbon nanotubes as indicated by Raman spectroscopy, dynamic mechanical analysis, electrical conductivity, optical microscopy and SEM. Varying the copolymer composition controls the amount of hydrogen bond interactions between components of the nanocomposite. The results are critical in understanding interfacial phenomenon in polymer and nanocomposites and will be discussed in the context of the applicability of this protocol in nanocomposites containing conjugated polymers.

8:30 AM ***W3.2**

Design of Responsive Conducting Polymers.
Timothy M. Swager, Chemistry, MIT, Cambridge, Massachusetts.

I will discuss our continuing efforts in the design of conducting polymers to be used as sensory, electrochromic, and actuating materials. For sensory materials I will describe how we utilize molecular recognition events to product changes in conductivity. In many cases we use transition metal ions are redox active elements in these materials and I will outline the design principles for producing conducting polymers that utilize the metal ions as part of the conducting pathway. The nature of the energy levels and bandgaps in

conducting polymers relevant to many applications and their electrochromic responses and new electronic structures will be discussed to modify these properties. I will present novel electroactive materials for actuator applications. In this effort we have developed new mechanisms for causing large dimensional changes in polymers by design of mechanical linkages and electronic properties.

9:00 AM **W3.3**

AFM characterization of electroactive polymer nanocomposites. Ricardo Perez¹, Zoubeida Ounaies¹, Peter Lillehei² and Joycelyne Harrison²; ¹Aerospace, TAMU, College Station, Texas; ²NASA LaRC, Hampton, Virginia.

Polymer-single wall carbon nanotube (SWNT) composites are processed and investigated as part of an effort to develop polymer nanocomposites with a unique combination of properties to advance space applications. The current study focuses on demonstrating the potential of the polymer-SWNT composites as actuators. Towards that end, characterization of their electromechanical properties using atomic force microscopy (AFM) is carried out. The set-up consists of a Digital Instrument AFM, a silicon nitride triangular probe, and a Glassman DC power supply. The experiment is conducted in the contact mode to determine the displacement resulting from application of a DC voltage. As a first step, polyvinylidene fluoride (PVDF) bulk film is tested using this technique and its piezoelectric strain coefficient, d₃₃, is computed from the displacement/voltage data. PVDF is a commercially available piezoelectric polymer, which has been widely studied in the last decades. Consequently, its piezoelectric performance is well-documented, making it the ideal material to use to verify the precision and reliability of the AFM measurement method. Next, the method is applied to the polymer-SWNT composites. The results are compared to displacement data obtained on the bulk composites using a fiber optic sensor. The composites have SWNT content varying from 0 vol% to 1 vol%. At lower volume content, the displacement/voltage curve follows a linear trend, indicating an enhancement in the piezoelectric response as compared to the unloaded polymer. At volume content exceeding the percolation threshold, the displacement/voltage curve is distinctly nonlinear, possibly indicating an electrostrictive response. The AFM method described here allows the probing of the electromechanical response of the polymer-SWNT at the nanoscale level. These findings, coupled with bulk film characterization and Raman spectroscopy, are used to shed light on the polymer-SWNT interaction and its effect on the electroactive mechanism displayed by the composites.

9:15 AM **W3.4**

Controlled gossamer structures deployment and stability using electroactive polymers (EAP) and Electrorheological Fluids (ERF). Yoseph Bar-Cohen¹, Zensheu Chang¹, Christopher H. M. Jenkins², Aleksandra Vinogradov³, Xiaoqi Bao¹ and Stewart Sherrit¹; ¹Jet Propulsion Laboratory, Pasadena, California; ²South Dakota School of Mines and Technology, Rapid City, South Dakota; ³Montana State University, Bozeman, Montana.

Recent technological advancements in ultra-lightweight structures, so called gossamer structures, enable new possibilities of producing large space structures. These structures are low in mass and can be packaged into small volumes, which can potentially reduce the overall programs cost by reducing the launch vehicle size. Reduction in total system mass and deployment complexity can also increase system reliability. The new structures typically consist in large part of highly flexible membranes that operate as load-carrying elements. This usually implies the use of thin, low-modulus materials, such as polymer films, having a very low inherent stiffness and they are used in either tensioned-planar or inflated-curved configurations. Changing the shape of gossamer structures is important for taking advantage of their flexibility for deployment, vibration suppression, control of figure of merit and many others. The change of shape can be best done by actuation materials that are imbedded in the membrane and provide contraction forces operating similar to muscles. Such characteristics can be obtained using the emerging electroactive polymer (EAP) actuators technology. An actuator can either be used to conduct reversible change or respond upon deployment of the structure and relax after it is rigidized. Out of all human-made actuators, EAP materials are the closest to resemble biological muscles and this characteristic earned them the name Artificial Muscles. Generally, EAP actuators are highly maneuverable, noiseless, and agile, with inherent ability to host imbedded sensors and micro-electro-mechanical-systems (MEMS). These unique characteristics are superior to any currently known practical actuator utilizing the properties of such materials as electroactive ceramics and shape memory alloys. Further in the paper, the use of electrorheological fluids (ERF) to provide controlled rigidization of gossamer structures is discussed. The essential functions of ERF in this regard are based on their ability to change viscosity when subjected to an electric field. Using EAP and ERF the structure deployment rates can be controlled and it allows mitigation of

negative post-deployment effects such as impact-induced vibrations and structural instability.

9:30 AM W3.5

Soft Actuators based on Polypyrrole and Polyaniline Composite Films. Keiichi Kaneto, Makoto Yano, Yuji Ishizaki, Miho Shibao and Vipul Singh; Graduate School of Life Science and Systems Engineering, Kitakyushu, Japan.

Composite conducting polymer films consisting of polypyrrole and polyaniline were examined for the performance of soft actuator due to the electrochemomechanical deformation. The polypyrrole (PPy) based films were electrochemically polymerized in molecular anions with various ratios of dodecylbenzene sulfonic acid (DBS) and poly(2-methoxyaniline-5-sulfonic acid), PMAS in aqueous electrolyte. With increasing the ratio of PMAS, the film contained large volume of water and exhibited gel like appearance. The film can be actuated in both aqueous and organic electrolytes, and showed a little different and complicated behavior. PPy/DBS film expanded by reduction, however, with increasing the ratio of PMAS the film showed the contribution of anodic expansion. The large expansion of film (composite PPy film of 97% DBS and 3% PMAS) reaching to 8% was observed by reduction of film (cathodic expansion) in organic solvent of TBACl/acetonitrile. This is the largest strain ever obtained for cathodic expansion).

10:15 AM *W3.6

Electrostrictive Polymers, Devices, and Applications. Ji Su¹ and Tian-Bing Xu²; ¹Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, Virginia; ²National Institute of Aerospace, Hampton, Virginia.

In recent years, a variety of electrostrictive polymers have been developed. These electrostrictive polymers usually offer significantly larger electrical field-induced strain than piezoelectric polymers. A relatively new electrostrictive graft elastomer (G-elastomer) developed at NASA Langley Research Center has demonstrated promising electromechanical properties. The properties include large electrical field-induced strain, high electromechanical output, and relatively high mechanical moduli. The elastomer is a two-component system that contains a flexible backbone chain and an electro-responsive polar grafted crystalline domain. This two-component system enables tailoring of the electromechanical performance by controlling the relative fraction of the components and the morphology. The investigation of the mechanism of electrostriction in the G-elastomer demonstrated that by controlling the morphology, a simultaneous increase in both the field-induced strain and the mechanical modulus is observed. Several types of electromechanical devices have been designed and fabricated using electrostrictive polymers. These devices have shown good performance and are attractive for aerospace applications. This presentation will provide a review of electrostrictive polymers, devices, and potential applications for NASA missions.

10:45 AM W3.7

Synthesis and Applications of Poly(phenylene ethynylene)s Containing Pendant Masked Michael Acceptors. Ghislaine C. Bailey and Timothy M. Swager; Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Poly(p-phenylene ethynylene)s (PPEs) are highly emissive polymers which are easily quenched by target analytes and, as such, have become increasingly popular for use in both chemo- and bio-sensors. To ensure their continued success, the versatility of PPEs will need to be expanded and will require taking advantage of the modularity of PPE synthesis. Incorporation of multi-functional handles along the polymer backbone is one such way to increase the PPE's value. These handles could be used to bind a wide range of targets, from small molecules to large ones, such as peptides or antibodies. They could also serve as sites for cross-linking to form a polymer network. To this end, a polymer has been designed and synthesized with the reactive maleimide group pendant along the polymer's backbone. The maleimide functionality contains an electro-deficient double bond capable of participating in Michael and Diels-Alder chemistries with thiols and dieneophiles, respectively. One major problem was the discovery of the need to shield the maleimide during polymerization reactions due to the reactive nature of maleimide's double bond. The synthesis of the monomers and polymers, along with the solution to the aforementioned problem, will be presented. Initial applications of the polymers in a biosensor utilizing molecular beacon DNA sequences will also be presented.

11:00 AM W3.8

Electrical Properties Of Electrospun Poly (Ethylene Oxide) - Polypyrrole Composite Fibers. Natarajan Tirupattur Srinivasan, Bibekananda Sundaray and Subramanian V.; Physics, Indian Institute of Technology Madras, CHENNAI, Tamilnadu, India.

Electrospinning is a simple method of obtaining ultra fine and nanometer diameter fibers of polymers. The increase in the ratio of surface area to volume in the case of such fibers, make them attractive in applications such as sensors, etc. Polypyrrole (PPy), is a well known polymer with potential applications in sensors and polymer devices and by itself it can not be spun to form fibers. Hence a composite formed with PPy and another polymer like Polyethylene oxide (PEO), Polystyrene (PS) etc., can be easily electrospun. The concentration of PPy can be varied to improve the electrical or sensing properties of the resulting composite polymer. In the present report, the PEO-PPy composite fibers with different weight percentages (10% to 50% w/w), are prepared by electrospinning process. The fibers obtained are characterized using SEM (Scanning Electron Microscope) and TEM (Transmission Electron Microscopy). I-V Characteristics are studied for single and multiple aligned fibers obtained on gold electrodes. The variation of electrical conductivity with different concentration of PPy is discussed in detail.

11:15 AM W3.9

Intrinsically Conducting Polymer Composites as Matrix Material for Molecular Actuators. Nathan Vandesteeg¹, Ian Hunter² and Timothy Swager³; ¹Materials Science and Engineering, MIT, Cambridge, Massachusetts; ²Mechanical Engineering, MIT, Cambridge, Massachusetts; ³Chemistry, MIT, Cambridge, Massachusetts.

Traditional actuators based on intrinsically conducting polymers such as polypyrrole, polyaniline, and poly(3,4-ethylenedioxythiophene) utilize the ingress and egress of ions to change bulk dimensions and perform work against an applied load. Considerable synthetic effort in our group as well as others has focused on novel polymer architectures capable of sustaining dimensional changes at the molecular level. The realization of materials of sufficient size and stability for mechanical testing has been slow in this area as many of the novel monomers do not polymerize as well as traditional conducting polymers. The goal of observing molecular displacements in a bulk material has remained elusive. With this goal in mind, a series of composite materials containing a matrix of electroactive monomer copolymerized with monomers that exhibit conformational changes with oxidation state have been synthesized. The actuation of these materials demonstrate the ion ingress and egress known to occur in conducting polymers as well as the conformational changes that occur at known oxidation/reduction potentials for the comonomers. By varying the ratio of monomers it is possible to elucidate the effects of each mechanism and understand the capabilities of molecular dimensional changes in the bulk material. A body of work comprising synthesis of novel monomers, copolymerization of composite materials, and active mechanical characterization of composite actuators will be presented.

11:30 AM W3.10

Application of Ab Initio Computational Methods to conjugated Electroactive Materials. Nicholas E. Miller, Damian Scherlis and Nicola Marzari; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Ab initio computational methods have been utilized to investigate at the molecular scale the properties of promising organic actuators. Our work has focused on reversible actuation through the oxidation and reduction of -conjugated thiophene oligomers. In particular, we have explored the intermolecular interactions between charged oligothiophenes as a function of the chemical potential, with an emphasis on the role of the counterions and on solvation effects. Our calculations show what are the factors determining repulsion or stacking of thiophene oligomers in different environments, and assess the role of the solvent and the counterions in the stacking phenomenon. This insight is fundamental to understanding the mechanisms leading to either molecular or bulk (counterion driven) actuation. Other actuating materials such as thianthrene and thianthrene-derived actuators are examined and contrasted to the oligothiophene systems.

SESSION W4: Polymer Actuator II
Chairs: Y. Bar-Cohen and T. Swager
Tuesday Afternoon, November 29, 2005
Gardner (Sheraton)

1:30 PM *W4.1

Fuel Powered Artificial Muscles. Von Howard Ebron¹, Zhiwei Yang¹, Daniel J. Seyer¹, Mikhail Kozlov¹, Jiyoung Oh^{1,2}, Hui Xie¹, Joselito Razal¹, John P. Ferraris¹, Alan G. MacDiarmid¹ and Ray Henry Baughman¹; ¹Chemistry and NanoTech Institute, University of Texas at Dallas, Richardson, Texas; ²Research Center of Dielectric & Advanced Matter Physics and Department of Physics, Pusan National University, Busan, South Korea.

We here experimentally demonstrate artificial muscles that convert the energy of a high-energy-density fuel to mechanical energy. These muscles are fuel cells that in some embodiments store electrical charge and use changes in stored charge for mechanical actuation. The highest demonstrated actuator generated strains and mechanical output power densities are comparable to natural skeletal muscle, and the actuator generated stresses are over a hundred times higher than for natural skeletal muscle. Since the energy density of fuels like methanol is ~ 7.5 times higher than for advanced Li batteries, this advance seems quite important for such applications as autonomous robots or prosthetic limbs, where long operation without recharging or refueling is needed.

2:00 PM *W4.2

DARPA Nastic Materials. John Main, Defense Sciences Office, DARPA, Arlington, Virginia.

The DARPA Nastic Materials Program seeks to develop a new class of active materials inspired by the structures and processes found in the motor organs of plants. Plants generate motion for activities such as prey capture and sun tracking by modulating the fluid pressure within 10-100 micron diameter structural cells. This pressure modulation is achieved by actively transporting fluid through the cell walls. Essentially these plant structures are highly distributed and redundant hydraulic actuation systems. The impetus for this work is the need for an active material that possesses the power density of conventional hydraulic systems and can be used to build smooth and adaptable structures such as aircraft wings, helicopter rotor blades, and submarine planes. The goal is develop a material system that can be used to build structures that can effect large and complex shape changes to optimize performance while still carrying significant mechanical loads.

3:30 PM W4.3

A Novel, Cost-Effective Fabrication Method for Ionic Polymer-Metal Composites. Michael J. Siripong, Susan A. Fredholm, Brian A. Shih and Jonathan D. Stolk; Franklin W. Olin College of Engineering, Needham, Massachusetts.

To date, many processes have been used for the preparation of ionic polymer-metal composite (IPMC) artificial muscle membranes from conductive metals and perfluorosulfonic polymers such as Nafion. Of the reported preparation methods, the platinum plating processes involving chemical reduction of ionic salt solutions are most widely used for production of IPMCs with outstanding surface electrodes and excellent performance characteristics, but these chemical electroding techniques can be relatively costly and time-consuming. We describe a novel fabrication process for fast preparation of low-cost Ni-Au-Nafion IPMCs. The process involves formation of an adherent surface layer on prepared Nafion through DC sputter deposition of a fine-grained gold film. The sputter coating is followed by electroplating of a thin and ductile nickel layer in a solution of aqueous nickel salts and boric acid. Preliminary results indicate that the Nafion-117-based IPMCs produced using this technique exhibit good surface conductivity and promising actuation performance, with a 30 mg cantilever bending sample showing remarkably high displacement and a tip force of approximately 430 mg at 4 V. Our current research efforts are focused on achieving repeatable synthesis techniques and evaluating the properties and performance characteristics of the Au-Ni-Nafion IPMCs, especially in comparison to the popular platinum IPMCs.

3:45 PM W4.4

The Effect of Temperature on Polypyrrole Actuation. Matthew Cole^{1,2} and John D. Madden^{1,2}; ¹Electrical & Computer Engineering, University of British Columbia, Vancouver, British Columbia, Canada; ²Advanced Materials & Process Engineering Laboratory, University of British Columbia, Vancouver, British Columbia, Canada.

Recent work on polypyrrole electrochemically driven actuators has shown significant improvement in strains, with $> 8\%$ strain at 1 MPa having been demonstrated in several studies. However, commercial use of polypyrrole requires reliability in a variety of conditions. In this study, the effect of thermal cycling on two differently synthesized polypyrroles was investigated. Films were cycled between 0°C and 100°C in order to study creep, electrochemomechanical strain, strain to charge ratio and modulus. Strips of polypyrrole were electromechanically cycled in a single compartment cell. Polypyrrole grown and cycled in tetrabutylammonium hexafluorophosphate, showed an initial contraction of 4.8% upon heating, significant creep at high temperatures and a drop in actuation of 80% after exposure to elevated temperatures. Polypyrrole grown in methyl benzoate with tetrabutylammonium tetrafluoroborate and actuated in aqueous sodium hexafluorophosphate showed no initial contraction, very little creep at high temperatures and a drop in actuation of 40%. Based on changes in modulus and charge to strain ratios, the changes can be attributed to a combination of film reconfiguration and an increase in

the rate of film degradation. Preliminary work with bilayers indicates that thermal effects may be minimized by reducing the average stress on the polypyrrole during cycling.

4:00 PM W4.5

Dynamics of Ionic Polymer-Metal Composites in the Linear-Response Regime. Victor V. Yashin¹, Steven P. Levitan² and Anna C. Balazs¹; ¹Chemical & Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; ²Electrical & Computer Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Theoretical modeling of the electromechanical properties of Ionic Polymer-Metal Composites (IPMC) is a challenging problem due to the presence of multiple physical-chemical processes, which are inherently coupled, with many of them being highly non-linear under the operating conditions. Furthermore, current understanding of the underlying mechanisms lacks many essential details, thus impeding significantly the development of reliable theoretical models of IPMC. Theoretical studies of the dynamics of IPMC in the linear-response regime might provide valuable insight into electromechanics of IPMC because the well-developed methods of statistical thermodynamics could be employed for an analysis of realistic physical-chemical models. Here, we apply the electrostress diffusion coupling model by Doi and co-authors for modeling the dynamics of an IPMC cantilever. The frequency-dependent dynamics of sensing and actuation is described in the linear regime. The results reveal the time scales and magnitudes characteristic to the basic transport and relaxation processes in IPMC.

4:15 PM W4.6

Nature and Dynamics of Electronic Excitations in Conjugated Polymers. David Beljonne^{1,2}, Emmanuelle Hennebicq¹ and Jean-Luc Bredas^{2,1}; ¹Chemistry of Novel Materials, University of Mons-Hainaut, Mons, Belgium; ²School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

Conjugated polymers are extensively exploited as active materials in a wide range of opto-electronic devices, including light-emitting diodes, solar cells and field-effect transistors. From the working principle of these devices, it turns out that the dynamics of charge and energy carriers are key aspects that need to be optimized for the design of improved materials and device architectures. Energy transfer is also involved in polymer-based (bio)chemical sensors relying on dramatic changes in the polymer luminescence properties in presence of a minute quantity of an analyte. The sensitivity of such polymer sensors is strongly increased with respect to the corresponding molecular structures, indicating fast excitation transport along and/or between the conjugated chains. We have applied quantum-chemical approaches to study the geometric and electronic structures of conjugated polymers and molecules in their ground and excited electronic states, and how this is affected by the presence of conjugation defects. Based on such an input, microscopic models taking into account the detailed chemical structure of the conjugated chains have been applied to investigate the dynamics of excitation motion in model systems. According to these calculations, the conjugated polymer chains should be viewed as ensembles of interacting chromophores resulting from the presence of chemical/structural defects and self-localization induced by coupling to vibrations. In the limiting case of weak interactions between the chromophores, transport then takes place via a sequence of incoherent hopping events between conjugated segments. We will show examples of incoherent transport in conjugated polymers and highlight the influence of structural organization and low-frequency vibrational modes on the hopping rates. Generalization of the model to account for excitation delocalisation among chromophores will also be briefly discussed.

SESSION W5: Poster Session: Polymers Sensors and Actuators

Chairs: Vivek Bharti and Z-Y Cheng
Tuesday Evening, November 29, 2005
8:00 PM

Exhibition Hall D (Hynes)

W5.1

A Greener Approach to Conducting Polymers Using Electrophilic Carbohydrate Reagents. Marcy Beth Keddy¹, Richard W. Gurney¹ and Daniel J. Sandman²; ¹Department of Chemistry, Simmons College, Boston, Massachusetts; ²Center for Advanced Materials, Department of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts.

The use of unprotected carbohydrate derived reagents to initiate the polymerization of appropriate monomers to form synthetic metals is an environmentally friendly method to carry out a potentially hazardous synthesis to obtain useful conducting polymers. Herein, the synthesis of conducting polymers such as polyaniline, poly

(2,3-dihydrothienol [3,4-b]-1,4-dioxin) (PEDOT) and poly(3-hexylthiophene) using a unique and sustainable approach is proposed and executed. The polymerization is initiated by an oxidation-reduction reaction using a sugar metal complex, copper (II) D-gluconate and zinc (II) D-gluconate in aqueous solution. Initial experimentation involved the optimization of polymerization parameters with the water-soluble form of aniline, namely aniline hydrochloride. A standard polyaniline sample was fully characterized by MALDI-TOF, FT-IR and UV/Vis methods, so that the products of our sugar initiated polymerizations could be directly compared and the reaction conditions could be optimized. The best experimental parameters to produce polyaniline by copper (II) D-gluconate and zinc (II) D-gluconate will then be applied to the synthesis of other conducting polymers such as PEDOT and poly(3-hexylthiophene).

W5.2

Ink-Jet Printing P(VDF-TrFE) Copolymer and Terpolymer for Sensors and Actuators. Shihai Zhang¹, Ziqi Liang², Qing

Wang² and Qiming Zhang^{1,3}; ¹Material Research Institution, Pennsylvania State University, University Park, Pennsylvania; ²Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania; ³Department of Electrical Engineering, Pennsylvania State University, University Park, Pennsylvania.

Ferroelectric P(VDF-TrFE) copolymers and its derivative electrostrictive terpolymers exhibit electromechanical properties attractive for a broad range of microdevices. However, because of the incompatibility of the conventional photolithography technology, few microdevices have been developed based on these active polymers. Recently, we investigate the ink-jet printing and micro-stamping for fabricating micro-structured devices for these polymers. By properly controlling and modifying the surface energy, ink-jet printing of solution of P(VDF-TrFE) copolymer and electrostrictive terpolymer can produce structure at size below 30 microns. It is also shown that these micron-sized P(VDF-TrFE) copolymer and terpolymer films exhibit high ferroelectric or electrostrictive response.

W5.3

Modelling of Polypyrrole Actuators. Geoffrey M. Spinks¹,

Mehrdad Barhami Samani², Philip Whitten² and Christopher Cook²; ¹School of Mechanical, Materials and Mechatronic Engineering, University of Wollongong, Wollongong, New South Wales, Australia; ²University of Wollongong, Wollongong, New South Wales, Australia.

Conducting polymer actuators with favourable properties such as linearity, flexibility, high power to density and flexibility are of increasing demand in micro robotic applications. However, a dynamic model of the actuator is required to enable it to be used in a real-time controlled system like a robot; moreover such a model can be employed in order to optimize the actuator performance. De Rossi, Mazzoldi and co-workers have described the mechanical behaviour of EAP film actuators presenting two viscoelastic linear models. These are the Continuum Mechanics modelling of Porous Systems based on Biot equations, and the Linear Lumped Parameter method. Their properties are modelled as having an electro-chemical active component and a passive viscoelastic component. Methods exist to model the passive component as a configuration of springs and dashpots and the electro-active effects as a strain generator simply proportional to the charge transferred and independent on viscoelasticity. Initially, this paper gives a brief description of the lumped parameters viscoelastic model and then applies it to a PPy fibre actuator. The results of stress relaxation tests using different isometric square wave strains are analysed by the Trust-Region methods for Nonlinear Minimizing in the MATLAB curve fitting toolbox. Wet stress relaxation tests at zero voltage with an Ag/Ag+ reference electrode were carried out. The results, which contain lumped damping and stiffness coefficients, demonstrate that the fibre actuator deviates from the linear model, used to describe the film actuator. Finally, we show that there is a considerable interaction between two viscoelastic and actuation components for polypyrrole actuators, using dynamic elastic modulus measurement during different actuation conditions. The elastic modulus was measured in-situ by applying a high frequency rectangular isotonic stress input and recording the corresponding strain output. Two set of experiments were carried out based on two potential control inputs, vs. Ag/Ag+ reference electrode: In the first experiment, a triangular voltage signal with different scan rates (1, 2, 4, 6, 8, 12 and 20 mV/s) is applied to the PPy helix tube actuator and in the second one; a step voltage signal (+0.5, -0.5, +0.7, -0.7, +1 and -1 V) is applied to the actuator after meeting steady state form for a long period of time. The value of total real modulus was calculated during both experiments in order to evaluate the effect of actuation on the mechanical properties of PPy micro actuator. The accuracy of measuring method was confirmed by comparing its results to that of a sinusoidal stress input during a temperature ramp through the glass transition of polyethylene terephthalate (PET). It is presented that polypyrrole actuators stiffen

during contraction (electrochemical reduction) and soften during expansion (electrochemical oxidation); linearly proportional to the actuation strain amount, which mimic skeletal muscle.

W5.4

Effect of Solvent, Hydrogen Bonding, and Thickness of Azopolymer Film on Surface Relief Grating. Woo-Hyuk Jung¹, Dong-Yu Kim², Jayant Kumar³ and Stephen P. McCarthy¹; ¹Plastics Engineering, University of Massachusetts Lowell, Lowell, Massachusetts; ²Materials Science and Engineering, Kwang-Ju Institute of Science and Engineering, Kwang-Ju, South Korea; ³Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts.

Epoxy-based copolymers were synthesized with N,N-diglycidyl aniline (DGA) and aniline (An), called poly(DGA-co-An), where azo coupling reaction was performed using amino benzoic acid (ABA) and nitro aniline (NA). Two azopolymers were dissolved with both tetrahydrofuran (THF)/Dioxane complex solvent and THF to compare the diffraction efficiency according to solvent. The thin film that was spin cast with THF/Dioxane showed the better diffractive efficiency than with THF due to the high boil point of Dioxane. The azopolymer of two azo bonds was spin coated at 800 and 1300 rpm where the thicker film showed the better diffractive efficiency. Epoxy-based azopolymer synthesized with diglycidyl ether of bisphenol A (DGEBA) and aniline or hydroxyl aniline was coupled with hydroxyl nitro amino benzene (HNAB). Hydroxyl group in chromophore helped to form hydrogen bonding with nitrogen atom in azo bond and prevented photoisomerization, showing no surface relief grating under normal raser intensity of 100 mW/cm². Polyurethane-based azopolymer was synthesized with disperse orange 17 (DO17) and toluene-2,4-diisocyanate (TDI), which was no hydroxide group in the main chain, and showed the better diffractive efficiency than the epoxy-based azopolymer with nitro substituent.

W5.5

Highly Thermal Stable Main-Chain Nonlinear Optical Polyimide Based on Two-Dimensional Carbazole Chromophores. Hsieh-Chih Tsai and Ging-Ho Hsiue; Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan.

In poled electro-optical (E-O) polymer systems, the relaxation of oriented chromophores is maintained by either introducing the guest chromophores into host polymers with high glass transition temperatures, or by confining the chromophores in polymer networks. Various highly stable NLO polymers have been prepared by grafting NLO-active chromophores onto aromatic polyimide backbones. 1-6 The pendent chromophores of side chain polyimides can be stabilized at low temperature because they have rigid rod-like structures. However, the orientation decays quickly at elevated temperatures because the local free volumes that surround the chromophores increase. Taking advantage of the multifunctional characteristics of carbazole along with rational molecular design, a new NLO-active lambda-shape main-chain polyimide that comprises the two-dimensional carbazole chromophore was synthesized. This polyimide exhibits high thermal and temporal stability. It can endure as high as 240 °C in a transient time and maintain large SH signal at 100 °C for a long time. The high-glass transition polyimide as a matrix and embedding the two-dimensional chromophore into the polymer backbone are the major reasons that effectively restrict randomization of the oriented dipole. Reference 1.F. Fuso, A. B. Padias, H. K. Jr. Hall, *Macromolecules* 24, 1710 (1991). 2.Z. Ni, T. M. Leslie, A. B. Padias, H. K. Jr. Hall, *Macromolecules* 24, 2100 (1991). 3.M. A. Mitchell, M. Tomida, A. B. Padias, H. K., Jr. Hall, *Chem. Mater.* 5, 1044 (1993) 4.G. A. Lindsay, J. D. Stenger-Smith, R. A. Henry, J. M. Hoover, R. A. Nissan, *Macromolecules* 25, 6075 (1992) 5.C. Xu, B. Wu, L. R. Dalton, P. M. Ranon, Y. Shi, W. H. Steier, *Macromolecules* 25, 6716 (1992) 6.I. Teraoka, D. Jungbauer, B. Reck, D. Yoon, R. Tweg, C. Willson, *J. Appl. Phys.* 69, 2568 (1991)

W5.6

Development of New π -Conjugated Small Molecules and Their Applications. Anne J. McNeil and Timothy M. Swager; Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Our focus is on the design and synthesis of new π -conjugated materials with interesting properties. Over the past decade we have demonstrated the utility of π -conjugated polymers as chemical and biological sensors. These sensory materials are engineered to provide both specificity and sensitivity to the desired analytes. Herein, we will discuss the design, synthesis, and photophysical properties of new π -conjugated small molecules and their applications.

W5.7

Synthesis and Properties of Polymers with Pendant Hexafluoroisopropanol Groups for Sensing Applications.

John P. Amara and Timothy M. Swager; Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

There is currently great interest in the development of novel conjugated-polymer (CP) based sensor technologies for the detection of certain components of plastic explosives. These include the high explosives RDX and PETN, as well as the International Civil Aviation Organization (ICAO) explosives taggant DMNB. Planar, electron-deficient analytes, such as trinitrotoluene (TNT), tend to have very strong electrostatic interactions with electron-rich CPs. As a result, TNT can be readily detected with CP-based sensors even though its equilibrium vapor concentration is quite low (≈ 1 ppb). Analytes such as RDX, PETN, and DMNB are expected to have much weaker binding interactions with CPs. Furthermore, RDX and PETN have extremely low equilibrium vapor concentrations (≈ 1 ppt), which makes sample collection an important challenge. We are currently investigating whether the incorporation of strongly hydrogen-bond acidic groups, namely hexafluoroisopropanol (HFIP) groups, into CPs can lead to stronger binding interactions with weakly hydrogen-bond basic analytes. Our results indicate that the incorporation of HFIP groups can lead to significant changes in the responses of CP-based sensors towards a number of analyte vapors. Furthermore, we have also developed a simple method for the surface functionalization of various polymer thin-films with HFIP groups. We are also interested in developing thermally stable, porous, and inert sorbent coatings with pendant HFIP functionality to serve in analyte collection and pre-concentration applications.

W5.8

Bicyclic Electron-Deficient Nitrogen Heterocycles as Novel Monomers for Low-K Dielectric Poly(Aryl Ethers) and Luminescent Conjugated Polymers. Jean Bouffard, Robert F. Eaton and Timothy M. Swager; Chemistry, MIT, Cambridge, Massachusetts.

The synthesis and properties of a family of monomers and polymers based on the novel 1,4-dihalo-9,10-dihydro-9,10[1',2']benzo-2,3-diazanthracene (halo = chloro, bromo) building blocks are reported. These monomers have been efficiently synthesized in a 61% overall yield over 5 steps from the readily available anthracene and dimethyl acetylenedicarboxylate. The synthetic route is easily scalable to multigram quantities using inexpensive reagents. Owing to the highly electron-deficient character of the pyridazine ring, the chlorides at the 1,4 positions are exceptionally activated towards nucleophilic aromatic substitution reactions. These undergo polycondensations with phenols such as triptycene hydroquinone in the presence of a mild base in polar aprotic solvents to generate novel poly(aryl ether)s that feature bulky iptycenes on every repeat unit. The resulting polymers display large internal free volume and increased oxidative stability due to their electron-deficient nature. These appear particularly promising for the development of low-K dielectric polymers. Activation of the 1,4 positions of the pyridazine ring also allows for the efficient functionalization using Suzuki-Miyaura and Stille palladium-catalyzed cross-coupling methodologies, even though other aryl chlorides are normally too unreactive for these approaches. The resulting pi-conjugated systems are predicted to show increased planarity and conjugation lengths owing to stabilizing hydrogen-bonding interactions between heteroatoms and acidic hydrogens on adjacent arene units. Several conjugated polymers, many of them luminescent, including poly(arylene ethynylene)s, poly(arylene vinylene)s, and poly(arylene thienylene)s have been prepared using these methods. Their tunable electronic properties appear aptly suited for the development of electroluminescent or electrochromic materials.

W5.9

Side Chain Liquid Crystalline Thermoplastic Elastomers for Actuator and Electromechanical Applications. Eric Verploegen¹, Lu Tian², Darren Verploegen² and Paula T. Hammond²; ¹Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Liquid crystalline block copolymers have attracted interest for their potential use as actuators. Recent research has focused on side chain liquid crystal siloxane polymers, which are crosslinked forming an elastomeric network. This type of actuator can produce reversible strains much greater than conventional ceramic piezoelectric actuators. Block copolymer self assembly allows for the creation of a thermoplastic elastomer where hard blocks, with a high glass transition temperature (T_g), serve as physical crosslinks for a low T_g block. These physical crosslinks can be removed by elevating the temperature and the material can be repeatedly reshaped and remolded, unlike chemically crosslinked systems. The synthesis of a polystyrene-b-polyvinylmethylsiloxane-b-polystyrene triblock copolymer functionalized with liquid crystals exhibiting a smectic C* phase on the PVMS central block is described. The synthetic route is

based on the anionic polymerization of styrene and trimethyltrivinylsiloxane monomers and the functionalization of resulting triblock copolymers. The resulting polymer can self assemble into a thermoplastic elastomer where the high T_g styrene blocks serve as physical crosslinks for a low T_g siloxane block. The proposed application for these materials is an actuator displaying piezoelectric properties. The smectic C* liquid crystals add a ferroelectric component to the system allowing for actuation to be controlled by the application of an electric field. In order for the ferroelectric switching of the liquid crystal to cause a macroscopic actuation the smectic layers must all be uniformly aligned so that the smectic layers are parallel to each other throughout the material. It is expected that the orientation of the smectic layers is affected by the block copolymer morphology, and understanding this relationship is of great interest for being able to achieve the desired properties. The effects of a variety of mechanical processing techniques upon this system's morphologies are being investigated. It is hoped that the application of shear fields upon the material will lead to a homogeneous morphology. The impact of morphological variations on the thermal, optical, and mechanical properties of this system are also being investigated in order to optimize actuator properties.

W5.10

Prepare organic/inorganic hybrid nonlinear optical material containing 2-D chromophore from sol-gel reaction.

Chang Po-Hsun¹, Hsiue Ging-Ho¹ and Kuo Wen-Jang²; ¹Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan; ²Applied Chemistry, National University of Kaoshiung, Kaoshiung, Taiwan.

The second-order nonlinear optical (NLO) materials have potential used in doubled-frequency laser source, and electro-optical modulation, etc. The chromophores designed as $-\lambda_{\text{dop}}^*$ -shaped have been reported to form transparent and phase-matchable noncentrosymmetric crystal structures that can exhibit large second-order NLO responses owing to the large off-diagonal β -tensor component. In this work, we developed 2-D NLO polyurethane (PU). 2-D structure was used to promote its stability included thermal and temporal. Because 2-D structure needed more free volume to reach array randomly. The result expresses that this material possessed of high d33 value ($d_{33}=33.8\text{pm/V}$), but this value still decayed as time or temperature increasing. In order to overcome aforementioned problem, we designed the chromophore with flexibility segment which could be poled easily. Then, we added tetraethyl orthosilicate (TEOS) to the polymer solution, and cast on the thin film. This organic/inorganic hybrid NLO material could be polarized easily by electric field due to its flexible segment. At that moment, the gels were formed by elevated temperature. Upon thermal curing, the stiff matrix behaves as a lock for the NLO-active chromophores, preventing relaxation to a random orientation at high temperature. So, this organic/inorganic hybrid NLO material could possessed of high d33 value and stability at the same time. Ref 1. Moylan, C. R.; Ermer, S.; Lovejoy, S. M.; McComb, I.-H.; Leung, D. S.; Wortmann, R.; Krdmer, P.; Twieg, R. J. J. Am. Chem. Soc. 1996, 118, 12950. 2. Wolff, J. J.; Ingled, D.; Hillenbrand, D.; Wortmann, R.; Matschiner, R.; Glania, C.; Kraemer, P. Adv. Mater. 1997, 9, 138.

W5.11

Electrical Bistable Behavior in the Current-Voltage Characteristics of Switching Devices Based on Polyaniline Derivatives. Sanghyun Hong¹, Dongjin Lee¹, Ohyun Kim¹, Jiyeun Kim² and Moonho Lee²; ¹Electronic and Electrical Engineering,

POSTECH, Pohang, Kyungbuk, South Korea; ²Chemistry, POSTECH, Pohang, Kyungbuk, South Korea.

We investigated polyaniline(PANI) derivatives and polythiophene derivatives for the purpose of using it in the active layer of the organic memory. For the most part, the conductance switching did not appear or low (ON/OFF ratio = 2~10) conductance switching was observed. However, we observed a large electrical conductance switching (ON/OFF ratio = $10^3\sim 10^4$) in self-doped PANI, which has the carboxylic acid groups in its molecules. This is comparable, if not better, than the results reported so far with complicated device architecture. The carboxylic acid groups were obtained by adding the antranilic acid to aniline. The (self-doped PANI) polymer film can be programmed between the two electrical states by an electric field. The device in the initial state was in a low conductivity state, that showed an extraordinary increase in current when the device was scanned to $V_c(\text{ON})$. The high conductivity state could returned to the low conductivity state at a voltage of $V_c(\text{OFF})$ in the reverse direction. In the device, switching voltages were very low as compared to those in a recently reported paper. ON-switching voltage is less than -1V and OFF-switching voltage is about 2V. Therefore the device has the advantage of low voltage operation and low power consumption for memory applications. For conductance switching in the device, the trigger operation must precede. Discussions about the switching mechanism and large ON/OFF ratio are also provided.

W5.12

Preparation of electrophoretic microcapsules using gelatin and gum Arabic for electronic ink. Jung Kun Song, Kwangsook Kim and In-Joo Chin; Polymer Sci and Eng, Inha Univ., Incheon, South Korea.

Microcapsule-type electrophoretic display using the electromigration phenomenon of charged nanoparticles in a dielectric medium shows high contrast and reflectivity, and it can be applied to the fabrication of flexible electronic paper. However, the aggregation of electrophoretic nanoparticles and their irregular motion in an electric field can cause many problems. In this study, the electrophoretic dispersion of TiO₂ was encapsulated by the coacervation of gelatin and gum Arabic to prevent the clustering, the agglomeration and the lateral migration of TiO₂ nanoparticles. The resulting microcapsules with the diameter ranging from 70 μm to 100 μm were shown to form monolayers without damaging of the capsules mainly due to elasticity. In order to protect the capsule from the environment, the outer shell of the capsule was crosslinked by reacting with glutaraldehyde. Both the reaction temperature and the concentration of the crosslinking agent were varied to obtain stable and elastic microcapsules.

W5.13

Hybrid Organic-Inorganic Light Emitting Diode Based Bio-Chemical Sensor. Sunil Kumar Penna¹, Sudhaprasanna Kumar Padigi¹ and Shalini Prasad^{1,2}; ¹Electrical and Computer Engineering, Portland State University, Portland, Oregon; ²Bio-medical Engineering, Oregon Graduate Institute, Hillsboro, Oregon.

Recently, there has been an increased interest in bio-chemical sensing via measurable visual detection schemes for a wide range of applications from environmental sensing to homeland security. We report the development of a tunable hybrid organic-inorganic light emitting diode (LED) based bio-chemical sensor. This detects various bio-chemical agents from an air based environment. The LED based sensor adopts the Opto-electronic technique for detection. It has a dual geometry, that of a planar and cavity based structures, with a multi-layer architecture. The individual organic, inorganic and contact layers are spin coated. Nano-ordered materials, more specifically semi-conducting nano wires are used as the active region which is sandwiched between organic layers. This is where recombination occurs resulting in light emission. The principle of operation of the device is such that, when a bio-chemical agent interacts with the functionalized surface of the contact layer, there is a significant alteration in the band gap properties of the OLED layers, leading to a change in the intensity of the emitted light from the active region. The interaction between the functionalized surface of the light emitting diode and the bio-chemical agent is similar to an enzyme-substrate interaction. The intensity of the emitted light was measured before and after the interaction of the bio-chemical agent. The electroluminescent plot showed a significant variation in the intensity of the emitted light in the presence of the bio-chemical agent. The output intensity was measured for both planar and cavity based structures. The cavity based structure resulted in a narrowing of the line width of output light resulting in better spectral purity. This has resulted in low-cost, compact and ultra-sensitive bio-chemical sensors, ideal for in-situ detection and monitoring of various chemical and biological agents.

W5.14

A New Series of Poly(ortho-Phenylazonaphthols) for Colorimetric Sensing and Chromogenic Image Patterning. Moon Soo Choi and Taek Seung Lee; Textile Engineering, Chungnam National University, Daejeon, South Korea.

The chromogenic derivatives sensitive to many different stimuli can be produced which might attract interest in sensing, imaging, and data storage applications. It especially has been focused upon the design of supramolecules which have the capacity to selectively recognize and sense anionic analytes through the naked eye, electrochemical, and optical signals. Color changes, as signaling an occurrence detected by naked eye, are widely used due to without resort to any spectroscopic instrumentation, easy methods and cost effectiveness. Such colorimetric optical sensor systems generally contain receptor and chromophore, which involve the binding of a specific analyte with receptor groups and a chromophore responsible for explanation the receptor-analyte complex into an optical signal. Here, we report the synthesis of a new series of copolymers containing ortho-phenylazonaphthol group to apply to colorimetric sensing and chromogenic image patterning. We performed colorimetric anion sensing based on the anion analytes binding of hydrogen bond donor group in polymer backbone resulting in naked-eye color change. It was found that solutions, initially bright yellow in color, became dark purple when exposed to anion, respectively. The color change itself is attributed to the formation of a charge-transfer complex as a result of these proposed solution phase hydrogen-bonding interactions.

Furthermore, we described the novel color imaging properties in the solid state using protection and deprotection of t-Boc groups in the polymer backbone. The polymers with free hydroxyl groups resulted from deprotection of t-Boc group exhibited considerable red-shift compared to t-Boc-protected polymers. After t-Boc protected polymer was immobilized on a silica substrate, t-Boc group was deprotected by directly contact a hot substrate. These results show that t-Boc protected zone is bright yellow in color, deprotected zone is purple. We expect the utility of the present polymer in applications such as colored thermal paper, marking, and labeling.

W5.15

Total RNA Dispersed Single-Walled Carbon Nanotubes. Jianjun Miao¹, Lichun Zhang², Phillip S. Baker¹, Lei Zhu¹, Mark Aindow² and Marie E. Cantino³; ¹Chemical Engineering, University of Connecticut, Storrs, Connecticut; ²Materials Science and Engineering, University of Connecticut, Storrs, Connecticut; ³Physiology and Neurobiology, University of Connecticut, Storrs, Connecticut.

We have studied RNA-dispersed swCNTs using high-resolution transmission electron microscopy (HRTEM). The low magnification bright-field TEM images showed that the polynucleotide-wrapped swCNTs existed in the form of small bundles as well as individual tubes. The small bundles contained up to 20 swCNTs. A high magnification TEM image showed a tight helical wrapping of RNA on a swCNT. The energy-filtered TEM experiments provided further evidence for RNA coating on swCNTs. In a neat swCNT sample, the O K-map and P L-map showed no evidence for significant levels of O and P. The images obtained from RNA-stabilized swCNTs showed markedly different O and P distribution; there were O-bearing materials on the exterior of the bundles, which might not distribute evenly on all of the swCNTs. There were also P-bearing materials on the exterior of the bundles, but the signals were weaker than those in the O-maps. This was consistent with the fact that the O and P contents of the RNA used are 20 and 13 wt.%, respectively.

SESSION W6/V7: Joint Session: Polymer Actuator III
Chairs: Z-Y Cheng and J. Su
Wednesday Morning, November 30, 2005
Independence W (Sheraton)

8:00 AM *W6.1/V7.1

High Dielectric Constant Nano-Phase Polymers and Nano-Composites. Qiming Zhang, Penn State, University Park, Pennsylvania.

High dielectric electroactive polymers have applications such as MEMS, artificial muscles, and capacitors. One challenge is how to significantly raise the dielectric constant of polymeric materials. By exploiting the delocalized electron organics and polymers, we show that nano-dielectric composites can have high dielectric constant, approaching that of the inorganic materials. Consequently, high electromechanical response can be realized with relatively low fields. Further more, experimental results show that in nano-composites, the interface effects such as the exchange coupling can have marked effect in enhancing the dielectric and electromechanical responses. Nano-composites, prepared using grafting, self-assembly, and nano-phase fully functionalized polymers will be discussed.

8:30 AM *W6.2/V7.2

Carbon Nanotube Reinforcement of Conducting Polymers and Hydrogels for High Strength Actuators.

Geoffrey M. Spinks¹, Vahid Mottaghtalab¹, Binbin Xi¹, Philip Whitten¹, Gordon Wallace¹, Seon Jeong Kim², Su Ryon Shin² and Sun Il Kim²; ¹School of Mechanical, Materials and Mechatronic Engineering, University of Wollongong, Wollongong, New South Wales, Australia; ²Hanyang University, Seoul, South Korea.

Practical devices for electromechanical actuators will only be realised when the actuator materials can generate sufficient movement (stroke) and forces within a suitable time frame. Low voltage actuators based on conducting polymers such as polypyrrole (PPy) appear attractive choices because of the relatively large strains (up to 26%) and stresses (to 5-10 MPa) that have been previously reported. However, the small size of the actuator materials used mean that the actual stroke (few mm) and forces (<1 N) are quite small. Many more applications become feasible if low voltage actuators could produce >10mm stroke and >1 N force- preferably within one second. A serious limitation to the maximum force that can be generated by actuator materials is their breaking strength. Several previous studies have shown that the breaking strength can be an order of magnitude lower than the static strength when tested under actuator conditions - that is, when the sample is being cycled between the contracted and expanded states. The practical maximum stress for conducting polymer actuators is then only a few tens of MPa and is much less in some cases. The

maximum stress that can be applied to hydrogels is also very small. In our recent work, we have considered the use of carbon nanotubes as strengthening reinforcement for conducting polymers and hydrogels. These high aspect ratio fibers are capable of significantly increasing the strength and stiffness of polymers when added in only small quantities. Although an increase in stiffness may reduce the amount of movement produced by the actuator, this deficiency may be compensated by the increase in load-carrying capacity. We report in this paper the effect of carbon nanotube additions on the actuation behaviour of both polyaniline and chitosan actuator materials. In both cases a significant increase in actuation strength was observed. In addition, the effect of the carbon nanotubes on the modulus and, therefore, actuation strain was also considered. A small reduction in strain was noted for the polyaniline, but little change in actuation strain was observed for the chitosan hydrogels. The results are further analysed in terms of actuation mechanisms occurring in conducting polymers and hydrogels.

9:00 AM W6.3/V7.3

Synthesis and Electronic Properties of Individual Single-Walled Carbon Nanotube/Polypyrrole Heterostructures.

James V. Ly¹, Xiaolei Liu³, Song Han², Alexander Lee⁵, Daihua Zhang³, Mark E. Thompson^{2,1}, Ari Requicha⁴ and Chongwu Zhou^{3,2}. ¹Materials Science, University of Southern California, Los Angeles, California; ²Chemistry, University of Southern California, Los Angeles, California; ³Electrical Engineering/Electrophysics, University of Southern California, Los Angeles, California; ⁴Computer Science, University of Southern California, Los Angeles, California; ⁵Chemical Engineering, University of Southern California, Los Angeles, California.

Heterostructures of individual single-walled carbon nanotubes (SWNT) coated with conducting polymer polypyrrole (PPy) were synthesized by electrochemical polymerization and its electrical properties were analyzed. Growth conditions were explored to controllably produce SWNT/PPy nanostructures. The resultant SWNT/PPy has a SWNT core and a PPy cladding ranging from 10-150 nm in thickness, as measured by AFM and electron microscopy. The PPy thickness has shown to be, among other factors, both voltage and time dependent. In a series of PPy deposition cycles performed on the same individual SWNT, it is found that the electronic properties are more complex than the simple additive effect of both components. Even with similar diameters, whether the heterostructure was synthesized by a single or multiple deposition cycles, resulted in different conductances and further underlines the complexity of this system. What has been discovered, however, is that the thickness of the PPy layer plays a critical role in dominating the conductance of the heterostructure itself. The high surface-to-volume ratio of SWNT/PPy heterostructures also provides an advantage over traditional films as potential chemical gas sensors. Electronic measurements have demonstrated an increased conductance when SWNT/PPy are exposed to NO₂ and, in contrast, a decreased conductance when exposed to NH₃.

9:15 AM W6.4/V7.4

Carbon Nanocones and Nanocapsules with

Metallo-Tetrapyrrole Tips. Petr Kral and Stanislav Stoyanov; Department of Chemistry M/C 111, University of Illinois at Chicago, Chicago, Illinois.

We predict the existence of novel types of nanocones and nanocapsules that can be realized by a combination of metallo-tetrapyrroles, with their unique binding properties, and carbon nanotubes, possessing a large mechanical rigidity and electric polarizability. Our ab-initio calculations demonstrate that the novel structures are stable and have many interesting features, with potential applications in material sciences, chemistry, molecular mechanics and electronics.

9:30 AM W6.5/V7.5

Suspended Carbon Nanotube Tunneling Switch for Wireless Communication. Youngsik Song and Jaewu Choi; Electrical and Computer Engineering, Wayne State University, Detroit, Michigan.

We fabricated carbon nanotube tunneling switch by direct and lateral growth of suspended carbon nanotubes and studied its characteristics and performance for future nano-scale wireless communication systems. Laterally suspended carbon nanotubes are very straight, ~3 μm long and strongly anchored to metal electrodes. The physical structure of carbon nanotubes was investigated by Raman spectroscopy and transmission electron microscopy. The onset of tunneling turn-on voltage is as low as 2.6 V. The switching behavior was studied by modulating back gate bias and impedance spectroscopy.

10:15 AM W6.6/V7.6

Effect of CNT on dipole orientation and electro-active

properties of polymer nanocomposite. Jinho Kang¹, Cheol Park¹, Kristopher E. Wise¹, Steven J. Gaik², Nancy M. Holloway³, Sharon E. Lowther⁴ and Joycelyn S. Harrison⁴; ¹National Institute of Aerospace, Hampton, Virginia; ²Department of Materials Science and Engineering, Penn State University, Philadelphia, Pennsylvania; ³Technology Development and Integration Branch, NASA LaRC, Hampton, Virginia; ⁴Advanced Materials and Processing Branch, NASA LaRC, Hampton, Virginia.

High performance electro-active materials are often required for aerospace vehicles and astronaut suits. Investigations of the dipole orientation at the microscopic and macroscopic levels are essential for understanding electro-activities of nano-structured materials. In this presentation, the effect of carbon nanotube (CNT) on dipole orientation and electro-active properties of a polymer matrix will be addressed as a function of type of CNT, CNT content, electric field, poling profiles and temperature. The relaxation of electric-field induced dipole orientation and dielectric relaxation strength were investigated by thermally stimulated current measurement (TSC) technique and an impedance analyzer. The preliminary study showed that the remanent polarization (P_r) was retained at temperatures close to the glass transition temperature (~200 °C) of the polymer. The high temperature stability of the remanent polarization is one of the keys of developing high performance electro-active materials for aerospace applications in ultra-extreme aerospace environments. Out-of-plane (d₃₃) and in-plane (d₃₁) electro-active responses were characterized using a fiber optic sensor and a modified Rheovibron. Other sensing characteristics under various stimuli will be also introduced. Analytical modeling and numerical simulation were performed to aid in understanding the experimental results.

10:30 AM W6.7/V7.7

Electro-Mechanical Actuation of Carbon Nanotube Yarns and

Sheets. Mikhail Kozlov¹, Vignesh Seker¹, Jiyoung Oh¹, Mei Zhang¹, Shaoli Fang¹, Ryan Capps¹, John Madden², Von Howard Ebron¹, John Ferraris¹ and Ray Baughman¹; ¹NanoTech Institute, University of Texas at Dallas, Richardson, Texas; ²Department of Electrical and Computer Engineering, University of British Columbia, Vancouver, British Columbia, Canada.

We report preparation of highly conductive SWNT and MWNT yarns and sheets. The materials aim at such applications as electronic textiles, electro-mechanical actuators, and ESD anti-static coatings. The electro-mechanical response of the specimens was measured using custom made force transducer operating in an isometric mode. The measurements were carried out at room temperature in aqueous and organic electrolytes; square-wave potential of variable amplitude was applied with a potentiostat. It was found that the maximum isometric stress generated by nanotube actuators could be as large as 12 MPa. This approaches the stress generation capability of commercial ferroelectrics and is significantly larger than that of natural muscles. A variety of applications of the materials is discussed.

10:45 AM W6.8/V7.8

Are the Possibilities Infinite for the Molecular Conductivities in Real Measurement?

Anirban Bandyopadhyay¹, S. Yagi², K. Nittou², K. Miki² and Y. Wakayama³. ¹International Center of Young Scientists, National Institute of Material Science, Tsukuba, Ibaraki, Japan; ²Nanoarchitecture Group, National Institute of Material Science, Tsukuba, Ibaraki, Japan; ³Nanoassembly Group, National Institute of Material Science, Tsukuba, Ibaraki, Japan.

Conductivity of a molecule measured in STM changes continuously due to change in molecular conformation under electric bias, thermal drift and change in the coupling factor between molecule and electrode as a change of the other two mentioned parameters. An experimentalist ends up with measuring several unique current voltage measurements with a single molecule in the same environment. But normally the response that resembles with theoretical prediction is considered others left as an artifact evolved from experimental systems. To find answers to degree of unpredictability of such phenomenon we considered the whole response as a stochastic event and went on measuring several current voltage spectrums under specific environmental conditions of a molecule. Instead of isolated single molecule we have considered cluster of molecules and targeted randomly as interaction of enthalpy and entropy would allow them to create infinite possible dimensional distribution of quantum wells while incubation to the atomically flat gold surfaces. Variation of conductivities has been classified into 10 different natures considering current voltage measurements for Xanthene dye molecules such as Rose Bengal, Eosin Y and Fluorescein Sodium. The result showed that the probabilities in the ionic states controlled by resonance structures of ions while neutral state seems to follow unique conductivity spectrum. The Xanthene dyes have already been reported to show molecular switching¹. It was also reported that multiple states exist for these molecular systems².

As previously it was not possible to detect multiple states of the molecular systems, now we have succeeded in detecting each possible states of such molecular systems. Our results have shown that single molecules can behave as semiconductors, switches, rectifiers and even showing negative differential resistance depending on which molecular state it exists. Further challenge in controlling a particular molecular state on gold substrate is being carried out by tuning supramolecular structures. So statistical dominance of a typical quantum well during growth of supramolecular structures under various pHs might be possible. 1. Large conductance switching and binary operation in organic devices: Role of functional groups. A. Bandyopadhyay and A. J. Pal, *J. Phys. Chem. B*, 107, 2531 (2003). 2. Multilevel conductivity and conductance switching in supramolecular structures of an organic molecule. A. Bandyopadhyay and A. J. Pal, *Appl. Phys. Lett.* 84, 999 (2004)

11:00 AM W6.9/V7.9

The Impact of Interfacial Modification on the Electrical Responses of In Situ Polymerized Polyimide / Carbon Nanofiber Composites. Michael J. Arlen^{1,2}, David Wang³, Marlene Houtz³, Gary Price³, Loon-Seng Tan¹ and Richard Vaia¹; ¹Polymer Science and Engineering, University of Akron, Akron, Ohio; ²Materials and Manufacturing Division, Air Force Research Laboratory, Dayton, Ohio; ³University of Dayton Research Institute, Dayton, Ohio.

The electrical response of in situ polymerized polyimide (PI) / carbon nanofiber (CNF) composites were investigated for use as high temperature ESD and EMI films and as thermal electric switches. The preparation of PI/CNF nanocomposites were conducted via a two-stage polymerization of 2,2-bis(phthalic anhydride)-1,1,1,3,3,3-hexafluoroisopropane (6FDA) and 1,3-bis(3-aminophenoxy)benzene (BAPB) in the presence of 0.1-5 wt% CNF or amine functionalized CNF (H2N-CNF) in DMAc at room temperature, followed by thermal imidization. This results in 2 PI/CNF systems, differing in the strength of association at the tube-polymer interface. The amine groups on the H2N-CNF participate in the polymerization leading to surface grafted PI chains to the CNFs as illustrated by SEM results. AC impedance results illustrate PI/H2N-CNF composites at 5 wt.% loading exhibit DC conductivity three orders magnitude lower than PI/CNF composites. In addition, PI/CNF with 5 wt.% loading demonstrate the negative temperature coefficient (NTC) effect of resistivity, while PI/ f-CNF composites of equal loadings exhibit the positive temperature coefficient (PTC) effect of resistivity. The difference in the conductivity temperature dependence between composites was attributed to the grafted PI chains formed on the H2N-CNF during the in situ polymerization process.

11:15 AM W6.10/V7.10

Investigation of the Physics of Transduction in Nafion / Ionic Liquid Composite Membranes. Matthew Bennett, Barbar Akle and Donald Leo; Mechanical Engineering, Virginia Tech, Blacksburg, Virginia.

Ionic polymer actuators are a class of electroactive polymers (EAPs) that exhibit large bending motion (1%) under the application of small voltages (1-5 V). The most common polymer membrane used for these actuators is Nafion. The actuation mechanism in these materials is believed to arise from the field-induced motion of mobile charges when a voltage is applied. In order for this charge motion to occur, the material must be swollen with a solvent. Typically, the solvent used has been water. However, the use of water imposes several limitations on the application of these actuators. Recently, Bennett and Leo have shown that these limitations can be overcome by replacing the water in these actuators with an ionic liquid (Sensors and Actuators A, 115, pp. 79-90, 2004). In the current paper, we investigate the physics of transduction in these ionic liquid-swollen Nafion membranes. Small-angle X-ray scattering reveals that the structure and properties of the ionic liquid have a strong influence on the morphology of the composites. Infrared spectroscopy is used to probe the ion associations within the films and shows that the ionic liquids are able to effectively mobilize the counterions of the Nafion membrane. Nuclear magnetic resonance spectroscopy is also used to investigate the composites and reveals that the mobility of the counterions increases as the content of ionic liquid within the membrane is increased. The results of these characterizations are compared to an experimental investigation of transduction in Nafion / ionic liquid composites to form an interpretation of the mechanisms of actuation. This comparison reveals that the counterions of the Nafion membrane are the primary charge carriers and that it is the motion of these mobile charges that gives rise to the actuation behavior of the films. Additionally, the use of ionic liquids has facilitated the development of a new type of electrode fabrication technique. This new "direct assembly" method allows for much larger strains to be generated than with previous electroding processes.

11:30 AM W6.11/V7.11

Modeling Chemomechanical Devices Based on a Reactive Polymer Gel. Victor V. Yashin and Anna C. Balazs; Chemical & Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

We model polymer gel based miniature chemomechanical devices such as pumps, actuators and sensors. The key element for these devices is a reactive polymer gel, which exhibits swelling-deswelling behavior in response to a chemical reaction, thus performing chemical-to-mechanical energy conversion. We consider a theoretical model of a reactive polymer gel, in which the reaction can proceed in an oscillatory regime and generates traveling chemical waves accompanied by waves of local swelling-deswelling. This type of gel could be used for fabricating chemomechanical devices with self-sustained rhythmic action, and gel-based pumps. We assume that the Belousov-Zhabotinsky (BZ) reaction takes place in the reactive gel. The BZ reaction generates periodic redox changes of a metal catalyst covalently bonded to a hydrogel soaked in a solution containing the rest of the BZ reagents. The metal redox changes affect the polymer-solvent interactions, resulting in variations in the gel volume. The self-oscillation of gel volume, and the traveling waves of local swelling in a hydrogel with the BZ reaction have been experimentally observed by Yoshida and co-workers. To describe the system theoretically, we employ the Oregonator model of the BZ reaction, and the two-fluid model of the gel dynamics. Propagation of one-dimensional wave trains through the reactive gel is simulated. Structure of the traveling swelling-deswelling waves, and transport of solvent through the gel induced by the wave propagation are studied.

11:45 AM W6.12/V7.12

A Novel Glucose Sensor Based on Deflection of a Thin Hydrogel Membrane. Sandeep Mariserla¹, Zayd Leseman² and Thomas J. Mackin²; ¹Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²Mechanical and Industrial Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Self-monitoring of blood glucose has become an important and critical tool for effective management of patients with diabetes. We describe here a novel MEMS sensor that can continuously measure, in real time, the concentration of glucose in a solution. The device utilizes a glucose-sensitive hydrogel membrane, which swells reversibly in the presence of a glucose containing solution. The amount of swelling is related to the concentration of glucose. The hydrogel is composed of 2-hydroxyethyl methacrylate (HEMA) functionalized with 3-acrylamidophenylboronic acid (AAPBA) groups as the glucose-sensitive moiety. Phenylboronic acid (PBA) derivatives interact with glucose by forming a charged complex, causing the hydrogel to swell by solvent intake. The resultant swelling in turn buckles the membrane and deflects a silicon island that is coupled to the hydrogel membrane. Signal transduction is performed by measuring the change in capacitance between the silicon island and a fixed plate. The presence or variation in the concentration of glucose can be observed as a change in capacitance of the device. The device was fabricated using standard microfabrication techniques. Initially, a Si wafer is processed to yield dies with a trench-like opening. Si islands are patterned from the bottom side of the die using photoresist. Subsequently, a coating of PDMS is applied to the bottom surface of the device as a barrier film. In the remaining steps the Si is etched away leaving behind released islands of Si attached to the PDMS membrane. In the final step, the glucose-sensitive hydrogel monomer is then processed onto the opposite surface of the PDMS membrane and UV-polymerized. We will present preliminary results detailing the fabrication of the device, the swelling properties of the AAPBA-containing HEMA hydrogel membranes, their adhesion to the PDMS protective membrane and the deflection caused by their expansion.

SESSION W7: Polymer Actuator IV
Chairs: J. Madden and Geoffrey Spinks
Wednesday Afternoon, November 30, 2005
Gardner (Sheraton)

1:30 PM *W7.1

Electroclinic Liquid Crystal Elastomers with Electrically Controlled Actuation as Shape Changing Materials. Jawad Naciri, Christopher Spillmann and Banahalli Ratna; Naval Research Laboratory, Washington, District of Columbia.

New high performance actuator materials capable of generating mechanical actuation induced by external stimuli such as electric field, temperature, and light are needed for a wide range of applications. Supramolecular ordered assemblies such as liquid crystal elastomers provide an excellent framework for incorporating anisotropy as well as functionalities in materials that respond to

external stimuli. Electroclinic Liquid crystal elastomers (ELCEs) are of particular interest due to their ability to exhibit linear actuation strain under an applied voltage. The elastomer network consists of chiral liquid crystal mesogens attached to a polymer backbone through a spacer. The system is then cross-linked by a suitable cross-linker to form the elastomer. We demonstrate for the first time anisotropic freestanding films of ELCEs from laterally attached side-chain polymers that show fast and reversible shape change under an applied electric field. The magnitude of the field applied is ten times lower than electrostrictive polymers. Mechanical properties as well as possible applications of these materials will be discussed.

2:00 PM W7.2

PVDF-TrFE-CFE Terpolymer: Ultra-High Energy Density Materials for Capacitor Application. Baojin Chu, Bret Paul Neese, Xin Zhou, Shihai Zhang and Qiming Zhang; Materials Research Institute and Department of Electrical Engineering, Penn State University, University Park, Pennsylvania.

Capacitor is one of the most important components in electrical or electronic systems. The increasing miniaturization of electrical and electronic systems requires high energy density and high efficiency capacitors for the applications of energy storage, energy filtering, power conditioning, etc. At present, the most widely-used capacitor materials are based on inorganic materials because of their high dielectric constant. However, the low dielectric strength limits their energy density. Currently, the state-of-art high energy density capacitors are polymer-based due to the high breakdown field ($>500\text{Mv/m}$) even though the dielectric constant is low (<10). Recently, a PVDF-TrFE-CFE terpolymer that exhibits relaxor ferroelectric behavior was developed at Penn State University. The low-field dielectric constant can be as high as 50-60 at room temperature, more than ten times larger than other dielectric polymer materials such as Polypropylene, which is the most widely used polymer material for capacitor applications. Due to the large change of electric field induced polarization and high breakdown field, the energy density of the terpolymer can reach $\sim 10\text{ J/cm}^3$. In this presentation, experimental results on the dielectric properties, energy density, non-linear dielectric behavior, frequency and temperature dependence of dielectric response and energy density of the terpolymer will be presented.

2:15 PM W7.3

Influence of Thermal Process on Structure and Properties of P(VDF-TrFE) and P(VDF-TrFE) Blends. Xin Yang and Z.-Y. Cheng; Mechanical Engineering, Auburn University, Auburn, Alabama.

The thermal transition behavior and crystal structure of P(VDF-TrFE)-P(VDF-CTFE) blends with different compositions were reported. The structure and its transition were studied using a X-ray diffraction and differential scanning calorimeter (DSC). The influence of the thermal process on the structure and morphology of the samples is reported. It is found that although the miscibility of the copolymers in amorphous range is high, the miscibility in crystalline regions is very limited. It experimentally found that there is a very narrow temperature where the miscibility of two copolymers in the crystalline regions is high. Additionally, the electric, mechanical and electromechanical properties of the blends are reported.

3:30 PM W7.4

Controlling Bending and Twisting of Conjugated Polymers via Solitons. Xi Lin¹, Ju Li² and Sidney Yip¹; ¹Nuclear Science and Engineering, MIT, Cambridge, Massachusetts; ²Materials Science and Engineering, Ohio State University, Columbus, Ohio.

A strong generic coupling between self-localized solitons and conformations of a pi-conjugated polymer chain is demonstrated through ab initio calculations and the underlying mechanisms revealed by using extended Hubbard models. We show that significant chain bending and twisting of trans- and cis-polyacetylene result from force imbalances among atom-centered orbitals and the steric instability at single-bond cis-centers, respectively. The soliton-induced conformational effects create sufficient strains and stresses to provide an intrinsic high-strain-rate actuation mechanism in optical excitation processes.

3:45 PM W7.5

Active NanoComposite Polymers: Enhancing Shape Memory Response and Actuation Performance. Richard Vaia¹, Michael Arlen⁴, Hilmar Koerner⁵, Zoubeida Ounaies³, Ricardo Perez³ and Ramanan Krishnamoorti²; ¹Air Force Research Laboratory, WPAFB, Ohio; ²University of Houston, Houston, Texas; ³Texas A&M, College Station, Texas; ⁴University of Akron, Akron, Ohio; ⁵University of Dayton, Dayton, Ohio.

The dispersion of nanoparticles, especially those with high aspect

ratio, into polymers has been shown through numerous commercial and academic ventures to yield an array of impressive property enhancements for a surprising low volume fraction ($<5\text{ vol}\%$) of nanoparticle addition, thus maintaining the inherent processibility of the polymer. By focusing on the design and optimization of the large polymer-nanoparticle interfacial area ($>500\text{ m}^2/\text{g}$); of the percolative network morphology of the nanoparticle; and of the impact of nanoscale compositional fluctuations on the local electric field, nanocomposite concepts offer opportunities to also enhance the performance of active materials, such as shape memory polymers and electroactive polymers. Specifically, carbon nanotube addition to shape memory polymers, such as polyurethane, increase blocking stress by at least 100% through increasing the rubbery state moduli by greater than a factor of five. In addition the unique optoelectronic properties of carbon nanotubes impart novel electrical and optical methods to trigger recovery of the shape memory system. Similarly, the polarizability of carbon nanotubes modifies the local electric field in the surrounding polymer matrix, resulting in a decreased actuation voltage for electrostrictive and ferroelectric polymers. These investigations promise to increase our understanding of the mechanisms involved, particularly as related to nanoparticle/polymer interaction. This in turn would allow us to tailor the polymer nanocomposites (by modifying dipole moiety, carbon nanotube content, and carbon nanotube distribution) to yield desired performance in terms of actuation voltage, electroactive strain, blocking stress and response time to name a few.

4:00 PM W7.6

High Conductivity Ionic Liquid-Nafion Mat Composites for High Speed Ionic Polymer Transducers. Barbar J. Akle¹, Donald J. Leo¹, Changwoon Nah² and Abdul M. Kader²; ¹Mechanical Engineering /CIMSS, Virginia Tech, Blacksburg, Virginia; ²Department of Polymer Science & Engineering, Chonbuk National University, Jeonju, 561-256, South Korea.

Ionomeric polymer transducers consist of an ion-exchange membrane plated with conductive metal layers on the outer surfaces and are saturated with a solvent usually is water. Such materials are known to generate large bending strain ($>9\%$ is possible) and moderate stress at low applied voltages (typically less than 5 V), and high sensitivity to mechanical deformation in charge-sensing mode. Recently it was demonstrated that ionomer-ionic liquid transducers can operate in air for long periods of time ($>250,000$ cycles) compared to few minutes for water hydrated transducers. The main disadvantage of ionomer-ionic liquid transducers is the slow speed of response. The speed of response in such actuators has been correlated to the ionic liquid content and the conductivity of the membrane. To increase the conductivity of the transducers a Nafion mat is hydrated with 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EmI-Tf) ionic liquids and high surface area RuO₂ electrodes are attached using the Direct Assembly Process (DAP). The Nafion mat is prepared from homogenous solution electrospinning. The solution is prepared by mixing 1 wt % of polyethylene oxide solution in methanol (PEO, Mol. wt 3×10^6) to 5 wt % Nafion 1100 solution under 40 C for 2 hrs. The electrospinning experimental setup is based on the apparatus described by Doshi and Reneker. 10 ml of solution is placed in a plastic syringe attached with a needle (26G, OD=0.46 mm) connected to a 15kV power supply and is placed 15cm away from the collecting drum. The measured conductivities of water hydrated Nafion electro-spun fibers are 16.8mS/cm and 13.7mS/cm for H⁺ and Li⁺ cations respectively, which are lower than the nominal 110mS/cm that of H⁺ Nafion membranes. The ionic liquids-Nafion mat composite is prepared by soaking a Li⁺ cation mat for 24hrs in EmI-Tf under room temperature. The uptake is measured to be around 250%(w/w) compared to 31%(w/w) obtained in Nafion films. The ionic conductivity ionic liquids-Nafion mat composite is computed to be 4.25mS/cm compared to 0.25mS/cm in ionic liquid-Nafion membrane composite. Scanning Electron Microscopy (SEM) images indicates that the space between the swollen fibers is filled with EmI-Tf. 1-Doshi J and Reneker DH, J Electrostatics 35:151 (1995).

4:15 PM W7.7

Poly(thienyl-1,1-bi-naphthol): Conducting Polymer Sensor for Chiral Amines. Changsik Song and Timothy M. Swager; Chemistry, MIT, Cambridge, Massachusetts.

Semiconducting polymers containing 1,1-bi-naphthol moieties were prepared and their chiro-specific electronic responses were tested. In conjunction with pH-dependency of the phenol containing conducting polymers, atropisomeric 1,1-bi-naphthol units in conducting polymers are expected to be an excellent platform for chiral molecular sensing, especially for chiral amines. Racemic and optically pure poly(thienyl-1,1-bi-naphthol)s (PBNTs) were electrochemically synthesized from corresponding monomers, which were easily prepared by Stille cross-coupling reaction. The thin films of resulting polymers were characterized via several electrochemical methods, such as cyclic voltammetry, in-situ conductivity measurement, and

spectroelectrochemistry. Potentiometric and coulometric responses of R- and S-form of polymer films were taken against various chiral amines.

SESSION W8: Polymers, Dielectrics and Charge Storage Properties
Chairs: S. Bauer and S.B. Lang
Thursday Morning, December 1, 2005
Gardner (Sheraton)

8:00 AM *W8.1

Correlation between Nonlinear Dielectric Response and AC Breakdown for High and Low Dielectric Constant Composite Materials. Jan Obrzut¹ and Kanji Kano^{1,2}; ¹Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland; ²Advanced Core Technology Laboratories, Fuji Photo Film Co., LTD, Kanagawa-ken, Japan.

Dielectric composites with an enhanced dielectric constant are being increasingly used in electronics as building blocks for functional circuits and as insulation materials for power distribution. With decreasing dielectric thickness, these materials are operating at higher electric fields that can induce nonlinear behavior. Under a sinusoidal electric field the nonlinear response consists of higher-order harmonics. We present the application of a waveform technique in determining the complex impedance and non-linear response of dielectric composite films at high AC voltages. The voltage waveforms are recorded in the time domain and analyzed by using the Digital Fourier Transform technique. It was found that conventional low dielectric constant materials exhibit a flat impedance characteristic, nearly independent of voltage, up to the material dielectric break-down. When the voltage approaches near dielectric break-down conditions, the second-order nonlinear dielectric susceptibility decreases abruptly while the third-order susceptibility increases, and the third harmonic response dominates the non-linear dielectric behavior. In comparison, the impedance of dielectric materials made of organic resins and ferroelectric ceramics decreases with increasing voltage. The drop in impedance is accompanied by a reversible transformation from dielectric to resistive. The non-linear dielectric effects are due to polarization reversal of the ferroelectric component. Consequently, the non-linear dielectric response is dominated by the third harmonic component of the specimen current. At near dielectric break-down conditions the second harmonic response decreases rapidly to a negligible value. The results demonstrate that the voltage break-down condition can be inferred from the non-linear dielectric response without ambiguity. The presented procedure can be utilized to analyze the non-linear dielectric response of materials and to determine the mechanism of their dielectric breakdown.

8:30 AM *W8.2

Bulk and Interface Charging Mechanisms in Organic Semiconductor-Gate Dielectric Bilayers. Howard Edan Katz¹, Cheng Huang¹ and James West²; ¹Materials Science/Engineering and Chemistry, Johns Hopkins University, Baltimore, Maryland; ²Electrical Engineering and Computer Science, Johns Hopkins University, Baltimore, Maryland.

Since the first reports of charge storage in the gate dielectrics of organic semiconductors, several groups have proposed charge-storing dielectrics that become polarized through varied mechanisms, and have offered various explanations for observed charge storage phenomena. These groups were concerned either with nonvolatile memories as an application, or with controlling hysteresis in conventional OFETs. This presentation will summarize measurements of surface charging, capacitance, and OFET threshold voltage shift that, taken together, identify contributions from bulk and interfacial charging to OFET current outputs. These contributions are highly dependent on the choice of materials. Dielectric materials include SiO₂, silicon network polymers, oxo-functionalized polymers, and ferroelectrics. Semiconductors, including thiophene oligomers, are designed so that results do not reflect contributions from impurity carriers, and so that side chain effects can also be evaluated. Experimental architectures focusing on integrated capacitors and OFETs on unitary substrates, which provide the best control of variables, will be emphasized.

9:00 AM *W8.3

Interfaces and space charge in polymeric insulating material. George Chen, School of Electronics and Computer Science, University of Southampton, Southampton, United Kingdom.

Interfaces are often encountered in practical insulation systems and have become a growing area of interest due to their influence on the electrical performance of whole system. Unlike the case of semiconductors where the interfaces (p-n junctions) are of great benefit, the interfaces in high electrically stressed materials, whether

polymer/metal or polymer/polymer, can cause the accumulation of space charge which can lead to unwanted electric field modification. For example, interfaces in joints and terminations of extruded high voltage cables have been identified as crucial parts as their failure probability is much higher than cable itself. It has been proposed that the accumulated space charge at the interface is a more significant factor with regard to electric field enhancement than in the bulk. Despite of increasing interests in the interfaces, the underlying mechanisms related to charge formation and ageing are not well understood and research into the best interfacial materials and its binding structure is becoming increasingly important. In this report, we investigate the space charge formation in polymeric insulation with different material interfaces. In particular, the influence of the interface between electrode and polymer or polymer and polymer on the space charge dynamics has been studied. Planar samples of low density polyethylene (LDPE) were subjected to high dc electric stresses for extended periods of time and space charge measurements were taken using the pulsed electroacoustic (PEA) technique. The report is divided into two parts. Initially, the effects of electrode materials on space charge formation in LDPE have been investigated. Common electrode materials used in either the laboratory or power cable industry were selected (i.e. aluminium (Al), gold (Au) and carbon loaded XLPE (Sc)) and space charge accumulation after the application of high electric stresses was monitored. Experimental results demonstrated that charge injection processes take place in all cases once the applied stress has exceeded a threshold. However, the amount of charge and polarity of the dominant injected charges showed a significant dependence on the electrode materials (under the same applied electric stress). Having established the influence of the electrode material on charge accumulation, our attention was paid to the effect of polymer/polymer interface on charge dynamics in the second part. Unlike our previous approach where two different polymeric materials were used, this time the polymer/polymer interface was formed by using the two layer of LDPE films cut from the same sheet. Sc and Al were used as electrodes to form different combinations. The results clearly indicated that the interface between two layers of LDPE acts as traps for electrons but not for positive charge carriers. The charge distribution in the bulk of the sample strongly depends on the electrode materials.

9:30 AM W8.4

A Leakage Current Model for "Flash-like", Non-volatile Resistive Switch Memory Device. Herbert Schroeder, IEM am IFF and cni, Forschungszentrum Juelich GmbH, Juelich, Germany.

For future ultra-large scale-integrated memory chips in cross-bar architecture simple non-volatile memory devices are desirable such as switchable resistors. Among a large variety of candidates such as magnetic RAM, phase change materials, ferroelectric and paraelectric oxides, molecules, polymers and other organic insulating materials the last have the advantage of simple and cost-efficient production. Some devices using these materials have a flash-like design, i.e. they consist of an insulating matrix between electrodes and some charge storage component within the insulator, e.g. a floating electrode (similar as in the floating gate of a flash transistor) or dissolved chargeable metal ions or defects dispersed in the matrix. Usually, a high voltage (or current) //write// pulse can change the charge in these embedded components giving rise to a different space charge distribution and thus a changed resistance of the insulator which can be read out at low voltages. An advanced leakage current model combining the electronic carrier injection /ejection at the electrode interfaces (described by thermionic emission) with the film conduction properties of the thin dielectric film (modelled as wide band gap semiconductor) was used to describe these devices. This model was successfully used to explain the field, temperature and thickness dependence of experimental leakage currents through paraelectric BST thin films between platinum electrodes [APL 83, 4381 (2003)]. This contribution reports simulation data of this model for I(V)-leakage curves dependent on contact and defect properties. The results show a large influence of the several parameters on the I(V)-leakage curves, characterized by the switching sensitivity S defined as $S = [R(\text{high}) - R(\text{low})] / [R(\text{high})]$: Increasing S with increasing switchable space charge density and higher spatial concentration of the space charge for completely symmetrical devices. In addition asymmetrical contacts and/or space charge distribution result in asymmetrical leakage and switching properties for opposite applied bias and may increase S for one polarity substantially. The simulation data will be compared to experimental leakage current in such devices.

10:15 AM *W8.5

Design, Synthesis, and Realization of Self-Assembled Dielectric Materials for Micro- and Macro- Applications. Tobin Jay Marks, Chemistry, Northwestern U., Evanston, Illinois.

We describe here several new approaches to the synthesis of dielectric materials for printed organic electronics and for high-performance capacitor applications. In both areas, nanoscopic control of

self-assembly motifs is employed to achieve very large capacitances, very large dielectric constants, and large charge storage capacities. For organic field-effect transistors, this results in devices with very low operating voltages, low leakage current densities, and very high breakdown fields. These dielectric structures can be assembled on a variety of substrates, including common plastics and metal foils.

10:45 AM W8.6

Space charge modelling in solid dielectrics under high electric field based on double charge injection model. George Chen and Su Han Loi; Electronics and Computer Science, University of Southampton, Southampton, United Kingdom.

One of the major issues in the electricity generation and supply industries is the catastrophic failure of the high voltage insulation in power equipment. The problem has received much interest over the last decade as the reliability of power systems has attracted attention of the public. Polymeric materials have been replacing traditional insulating materials due to their excellent mechanical, chemical and electrical properties. However, like any other materials, they are prone to develop an inevitable effect of electrical and chemical degradation after some long-standing operation. Due to the physical and engineering importance of this phenomenon, significant effort has been made to tackle the problem, using approaches relevant to the interference of ageing mechanisms, to space charge measurement and to the identification of the chemical nature of traps. It is generally believed that the occurrence of space charge within polymeric materials would introduce an early ageing effect in which the life expectancy of the insulation is greatly affected. Consequently, space charge measurements in polymeric materials have been extensively explored in last two decades. Various mechanisms have been proposed in the process of pursuing understanding observed phenomena. Present study aims to develop a clear insight on factors that influence space charge dynamics in solid dielectrics through a numerical simulation. The model used for the simulation is proposed by Alison and Hill [1] which describes charge dynamics as a result of bipolar transport with single level trapping. In this model, a constant mobility and no detrapping have been assumed. Schottky injection at the interface between electrode and insulating material is considered to be the source of charge carriers in the present simulation. Mathematical interpretation of the transport, continuity and Poisson's equation is carried out where splitting method has been introduced. With this, a programming pseudo-code is designed where the effect on varying each modelling parameter is examined. The simulation results show that carrier mobility, trapping coefficient and Schottky barrier have a significant effect on the space charge dynamics. Our simulation shows many features of space charge profiles observed by experiments in despite of over simplistic model. More importantly, the simulation allows us to study the role of each individual parameter in the formation of space charge in solid dielectrics. Reference: I. J. M. Alison and R. M. Hill, "A model for bipolar charge transport trapping and recombination in degassed crosslinked polyethylene", J. Phys. D: Appl. Phys. Vol. 27 pp. 1291-1299, 1994.

11:00 AM W8.7

Charge-Storage and Dipolar-Polarization Induced Threshold-Voltage Shift and Current Modulation in Organic Field-Effect Transistors and Their Organic Circuit Applications. Cheng Huang¹, Howard E. Katz¹ and James E. West²; ¹Whiting School of Engineering, Materials Science and Engineering Department, Johns Hopkins University, Baltimore, Maryland; ²Whiting School of Engineering, Electrical and Computer Engineering Department, Johns Hopkins University, Baltimore, Maryland.

By incorporating dielectrics with stored electric fields and organic semiconductors, new organic electronic components such as circuits with controlling voltages "prestored" for memory and tuning can be developed. We have successfully used excellent electret materials including surface-treated silicon dioxide and silsesquioxane polymers as the dielectric layer in organic field-effect transistors (OTFTs). Charge injection and charge storage induce threshold voltage shifts and current modulation, which results from the built-in electric fields in the conduction channels. Static and dynamic characteristics of OTFTs such as charging conditions and voltage/current retention were evaluated. In addition, self-assembled monolayers (SAMs) of dipolar molecules and domain polarization of ferroelectric polymers have been utilized in the dielectric layer, with different mechanisms but similar effects compared to charged dielectrics. In this talk, we also discuss new OTFT inverters, comprised of only two simple OTFTs with enhanced-mode driver and depletion-mode load to implement full-swing organic logic circuits.

11:15 AM W8.8

Thermal analysis evaluation of optical, electrical and mechanical properties changes promoted by different spectral radiations on commercial engineering polymeric textiles. Mohamed Mohamed Saad¹, Gamal Abdel-Wahed Abbas², Lobna Aly

Abdel-Wahab³, Mahmoud Sayed Morsy⁴ and Mohamed Hassan Talaat⁵; ¹Physics, Queen's University Belfast, Belfast, United Kingdom; ²Physics, Ulster University, Ulster, United Kingdom; ³Solid State & Accelerators, National Centre for Radiation Research & Technology, Cairo, Egypt; ⁴Textiles, National Institute for Standards, Giza, Egypt; ⁵Physics, Ain Shams University, Cairo, Egypt.

The present study is mainly applied for the investigation of the effect of the artificial γ -irradiation and the natural daylight on some of the engineering materials, such as the fabricated textile polymers (cotton, nylon-6, polyester/cotton blend and wool/polyester blend). The differential thermal analysis (DTA) and thermogravimetry (TGA) techniques show that γ -irradiation in air atmosphere on cotton and nylon-6 fabrics enhances the loss in their activation energy faster than what happened by natural exposure. Thus, the ionizing γ -irradiation has a strong effect on the rate of degradation and also the thermal stability of cotton and nylon-6 than the natural solar irradiation. Also γ -irradiation, at high doses, tends to induce crosslinking for the polyester/cotton blend while natural daylight can only induce degradation. On the other hand, all the examined fabrics tend to be more yellow in colour on exposure to the γ -irradiation, resulting in less white and bright. With the natural daylight exposure it is observed that, nylon-6, polyester / cotton blend and wool/polyester blend show the same behaviour but with small values. Only cotton samples when exposed to the natural solar energy tend to be more white and less yellowness up to three months of exposure, because of the photo-oxidation of the natural creamy dye of the cotton. The γ -irradiation for all engineering polymers reduces their electrical conductivity with different rates and ranges depending upon the nature of the fabric under test. Cotton and nylon-6 fabrics lose their tensile strength (T.S.) and bursting strength, respectively at rapid rates under the effect of γ -irradiation while the rates of loss become slower with the natural daylight exposure. The blend fabrics [cotton/polyester and wool/polyester] show stability of the mechanical properties with respect to γ -irradiation while the loss percent in T.S. increases with increasing the exposure of daylight. The elongation % at break showed that the effect of γ -irradiation is less than that of the natural weathering.

11:30 AM W8.9

Characteristics of Polythiophene Base Field Effect

Transistors. Keichi Kaneto, Graduate School of Life Science and Systems Engineering, Kitakyushu, Japan.

Polythiophene field effect transistors (FET) have been fabricated to investigate the mobility, on/off ratio, frequency dependencies and potential profile along the channel between source and drain. The polythiophene channel has been also modified by mixing fullerene.