

WorldWide ElectroActive Polymers



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WW-EAP Newsletter

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FROM THE EDITOR

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The last year of the 2nd Millennium, 1999, has been marked with important milestones for the field of EAP in terms of communication platforms. I am please to state that as of this year we have established **2 international conferences**: SPIE – emphasizing actuators, mechanisms, smart structures and robotics; and MRS – emphasizing materials science aspect of EAP. In addition, we have (a) this **WW-EAP Newsletter** offering timely report of progress and information exchange among the developers, users and potential sponsors; (b) **WW-EAP Webhub**, which is a website linking all the worldwide EAP research facilities; (c) **WW-EAP Newsgroup**, which was established on November 19, 1999 to allow direct e-mail link among the experts.

As an emerging field, it is becoming well recognized that current EAP actuators have numerous weaknesses and unknowns. However, EAP materials are offering unique capabilities attributed to their performance similarity to biological muscles, gaining them the name artificial muscles. Considering the potential of these materials, the Editor of this Newsletter posed a challenge to the EAP science and engineering community to develop a robotic hand that is actuated by EAP and able to win against a human in an arm wrestling match (see figure on page 16).

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GENERAL NEWS

Since the first issue of this WW-EAP Newsletter, two events of significance to the field have taken place: (a) MRS symposium was held for the first time ever. (b) WW-EAP Newsgroup was formed allowing e-mail interaction among the members. Moreover, the WW-EAP webhub was further enhanced to provide significantly more information to meet the needs for the transition EAP materials to practical applications.

MRS FALL MEETING

To address issues related to the material science of electroactive polymers, an MRS Symposium FF, was organized by Qiming Zhang, Yoseph Bar-Cohen, Takeo Furukawa, and Jerry Scheinbeim. This Symposium was held as part of the MRS Fall 1999 Meeting in Boston, MA, from Nov. 29 to Dec. 3, 1999. More than 75 abstracts were submitted (a record number), covering topics such as IPMC, ferroelectric polymers, polymer composites, polymer gels, and thin polymer films for applications to smart materials, actuators, transducers, and microelectronics.

<http://www.mrs.org/meetings/fall99/progbook/ProgramBookFF.html>

WW-EAP NEWSGROUP

Last month the WW-EAP Newsgroup was launched to allow direct e-mail interaction between the users. This Newsgroup is a platform through which anyone who sends an e-mail message to eap@artemis.arc.nasa.gov will reach everyone who is subscribed to the Newsgroup. There is no cost to subscribe and the subscription is done by sending an e-mail with the single line "subscribe eap" in the body of the message to:

eap-request@artemis.arc.nasa.gov.

For further information please visit:

http://ndea.jpl.nasa.gov/nasa-nde/lommas/eap/WW-EAP_Newsgroup.html

WW-EAP WORLDWIDE WEBSITE

The WW-EAP Wehub has been further enhanced to include more links to EAP research and development facilities as well as databases, and other useful information. The address is <http://ndea.jpl.nasa.gov/nasa-nde/lommas/eap/EAP-web.htm>.

SPIE CONFERENCE

The 2nd Conference on EAP Actuators and Devices will be held as part of the 7th SPIE Conference on Smart Structures and Materials in Newport Beach, California. The program of this EAPAD Conference #3987 is accessible via: <http://www.spie.org/web/meetings/programs/ss00/confs/3987.html>. This upcoming conference will be focused on electro-mechanically-active polymers and will include an hour of open discussions with a panel that consists of the invited speakers and the Conference chairs. The potential to make EAP actuated robots that emulate insects is one of the areas that EAP actuators offer an edge over other technologies. To improve the understanding of the challenges associated with developing such biologically inspired robots, the Keynote speaker, Robert Full of Berkeley University, will describe his studies of insects and the requirements for artificial muscles (see

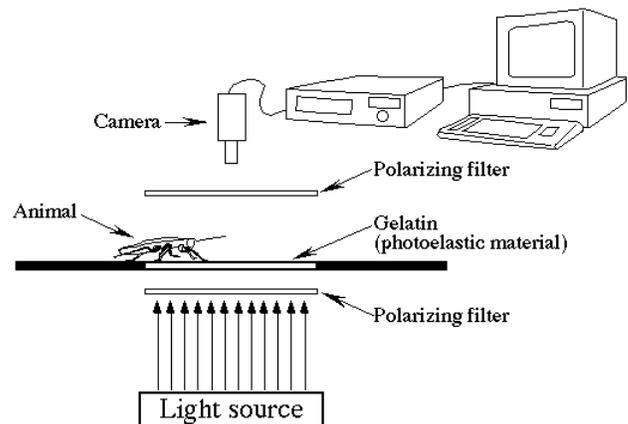


Figure).

RECENTLY HELD WORKSHOPS

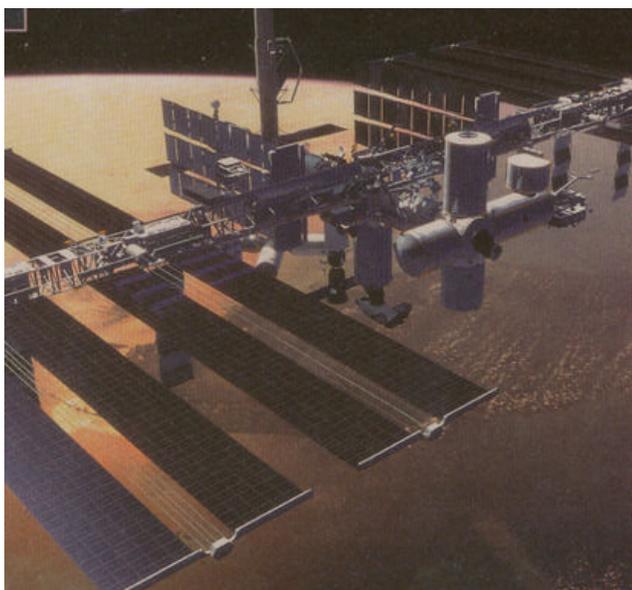
Besides the two international conferences that were organized this year under the auspices of SPIE and MRS, several workshops were held on subjects related to EAP. Some of the workshops include.

- 4th Workshop on Multifunctional & Smart Polymer Systems, Dublin, Ireland, Sept. 20-23, 1999
- 6th International Seminar on the Technology of Inherently Conductive Polymers, Commercialization, Advances and Opportunities, September 26-29, 1999, Toronto, Ontario, Canada

- Workshop, The Knowledge Foundation, Inc., San Diego, October 25-26th, 1999
- Organic Electronics Workshop, ATP National Meeting, November 17, 1999; San Jose, CA

INTERNATIONAL SPACE STATION - MISSE EXPERIMENT

Soon the International Space Station (ISS) will become a reality and will offer unprecedented opportunities for long-term experiments in space. One of the first of such experiments is the Materials International Space Station Experiment (MISSE) sponsored by the AFRL/ML and the NASA SEE Program that is a cooperative effort between the Air Force, NASA and industry. Material specimens will be placed in four separate Passive Experiment Carriers (PECs) that were previously used to contain the MIR Environmental Effects Payload experiments on MIR from March 1996 to September 1997. The MISSE PECs will be installed external to the ISS in late 2000 to early 2001, subject to approval by the NASA ISS program and flown for periods of 1 to 3 years. The experiment time frame will correspond to solar maximum conditions, providing as severe a test environment in low earth orbit as possible. EAP was offered an opportunity to fly on the autonomous experiment and a small area was allocated. If you have an EAP material that you believe is sufficiently robust and possibly ready for such tests please send an e-mail to the Editor of this Newsletter at yosi@jpl.nasa.gov.



FRANCE COLLÈGE DE FRANCE

Electromechanical effects in wet Nafion

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Researchers [1-2] have developed actuators based on fluorocarbon networks ("nafions") carrying bounded sulfonate groups having mobile counter-ion (Li^+ , Na^+ , etc.) slightly swollen by water. Efficient electro-activation requires highly divided electrodes made with conducting nano-particles. Making an effective EAP actuator using such materials requires a compact model of the actuation mechanism. For weak gels, strongly swollen by water, the classical interpretation of electric field effects is based on the osmotic pressure of the transported ions [3]. For Nafion, another effect is important [1], *electroosmosis*, where each cation drags some water with itself. In particular, replacing Na^+ by Li^+ , dramatically reduces the efficiency, while osmotic pressure effects should be essentially unaltered. The classical picture of electro-osmosis [4] is based on shear flows, occurring inside a double layer near a solid wall (capillary wall, or colloidal particle). For our purpose, this is not adequate: the water pockets in Nafion are very small [5]. This led us to a more phenomenological description based on irreversible thermodynamics [6] with two coupled currents: electric and hydraulic.

An estimate of the relevant transport coefficient can be obtained by assuming that each Na^+ ion carries a fixed number of water molecules. On the whole, this description is very compact, and probably adequate for static effects. The limitations in frequency for AC operation remain to be examined.

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GERMANY

ENERGETIX SYSTEMS

Start Up EAP Company

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Energetix Systems is a new start-up company that was recently founded in Germany near Munich. The activities of the venture are related to research, development and production of practical solid state actuators based on polymers with electrostrictive properties mainly for industrial applications. Efforts are sought to fill actuators performance gap between piezoelectrics and shape-memory alloys on one side and conventional pneumatic and hydraulic actuators, on the other. The company founder, Mr. Matthias Grosse, is an experienced aerospace engineer and an expert in rocket propulsion and guided missiles. His efforts are focused on seeking relative short or medium R&D tasks that can lead to marketable products. Collaboration is currently being sought with partners in industry and universities and the effort is open to partnership.

TITK RESEARCH INSTITUTE, RUDOLSTADT, TU ILMENAU

Force Measurements on Polypyrrole Bilayers

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Measuring the actuation force of EAP actuators is not simple to perform because the forces are often very small (~mN) and many times the actuators are operated in a liquid environment. Force measurements reported in the literature are made on relative large strips of EAP unimorphs [1] or by mounting a known mass on the tip of an actuator [2]. Using a special sensor, our groups at the Thuringian Institute of Textile and Plastics Research (TITK) and at the Technical University of Ilmenau jointly developed a force measurement technique allowing to measure forces in the range

of mN with a resolution of 0.1 mN. The measurement is isometric because the sensor generates an electromagnetic counter force equivalent to force generated by the actuator. The sensor is coupled to the actuator and is operated in an electrolyte with the aid of a graphite rod through a glass capillary. Figure 1 shows the forces generated by polypyrrole bilayers of several thicknesses operated in a 0.1-M NaCl electrolyte. The bilayers are made by depositing polypyrrole potention-statically on a 50- μm thick polyimide film with a mixture of chlorate, dodecylbencen-sulfonate and tosylate as counter ions. The thickness is controlled by the polymerization time.

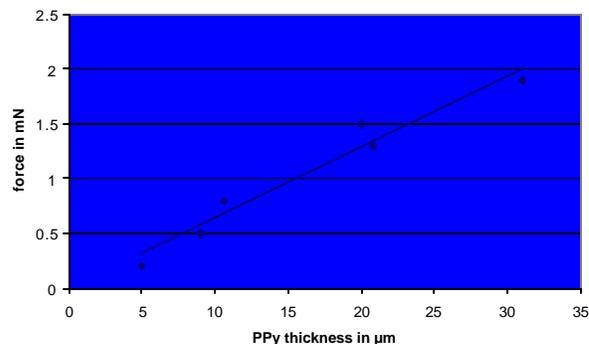


FIGURE 1: force of a PPy bilayer as a function of the PPy thickness.

The forces of the bilayers depend linearly on the polypyrrole thickness. The specific force related to the PPy mass is about 0.7 N/g, which is in the range of biological muscles (about 0.2 N/g). Taking into account that force is also necessary to overcome the friction of the graphite rod and to bend the passive polyimide, this value is only a lower limit of the force generated by the PPy.

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ITALY

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Realization, characterization and modeling of electroactive polymer actuators

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The demand for actuators featuring biomimetic properties, including direct drive, high power density and compliance, is growing in robotics and bioengineering. Our experience in the field has been involved with electro-mechano-chemical measurements and modeling of various EAP materials, in particular polymer electrolyte gels and conducting polymers. Recently, in a project funded by DARPA and led by AlliedSignal we extended our studies to carbon nanotube artificial muscles.

We proposed a methodology for the mechanical characterization of polyelectrolyte gels and the experimental work permitted the validation of a continuum poroelastic model that we developed to describe their passive mechanical behavior [1]. Different configurations can be developed using these gels. Two possible configurations were considered including fibers or layers of polyelectrolyte gels and disposed together with conducting polymer elements [2].

The same proposed methodology and model were adapted to the study of conducting polymer (CP) actuators [3]. In this case, we performed and validated a lumped parameter muscle-like model which provides favorable indications for the practical utilization of the materials as a muscle-like linear actuator, once the response time is decreased by a suitable scaling down characteristic dimensions of the actuator [4].

Several studies were dedicated to the development of conducting polymer dry actuators in the shape of fiber and film [5]. Figure 2 shows a dry actuator consisting of a polyaniline (PANi) fiber covered by a solid polymer electrolyte and using a Cu wire as counter electrode. The actuator was examined at several different stimulation conditions, including cyclic voltammetry CV, square wave potential SWP, square wave current SWC, and showed interesting performance. The tensile isometric stress exerted by the contractile fibers is about 10 times higher than typical human skeletal muscles. Under low voltage drive (< 2 V), the linear isotonic strain is 0.3% is obtained during CV and 0.2% during SWP. The use of the polyelectrolyte gels and of CP is important

because they are naturally predisposed to reciprocal interaction. The ionic exchange process of these components can be used to realize actuators with characteristics of strain and stress to support various applications. In the case of CP, the actuation strain can reach several percents and stress of >100 -MPa. In the case of polyelectrolyte gels, a strain of $< 50\%$ and stress of 20 MPa can be obtained. Tests on polypyrrole and PAN showed work density of 7×10^5 J/m³ for polypyrrole [6] and 4×10^5 J/m³ for PAN [7].

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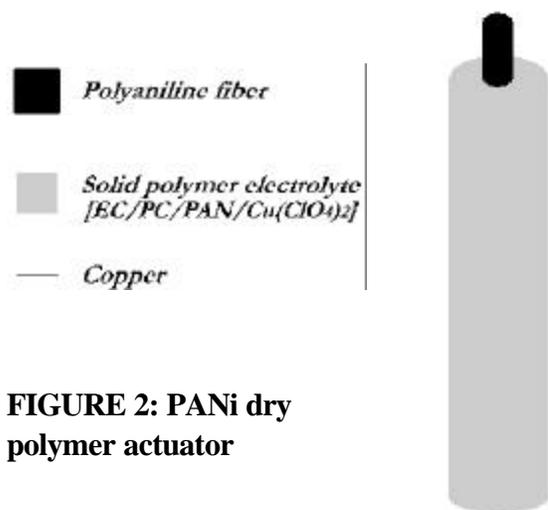


FIGURE 2: PANi dry polymer actuator

JAPAN

KOBE UNIVERSITY

EAP Application to Micro-manipulators with Multiple Degrees of Freedom

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Nafion-Platinum composite type EAP actuator (IPMC or ICPF) was applied to micro motion

devices with multiple degrees of freedom by S. Tadokoro, S. Yamagami, T. Takamori, Kobe University, and K. Oguro, Osaka National Research Institute, Japan. In manipulation of MEMS structures, it is essential to prevent damage due to excessive forces and the softness of EAP makes it attractive actuator. For this purpose four actuators were used having a concentrating perpendicularly at their tip forming a bridge with an end-effector (see Figure 3). Controlling 4 input voltages to this device allowed realizing 3-dimensional motion of the end-effector.

To avoid the use of adhesives, a pattern plating method was developed to support the manufacturing of this device. To assure electric isolation of the electrodes, the bridge was masked at its center during the application of the platinum onto the produced EAP. Cross-shaped membranes were made of four IPMC actuators 0.4 mm wide 27 mm long and the bridge was cut out using a thin edged tool after the plating. To control the micro-manipulator a setup was used consisting of a joystick with 6 degrees of freedom and a microscopic image feedback to the operator. Experiments have shown that the device is capable of high speed 3-dimensional micro-manipulation with maximum displacement of 2 mm. The available frequency reached up to 13 Hz. However, when the joystick stopped, the device did not stop and returned to the initial position because of IPMC characteristics. Manual control of input cannot maintain a constant arbitrary position longer than 3-seconds. Therefore, using an IPMC as an actuator can only support dynamic operations (pushing and snapping), and it is not suitable for static

operations (gripping and grasping).

Gray Box Modeling of IPMC Motion

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To allow effective design and prediction of the response of IPMC, the material characteristics and the mechanical constrains need to be modeled. Using experimental input-output relations Satoshi Tadokoro and Ryu Kanno, Kobe University, developed the Kanno-Tadokoro model, which is a gray box model. This model is

$$\sigma = D(s)\varepsilon - e i \frac{\omega_n^2 s}{s^2 + 2\zeta\omega_n s + \omega_n^2}$$

effective for mechanical and control design when a chemical modeling cannot be used. The voltage applied to an actuator is transformed to current distribution through the membrane. This current generates distributed internal stress causing strain by a viscoelastic property of the IPMC.

The resistance of the surface layers and RC elements approximate the experimental voltage-current response as the electric property. The stress generation property and the viscoelasticity were expressed by an equation similar to the piezoelectric equation as follows.

In IPMC, it is natural that the current causes internal stress because it is involved with a hydrated ionic flow. A 2nd order delay approximates the time delay to reaching equilibrium of the ionic distribution and internal stress is generated by swelling and electrostatic force. Kanno-Tadokoro model was applied to the design of a visual window wiper of MUSES-CN Nanorover by Satoshi Tadokoro and Masahiko Fukuhara, Kobe University. Figure 4 (a) shows simulation results for a 15-mm long 8-mm wide IPMC actuator. Analysis of the model shows that current concentration near the electrodes causes imbalance of strain distribution. The response speed is faster near the electrodes because of the RC elements. Therefore, the actuator length should be designed short. The membrane itself deforms to curve in two dimensions, where the lateral deformation obstructs the wiper bending. When a 2-mm long section is used to constrain the tip this lateral displacement is minimized improving the bending of the wiper (see figure

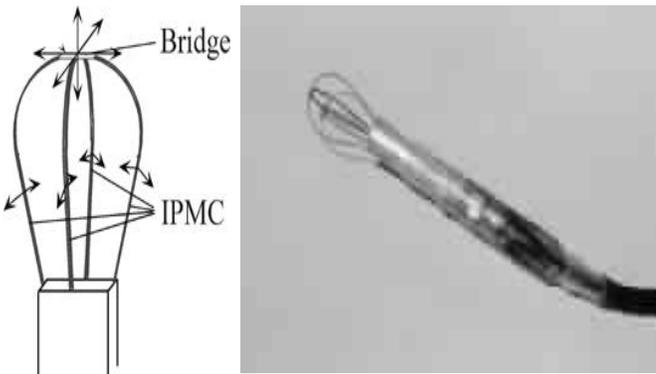


FIGURE 3: A schematic and a photographic view of the Micro-manipulator.

4b). These results show that crosspiece design is important to improving the wiper efficiency.

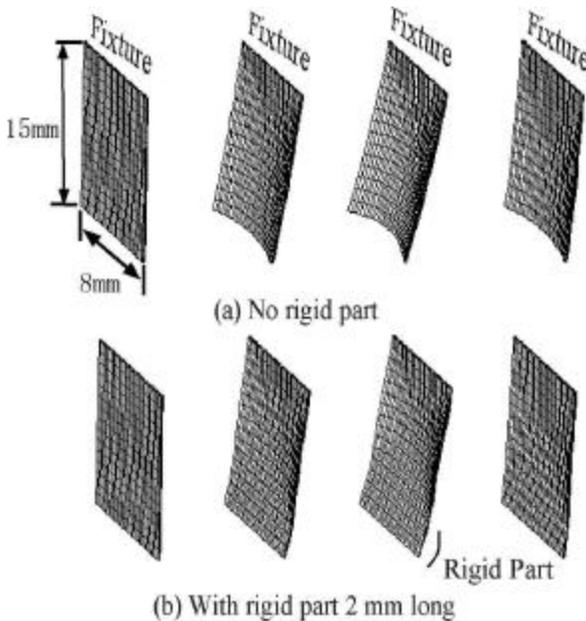


FIGURE 4: Simulation results of motion of the dust wiper for the MUSES-CN Nanorover.

OSAKA NATIONAL RESEARCH INSTITUTE
Soft Gripper Using Polymer Electrolyte Gold Composite
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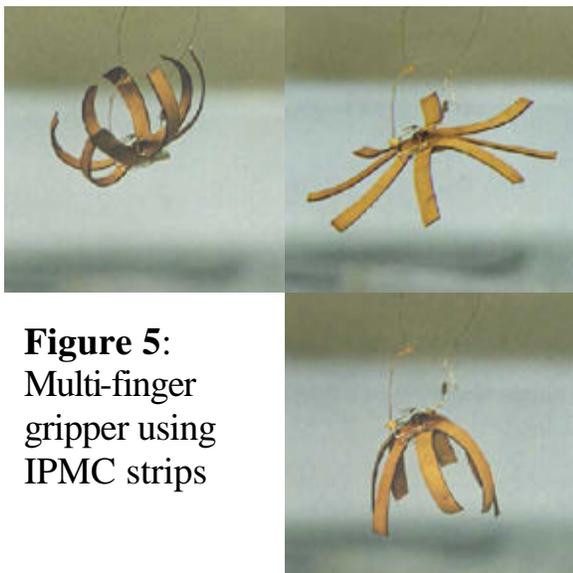


Figure 5:
 Multi-finger gripper using IPMC strips

A group of Osaka National Research Institute and Japan Chemical Innovation Institute has demonstrated a biomimetic device that acts like a small hand using polymer electrolyte gold composite, also known as IPMC. The device has eight fingers, 15-mm long each, made of a single sheet of a perfluorocarboxylic acid membrane plated with gold on both sides (Figure 5). The sheet was cut into a star configuration with eight fingers and fine platinum wires were bonded to both electrodes at the center of the sheet. The cut sheet was soaked in aqueous tetraalkyl-ammonium ion solution to enhance the response. The produced device acts in water as a small soft gripper. A 2.5 V electric signal was used to close or open the finger and the time response has been one second.

SHINSHU UNIVERSITY
PVC Gel Deforms Like a Tongue by Applying an Electric Field

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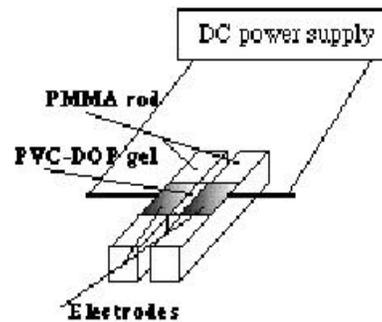


FIGURE 6: Experimental setup used for the deformation of PVC-DOP gel. The thickness of the gel is 2-mm and the width of the electrodes is 10-mm

Poly(vinyl chloride) (PVC) nonionic gel has been considered inactive to electric field. In this Newsletter we are reporting that we have successfully actuated such material by an electric field. PVC is plasticized with dioctyl phthalate (DOP), which is a typical plasticizer containing 90 wt% and can maintain its shape and behaves as an elastic nonionic gel. The gel was placed between a pair of electrodes as shown in Figure 6. When an electric field was applied, the gel is curved onto the anode like a tongue (see Figure

7), and held the deformation as long as the field was on. The deformation was restored as soon as the field was off. The deformation rate is much slower compared to that of PVA-DMSO gel (reported in the previous issue of this Newsletter), and the mechanism of the deformation was suggested to be similar to PVA-DMSO gel. The details of this progress will be reported in the open literature.

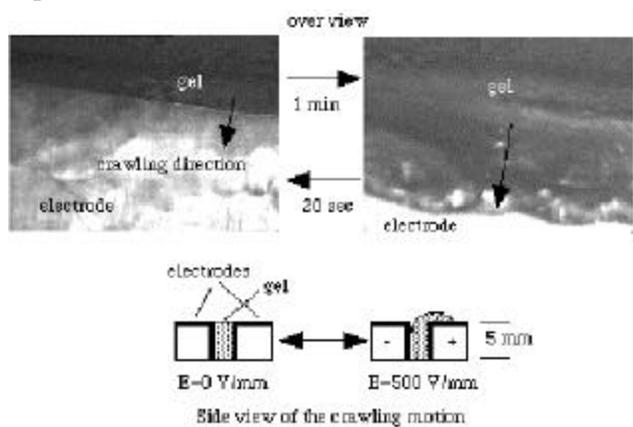


FIGURE 7: Electrically induced reversible deformation of PVC-DOP gel

RUSSIA

MOSCOW STATE UNIVERSITY

New type of photoaddressable copolymers with photoregulated supramolecular structure and optical properties.

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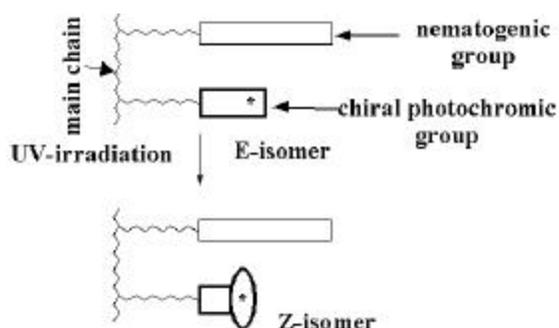


FIGURE 8: Schematically representation of chemical structure and photoisomerization process of chiral-photochromic copolymers.

We have developed an approach to the synthesis of liquid crystalline (LC) acrylic copolymers with light-controlled supramolecular structure and optical properties. These copolymers

consist of mesogenic and chiral-photochromic monomer units (Figure 8) and display chiral nematic (cholesteric) phase with helical supramolecular structure. The planarly-oriented films of such copolymers are characterized by the selective reflection of light (λ_{\max}) according to the equation

$$\lambda_{\max} = nP \quad (1)$$

where P is the pitch of helix and n is the refractive index of polymer. Depending on the composition λ_{\max} may be changed in the spectral region from 400 nm till 1.5 μm . These films can be used as optical filters and reflectors of circularly-polarized light in optics and optoelectronics. The pitch of the helix also depends on the so-called helical twisting power β , which is expressed by the equation:

$$\beta = n(d\lambda^{-1}/dX)_{X=0} \quad (2)$$

where X is the concentration of chiral units. In other words β is a measure of chiral fragments to produce the helical structure and it depends on configuration and conformation of the chiral fragments.

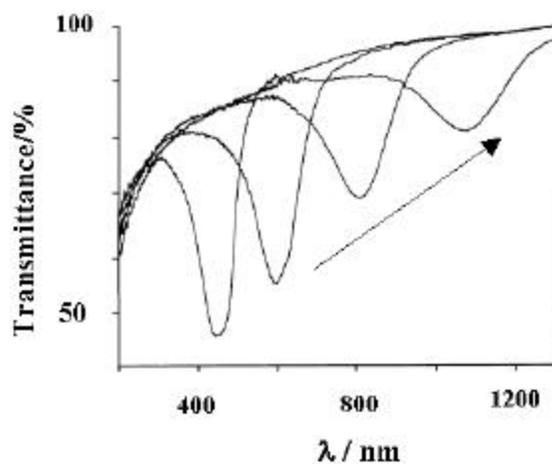


FIGURE 9: Changes of transmission spectrum of copolymer during UV irradiation. Spectra were recorded each 2 min of irradiation (light wavelength-366 nm, light intensity-4.1 mW/cm²).

Using a light (for example UV-irradiation) one can change the β value due to the E-Z isomerization process taking place in the chiral-photochromic side groups (Figure 8). As far as these groups - they are chemically combined and the same monomer units E-Z isomerization is

accompanied by the dramatic change of the β - values (one order of magnitude).

As a result the maximum of selective reflection of light λ_{\max} is changed during the irradiation process (Figure 9). This phenomenon opens the possibilities of creating new photooptical active media and materials for colored recording of information and optical data storage.

Acknowledgment

This research was supported by the Research Program of "Russian Universities" (Grant 5177), INTAS Project 96-922 and International Soros Science Educational Program (Grant a98-2199), as well as Russian Foundation of Fundamental Research (Grant 99-03-33495).

SWEDEN

CELSIUS AEROTECH

Anti-G suit based on smart materials

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Celsius Aerotech in Linköping has developed and obtained a patent for a "Device to apply pressure on a human body". Primarily the invention was meant to be the basis for new design of anti-G suit, i.e. a suit that makes it possible for pilots to sustain high forces of acceleration (positive G-forces). Later, other applications like for medical purposes have been considered. In all applications, threads or bands of smart materials are used as active elements. During the original studies and experiments, these elements were made of threads of smart metal, but gradually we have found that polymers with equal or better qualities are more suitable.

A G-suit based on smart materials has a structure with active threads, woven into the parts around legs, waist, body, and if needed, also arms. The latter are needed to prevent pain in the arms during extreme G-forces. By using smart materials, this function can be designed into the suit without degrading the pilot's comfort or mobility. The threads are activated by electric current, which makes them contract. The process is reversible. The advantages of this design are:

- Superior comfort for the pilot (no tubes or valves, not tight, and lower weight).
- Many possibilities to control the application of pressure, i.e. not only as a function of

acceleration but also of time and place on the pilot.

- Prevention of arm pain during high G-exposure.
- Replacement of the present chest counter pressure garment.
- Short time of reaction, e.g. it is possible to activate a "corset-effect" during an ejection process to protect the pilot from spinal injuries.

Medical applications (active bandage):

Treatment in hospital to assist blood circulation in legs, to-day performed by compressed air bladders, very much like the principle for present anti-G units, could preferably be replaced by "smart trousers", using modern control technology. For example, the pressure application could be adapted to heart frequency and varied along the legs. The patient can perform the treatment at home. Also, this method can be used to widen blood vessels without surgery.

TAIWAN

INDUSTRIAL TECH. RESEARCH INST.

EAP Smart Noise Reduce System & Heat Dissipation Device

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In recent years, the concern of acoustic noise has grown significantly. Two methods were introduced to reduce the sound intensity of unwanted noise, including passive and active noise control (ANC). ANC has become a widespread and popular for reducing low frequency noise, which are difficult to deal with by passive control methods (including sound absorbers such as fibers). However, ANC techniques are difficult to apply to high frequency noise.

Recently, we develop an EAP smart system using hybrid passive-active control to address noise over a wide frequency range. The constructed smart system uses an EAP film, an air gap and fibrous layer. The EAP film minimizes the reflected acoustic wave and

operates as a loudspeaker. The fibrous surface on the backside provides a feed forward LMS control. The EAP film consists of miniature, lightweight, low-cost actuators taking advantage of the large actuation displacement and high power energy output.

We also designed a device for heat dissipation from computers using EAP materials. It has many advantages, such as high efficiency, low noise level, etc.

USA

JPL

Identified Issues Critically Affecting the Application of IPMC as an EAP Actuator

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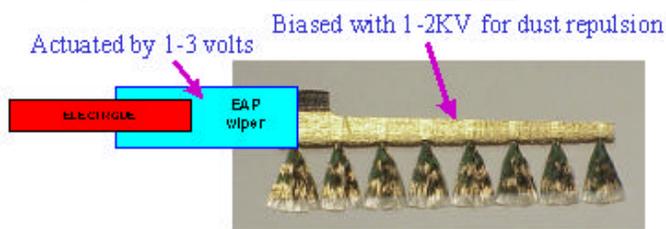


FIGURE 10: Schematic/photographic view of the EAP dust wiper.

As reported in the previous issue of this WW-EAP Newsletter, the application of the Ion Exchange Polymer Metal Composite (IPMC) EAP was explored for the development of a dust wiper. The dust wiper was intended to become part of the Nanorover, which will be launched to an Asteroid in 2002 with the NASA/NASDA MUSES-CN mission. This task was pursued under the lead of the author and the following investigators S. Leary, JPL; J. Harrison, J. Smith and J. Su, NASA-LaRC; T. Knowles, ESLI; in cooperation with K. Oguro, Osaka National Research Institute, Japan, and S. Tadokoro, Kobe University, Japan. A combination of mechanical brushing, driven by an EAP actuator, and high voltage dust repulsion mechanisms were incorporated. The use of IPMC with highly effective species, mechanical modeling, unique elements and a protective coating were explored to overcome the critical challenges to the application of this emerging technology. A schematic/photographic view of the EAP wiper blade is shown in Figure 10.

A 0.104-g blade was constructed of Graphite/Polyimide beam with a gold-coated fiberglass brush. The IPMC wiper is driven by about 2 to 3 Volts and the dust repulsion is obtained by about 1.5-KV DC voltage (Figure 11). Significant improvements were made to the IPMC where two types of cations, that induce large bending, were used including tetra-n-butylammonium and lithium. Issues that can affect the application of the dust wiper at the harsh environment expected in space and on the asteroid were investigated. Serious obstacles were identified including (1) Permanent deformation when applying a DC voltage; (2) The developed protective coating is permeable to water and would not prevent losing the critical ionic content of the IPMC; and (3) Hydrolysis occurs at $>1.23\text{-V}$ producing hydrogen as well as irreversible processes. Unless these challenges can be overcome it would not be feasible to assure the successful application of IPMC as an actuator of a dust-wiper or other practical mechanisms.



FIGURE 11: A view of the dust wiper activated with high voltage to repel dust.

Establishing an EAP Characterization Laboratory at the JPL'S NDEAA LAB

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One of the critical issues that need to be determined for EAP materials is their characteristics as electroactive materials and the need to provide a performance matrix that allows comparing their performance to other actuators (e.g., piezoelectric ceramic, shape memory alloys, hydraulic actuators, and conventional motors). For this purpose, it is essential to define

a unified matrix, establish test capability and provide a centralized independent test lab. These objectives are being currently pursued at the JPL's NDEAA Lab under a DARPA contract. A preliminary database using data that was provided by SRI International was posted on the WW-EAP Webhub to be challenged by the worldwide EAP community as well as the JPL team. Key parameters were identified and are currently being peer reviewed. Also, test methods are being developed. A view of the test setup that was established so far is shown in Figure 12.

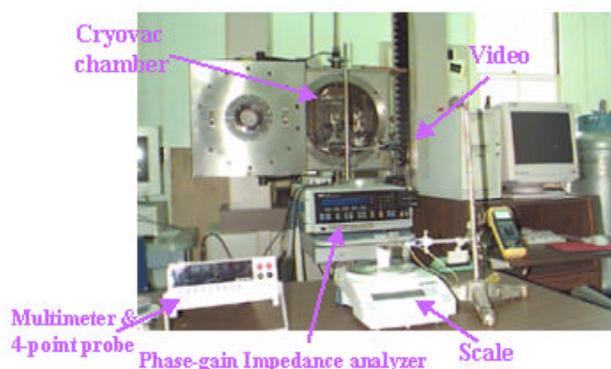


FIGURE 12: A view of the EAP characterization capability established at JPL.

JOHNS HOPKINS UNIVERSITY

Mechanical characterization of active polymer gels

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The Laboratory for Active Materials and Biomimetics at the Johns Hopkins University is currently working to characterize the mechanical properties of ionic polymer gels and to describe how these properties evolve as the gel actuates. Mechanical testing is being conducted on poly(vinyl alcohol)-poly(acrylic acid) gels, which shrink in acidic environments and swell in basic environments. Experimental results of uniaxial tests have shown these materials to be slightly viscoelastic and compressible and capable of large recoverable deformations. The gels also exhibit similar stress in response to mechanical deformation in both acidic and basic environments (see Figure 13).

The stress-deformation behavior of these polymer gels is described through a finite elastic constitutive function. The mechanical and actuation properties of the gel are coupled through a strain-energy function. This approach is analogous to that of finite thermoelasticity, in which a relatively small change in volume accompanies a change in temperature. In the case of polymer gels, however, a large change in volume results from a change in environmental conditions (pH, electric field, etc.). An application of this model to the problem of a bending actuator will be presented at the upcoming SPIE symposium.

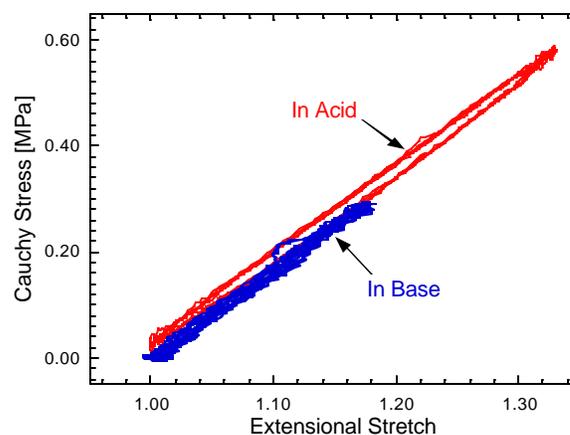


FIGURE 13: Cauchy stress versus extensional stretch for separate PVA-PAA specimens in 0.1M citric acid and in 0.5M sodium bicarbonate (multiple cycles are presented).

MIT

Conducting Polymer Actuators and Devices

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The BioInstrumentation Laboratory at MIT creates instruments and devices for biological and medical applications (test bed is shown in Figure 14). Conducting polymers are key materials in the creation of compact, autonomous and low cost instruments due to their wide-ranging electrically, chemically, thermally, mechanically and optically modifiable physical

properties. As part of the effort to generate such polymeric devices, we are exploring the performance and underlying physics of conducting polymer actuators.

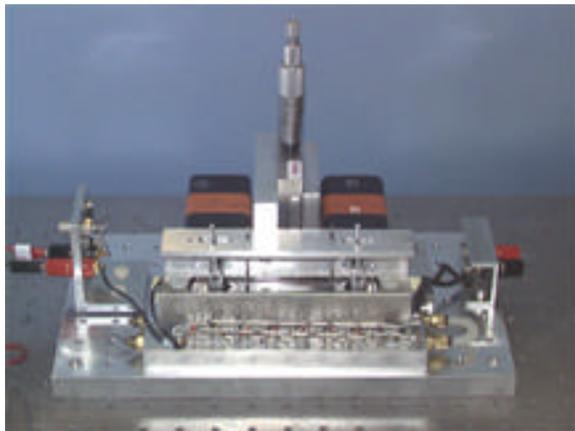


FIGURE 14: Photograph of an isotonic actuator test bed. Two galvanometers apply force to polymer specimens immersed in a temperature-controlled bath.

Key muscle-like actuator figures of merit include stress, strain, power to mass efficiency, and lifetime. In polypyrrole strains of 1-2% at stresses of 5-10 MPa are readily achievable. Recoverable strains reach 6 %, and maximum stress is 30 MPa. In conducting polymer actuators the strain is proportional to the amount of charge transferred. Interestingly, the strain achieved per unit charge is relatively independent of stress. Power to mass is approaching that of mammalian skeletal muscle at $40 \text{ W}\cdot\text{kg}^{-1}$. The electrical to mechanical efficiencies of conducting polymer actuators reported to date are less than 2 %. Recent results show that 18 % is possible with energy recovery, and suggest that higher efficiencies will be obtained. Cycle life is currently under investigation. Many applications require large displacements at moderate stress levels. This has led to an ONR supported collaboration with Timothy Swager's group at MIT, in which molecules are designed to optimize actuator mechanical response.

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3. <http://bioinstrumentation.mit.edu>

PENN STATE UNIVERSITY

Electroactive Polymers with High Electrostrictive Strain and Elastic Power Density

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Making use of high energy electron irradiation to break the macroscopic coherent polarization, a normal ferroelectric poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) copolymer can be converted into a relaxor ferroelectric, which possesses a high room temperature dielectric constant (>60) with a giant electrostriction (strain $>5\%$). The polymer has a high elastic modulus ($\sim 1 \text{ GPa}$) and the field induced strain can operate at frequencies higher than 100 kHz, which result in a very high elastic power density compared with any electroactive polymers reported. Interestingly, the transverse strain of the copolymer can be tuned over a broad range and in properly stretched films, the transverse electromechanical coupling factor k_{31} can reach 0.45. The new polymer actuators can be operated in air, vacuum, or water and in a wide temperature range. Mechanical load test was also performed and the results show that the polymer can withstand load to 40 MPa while still retain high strain level. Since the function of high-energy electron irradiation in converting the copolymer from a normal ferroelectric to a relaxor is to break up the macro-polarization domains, similar changes can also be induced by non-irradiation approaches. Recently, we showed that adding bulky side group to the copolymer main chain can also result in a reduction of the coherent polarization domain size and increase the field induced strain response. Using this approach, a strain of 2.5% can be induced under an applied field of 50 MV/m. Performance analysis indicates that this non-irradiation approach should be more promising than the irradiation approach in generating high strain with low excitation fields.

RUTGERS UNIVERSITY & JPL
Application of Electro-Rheological Fluids in Haptic Interfaces

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A novel haptic interfacing capability called MEMICA (remote MEchanical Mirroring using Controlled stiffness and Actuators) is being developed by Rutgers University and the Jet Propulsion Laboratory (JPL) using liquid EAP. This effort was initiated under the JPL's LoMMAs task. The developed MEMICA is intended to provide human operators intuitive and interactive feeling of the stiffness and forces at remote or virtual sites in support of space, medical, underwater, virtual reality, military and field robots performing dexterous manipulation operations.

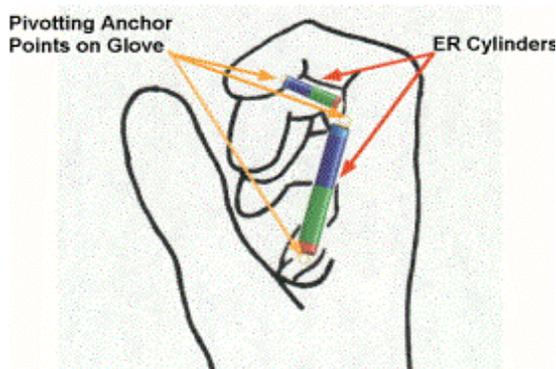


FIGURE 15: Glove with ECS Elements

One of the key aspects of the MEMICA system is a miniature Electrically Controlled Stiffness (ECS) element that mirrors the stiffness at remote/virtual sites. The ECS elements, which make use of Electro-Rheological Fluid (ERF), will be attached on a commercially available glove as it is schematically shown in Figure 15.

Electro-rheological fluids (ERFs) are electroactive fluids that experience dramatic changes in rheological properties, such as viscosity, in the presence of an electric field. The fluids are made from suspensions of an insulating base fluid and particles on the order of one tenth to one hundred microns in size. In the presence of an electric field, the particles, due to an induced

dipole moment, will form chains along the field lines. This induced structure changes the ERF's viscosity, yielding stress and other properties, allowing the ERF to change consistency from that of a liquid to something that is viscoelastic, such as a gel, with response times on the order of milliseconds.

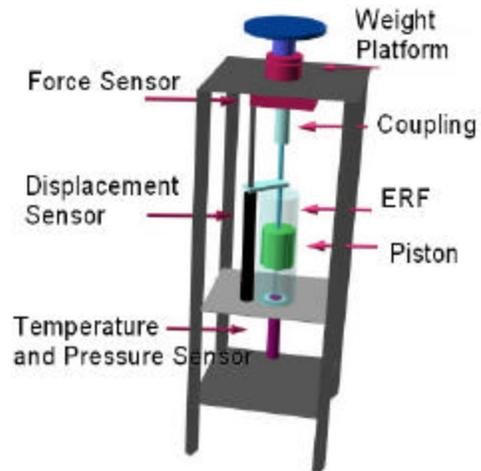


FIGURE 16: Experimental Test-Bed

In order to test the concept of controlling the stiffness with a miniature ECS element, the team began experiments and a larger scale test-bed (see Figures 16 and 17) was constructed at the Rutgers Robotics and Mechatronics Laboratory. This test-bed is equipped with temperature, pressure, force and displacement sensors that are used to monitor the ERF's state. Initial experiments showed that when the electrical field is enabled, the viscosity of the ERF is such that the ECS element can resist external forces.



FIGURE 17: Actual Prototype

RUTGERS UNIVERSITY
POLYMER ELECTROPROCESSING
LABORATORY

Giant Electrostrictive Response in Poly(vinylidene fluoride - hexafluoropropylene) Copolymers

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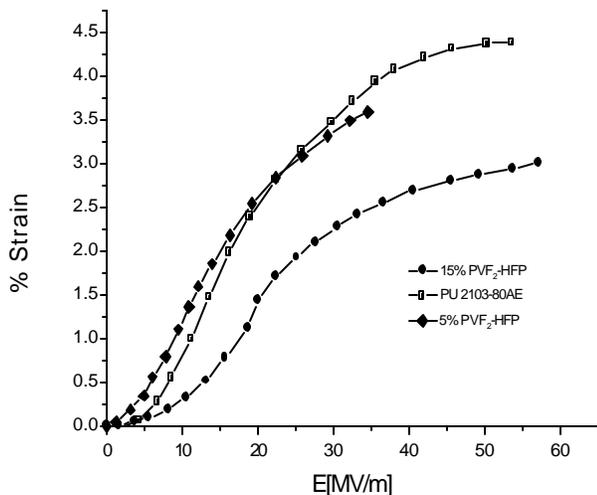


FIGURE 18: Strain response of PVF₂/HFP 5% ice water quenched, polyurethane and PVF₂/HFP 15% ice water quenched with applied electric field.

Electrostrictive strains were measured in three different polymeric materials: a low modulus polyurethane elastomer, previously studied by Scheinbeim, et al. [1] and two higher modulus random copolymers of poly(vinylidene fluoride/hexafluoropropylene) - [PVF₂/HFP]- with 5% and 15% HFP content. Measurements at increasing voltage (electric field ranging from 0 to 60 MV/m) were taken using an air-gap capacitance system, and converted to sample thickness. Copolymer samples having different thermal treatments were compared: ice water quenched, air quenched and slowly cooled, for both compositions. The ice water quenched 5% PVF₂/HFP copolymer exhibited the highest strain response (>4%) and the highest dielectric constant (13.5). The previously studied polyurethane exhibited the second highest strain response (>3%) with the lowest dielectric constant (8.5). The ice water quenched 15% HFP copolymer exhibited the lower strain response among the three polymeric materials (\approx 3%), with a dielectric constant of 13.1. The energy density

of the 5% HFP ice water quenched copolymer ($1/2$ Young's modulus times the maximum electrostrictive strain squared) is the largest known for any semi crystalline polymer: 0.88J/cm³. Results are shown graphically in Figure 18.

References

1. J. I. Scheinbeim, B.A. Newman, Z.Y. Ma and J.W. Lee, "Electrostrictive Response of Elastomeric Polymers", Polymer Preprints Vol. 33, No. 2, 385 (1992).

UNIVERSITY OF ARKANSAS AT LITTLE ROCK

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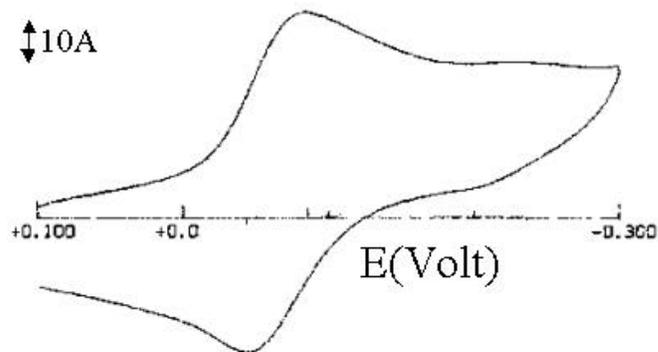


Figure 18. Cyclic Voltammogram of ligno-pani in an aqueous solution.

Lignosulfonic acid-doped polyaniline (ligno-pani), a water dispersible ICP, was synthesized by oxidative polymerization of aniline with sodium persulfate as the oxidant. The oxidant most commonly used in literature is ammonium persulfate. Ammonium persulfate, however, is less stable and more expensive than sodium persulfate. Electrochemical studies were performed on the synthesized ligno-pani in aqueous media (Figure 18). The pH of the media was varied from pH 2-12 using a three component wide range buffer. The redox capability of the polymer can be associated with its ability to protect against corrosion. Preliminary studies indicate that ligno-pani remains redox active above a pH of 10.0. This is significant since previous studies have indicated that HCl-doped polyaniline becomes redox inactive at pH values greater than 5. For this reason, polyaniline has not been considered for

use in marine environments, which have a pH of approximately 9. These new findings, however, open a new area of application for ligno-pani. Once corrosion studies are performed, ligno-pani could become useful for corrosion protection of ocean vessels as well as other applications that require corrosion prevention in both acidic as well as basic environments.

UNIVERSITY OF NEW MEXICO Conductive Polyacrylonitrile (C-PAN) Fibers

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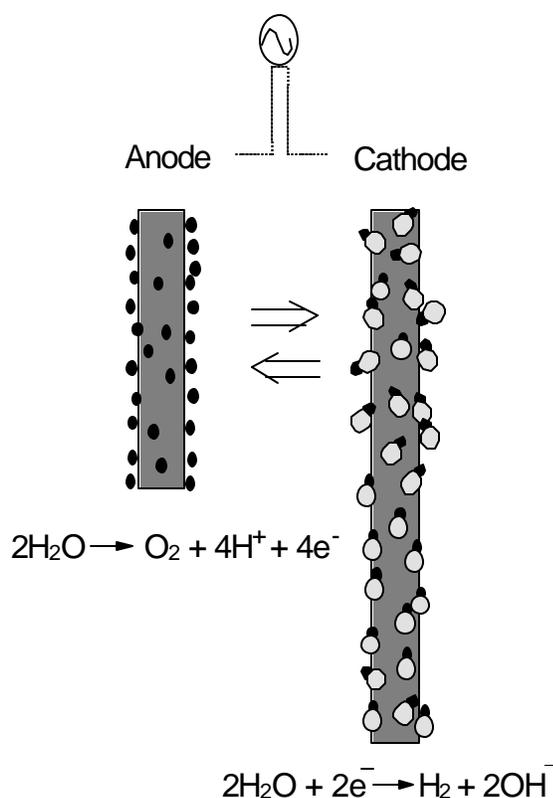


FIGURE 19: Operating principle of C-PAN

Activated PAN fibers are known to contract and elongate when immersed in acidic and alkaline solutions, respectively. The key engineering features of PAN is its capability of changing length more than 100% and comparable strength to human muscle. Artificial Muscles Research Institute (AMRI) of the University of New Mexico (UNM) is developing a new technique that electrically activates PAN. Increasing the conductivity of PAN by making a

composite with a conductive medium such as platinum, gold, graphite, and polypyrrole has allowed for electric activation of PAN when C-PAN is placed in a hydrolysis cell. A change in pH in the vicinity of C-PAN leads to contracted and elongated C-PAN depending upon applied electric polarity. Typically close to 100% change in C-PAN length in a few seconds is observed in a 10 mM NaCl electrolyte solution with a 20-Volt power supply (Figure 19). These initial results indicate a great potential in developing electrically activated C-PAN muscles and linear actuators, which would be more applicable than that of chemically activated PAN. These results present an excellent potential for using electrically activated C-PAN as artificial sarcomere and artificial muscle [1].

References

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UNIVERSITY OF CALIFORNIA AT RIVERSIDE Toward Single-Molecule Electromechanical Actuators

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and Rodney J. Reid

Electromechanical (EM) actuators derived from conducting polymers (CPs) typically function via the reversible counter-ion intercalation and expulsion that occurs during redox cycling. As such, EM actuation in traditional CPs is a bulk property of the material, and is thus not expected to function at the single-molecule level. We are interested in designing CPs in which EM actuation is an intrinsic property of the individual polymer chain, thus allowing EM actuation at the single-molecule level as well as in the bulk. Our preliminary results in this area of research have been recently reported [1], and are summarized herein. Our design utilizes established {4n}annulene chemistry as the method to accomplish the task of "encoding" EM actuation into individual polymer chains. It is well known that cyclooctatetraene (a tub-shaped {8}annulene) becomes planar upon oxidation or reduction.

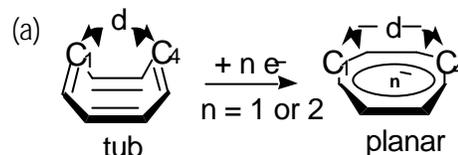
During such a process, the distance between carbons 1 and 4 (as depicted in Figure 1a) is altered. By utilizing an {8} annulene as a polymer repeat unit, such redox-induced conformational changes can be translated into a change in the effective monomer length. It follows that altering effective monomer length will ultimately alter effective polymer chain length. Thus, a single molecule EM actuator can be achieved. As stated, we have already reported our design, synthesis, and preliminary characterization (electrochemistry, conductivity, and molecular modeling) of poly(cyclooctatetrathiophene), a "masked" poly({8}annulene) (see poly(1), Figure 20) [1]. We are currently developing new analytical techniques to measure real-time dimensional changes in CP-based EM actuators. We are also investigating other poly({4n}annulene)s such as poly(2), a regioisomer of poly(1), for EM activity (Figure 1c). Note that both connectivity and conjugation are altered on going from poly(1) to poly(2).

References

1. Marsella, M. J., Reid, R. J. *Macromolecules*, 1999, 32, 5982-5984.

UPCOMING EVENTS

March 6-7, 2000	SPIE joint Smart Materials and Structures and NDE, Newport Beach, CA., Pat Wight patw@spie.org Website: http://www.spie.org/web/meetings/calls/ss00/ss04.html
June 5-6, 2000	International Seminar on Technology of Inherently Conductive Polymers, Napa, CA, fractals@infobridge.com , website: www.conductivepolymers.com



$C_1 - C_4$ distance (d):
planar > tub

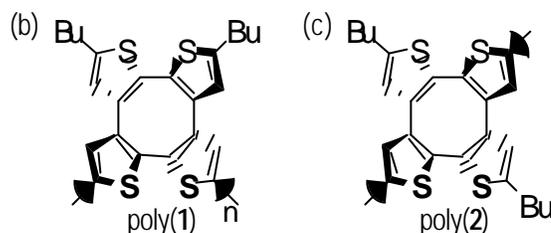
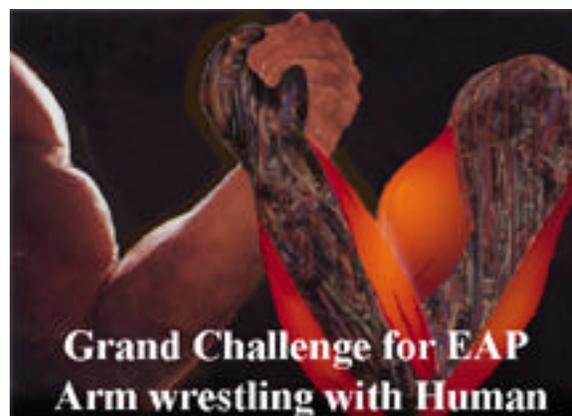


FIGURE 20. (a) Illustrating the redox-induced conformational change of cyclooctatetraene. (b and c) Two regioisomers of poly(cyclooctatetrathiophene).



WorldWide Electroactive Polymers (EAP) Newsletter

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