Actuators based on electroactive polymers

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Conducting polymers and ionic polymer–metal composites (IPMCs) are among those electro-active polymer materials that have shown tremendous potential to make efficient actuators. The volume change that a conducting polymer undergoes upon electrochemical oxidation and reduction is used to make microactuators, which find various biomedical applications and can be used for manipulation of particles of micrometre dimensions. IPMCs undergo strong bending on application of an electric field. Actuators using IPMCs have space applications. Further development of IPMCs is being done to make it overcome the present obstacles. Conducting polymers and IPMCs have gained recognition due to their low cost, low operating potential and high efficiency.

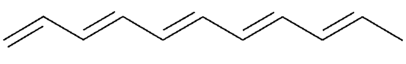
Since ages, man has tried to imitate nature. He has tried to make materials that emulate the working of a biological muscle, since it is a highly optimized system. Materials that come close to working like a muscle are ferroelectric polymers, piezoelectric polymers, electrostatic polymers, ionic polymer–metal composites and conducting polymers[1]. All these are collectively known as electro-active polymers (EAP). These show a change in shape or size or both upon application of electrical voltage.

The use of conducting polymers and ionic polymer–metal composites as actuators in the microscale and the macroscale respectively, will now be discussed. An actuator is a device that communicates motion. A prerequisite for these materials is that they should bend and straighten as and when required, thus resembling a biological muscle.

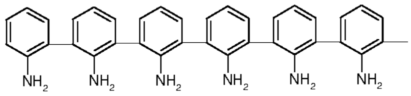
Conducting polymers

Conducting polymers are conjugated polymers, namely organic compounds that have an extended *p*-orbital system, through which electrons can move from one end of the polymer to the other. Polyacetylene is the conducting polymer with the simplest structure (Scheme 1). The most common conducting polymers are polyaniline (Scheme 2) and polypyrrole (Scheme 3).

Suppose polypyrrole is in an electrolytic solution. Let the electrolyte

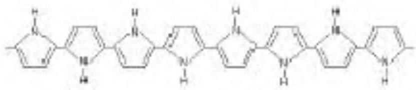


Scheme 1.



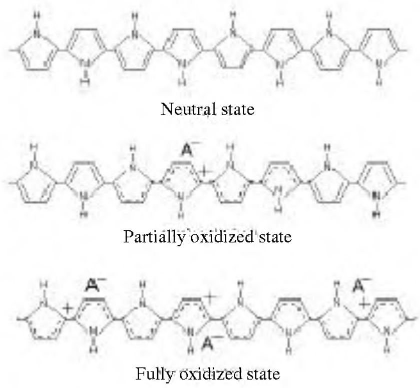
Polyaniline

Scheme 2.



Polypyrrole

Scheme 3.



Scheme 4.

C^+A^- be in contact with polypyrrole. On application of electric current, polypyrrole is oxidized (Scheme 4).

To maintain charge neutrality, the anion enters the polymer. This increases the volume. During reduction, the anions leave the polymer, thus resulting in contraction of the polymer. It is the redox reaction that brings about volume change. When the anion A^- is small, it is the mobile ionic species.

$$P^+(A^-) + C^+ + e^- \leftrightarrow P + A^- + C^+$$

However, if the anion A^- is large and bulky, then it is immobile and it is the cation C^+ that enters to maintain charge neutrality upon reduction, resulting in volume expansion. In this case the anion A^- resides in polypyrrole and the cation moves in and out. Usually NaDBS is used as an electrolyte, where DBS^- (dodecylbenzenesulphonate) is the large immobile anion (Scheme 5).

$$P^+(A^-) + C^+ + e^- \leftrightarrow P^\circ(AC)$$

Both processes may occur simultaneously for an intermediate-size anion, which makes bad actuators because the volume change is not predictable. In the oxidized state, the anion resides in polypyrrole and this is called the doped state. Correspondingly, the neutral state of polypyrrole is called the undoped state.

Bilayer

If a film of volume-changing material (like a polymer) is attached to a film that does not change its volume, then it forms a bilayer[2,3], which will bend on oxidation and reduction of the polymer film.

Dodecylbenzenesulfonate – DBS

Scheme 5.

An Au/PPy bilayer is shown in Figure 1. PPy is doped with DBS^- anions (PPy (DBS)). The microactuator is operated in an aqueous solution, usually of NaDBS. During reduction ($V = 0$ volt) of the PPy layer, Na^+ ions surrounded by water molecules enter the PPy layer to achieve charge neutrality in the PPy film. The PPy film swells and thus the bilayer straightens. On oxidation, the Na^+ ions are expelled from the PPy film, which in turn shrinks and causes a bending motion ($V = -1$ volt). Intermediate positions can be obtained by varying the voltage. Fabrication of the bilayer is done using the differential adhesion method or the sacrificial layer method[3].

Devices

Some interesting examples of devices based on PPy/Au bilayer microactuator are: (a) Simple array of fingers for positioning or holding small fibres, blood vessels, or nerve fibres; (b) A microvial that can be closed by a lid operated by microactuators; (c) A microrobot for the manipulation of micrometre-sized objects.

Presently, these microactuators can only be operated in a wet environment, but fortunately, most of the applications are in wet environment like salt solution, blood plasma, urine and cell culture medium.

Fingers: An array of bilayers can be used as fingers to grab micrometre-sized objects such as fibres. Such fingers have been found to be rather strong and resistant to damage in case the fibres are pulled, when the fingers are holding onto the fibre. Practical use of such fingers can be to hold small nerve fibres under study, for measurements or surgery. Figure 2 shows an actuator holding a fibre by an array of fingers.

Sealable microvials: There is an increasing need for confinement of small sample volumes in cell biology, chemistry and related fields. For example, one would need to isolate a single cell in a confined volume and study its characteristics and responses to external signals. The field of nanochemistry mainly deals with small sample volumes. The advantages of small sample volumes are reduced sample costs and lesser losses; detection of small amounts of reagents becomes more probable. However the main problem faced while dealing with small sample volumes is that of evaporation. A solution to this problem is to have a small chamber with a lid.

For such applications, a sealable microvial (Figure 3) has been developed. The fabrication of this device is done using differential adhesion method[3]. It is a micromachined cavity that can be closed or opened by a lid activated by microactuators. An electromagnetic locking mechanism is used to seal the closed lid. As added accessories, one could have micromachined sensors and actuators inside the vial, in order to stimulate and analyse the cell.

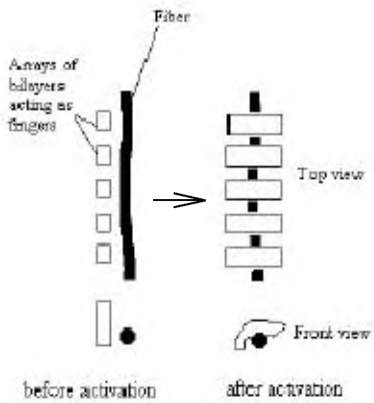


Figure 2. Actuator holding a fibre by an array of fingers.

Microrobots: The development of microrobots[4] is the most exciting application of PPy microactuators. A microrobotic arm has been fabricated which can be used to manipulate microscale objects. The robot consists of PPy/Au bilayer and rigid elements formed of BCB (benzocyclobutene). All the joints are individually controlled. Each joint consists of two separately controllable micromuscles. The fabrication of the microrobot is based on the sacrificial layer method[3].

The robots are activated using a triangular potential waveform on all joints, simultaneously. It is possible to control and bend each individual joint and finger at any angle by suitable application of potential at the respective joint. With proper combination of bending and coordination, the arm can be rotated. The fingers of the arm can be bent backward as well as forward.

Microrobots have successfully performed the lifting and displacement of a 100-μm glass bead over a distance of 200–250 μm (Figure 4). The microrobot seems to be a promising device in single-cell diagnostics. The robot arm could arrest biological entities like infected cells or bacteria and transfer them to other areas, as demonstrated by the transfer of the glass-bead experiment. These microrobots could also be located in the microvials themselves, to carry out single-cell operations. Thus, possible future applications of the microrobot are many and varied.

Ionic polymer metal composite

Polymers containing ions are called ionic polymers. An ionic polymer metal composite (IPMC) actuator consists of an ionic polymer[5–8]. IPMC is an EAP that bends due to mobility of ions in the ionic polymer. The IPMC is composed of a

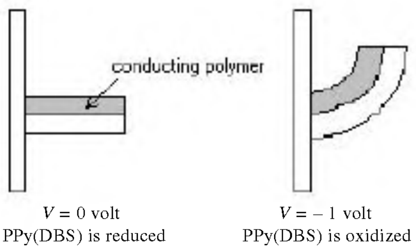


Figure 1. Au/PPy bilayer.

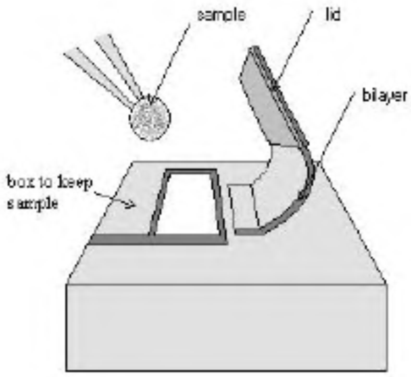


Figure 3. Sealable microvial.

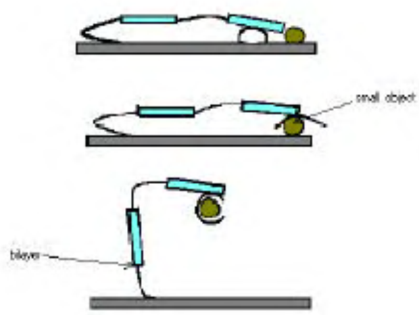
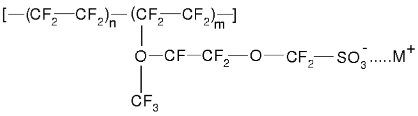


Figure 4. Schematic representation of the robot lifting a glass bead.



Scheme 6.

perfluorinated ion-exchange membrane (PIEM; Figure 5), the surface of which is deposited with platinum particles, that act as microelectrodes for electrical contact.

The base polymer used to form the IPMC is *Nafion*® (perfluorosulphonate made by DuPont) or *Flemion*® (perfluorocarboxylate made by Asahi Glass, Japan). This base polymer provides channels for mobility of positive ions in a fixed network of negative ions on interconnected clusters. In case of *Nafion*® (Scheme 6) the counter ion can be K^+, Na^+, H^+ or Li^+.

When a voltage is applied in the anionic polymer, an electric field is set up inside the polymer causing the cations along with the hydrated water molecules to move towards the cathode. This movement of bulk mass produces a bend in the EAP towards the anode (Figure 6).

This movement of ions causing bending is akin to electrophoresis. The extent of bending is directly related to the amount of hydration of the cation. Cations with greater amount of hydration produce greater displacement and higher stress, relative to cations with smaller hydration shells. Therefore, membranes with Li^+ show better actuation performance compared to Na^+ or K^+.

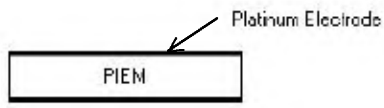


Figure 5. Perfluorinated ion-exchange membrane.

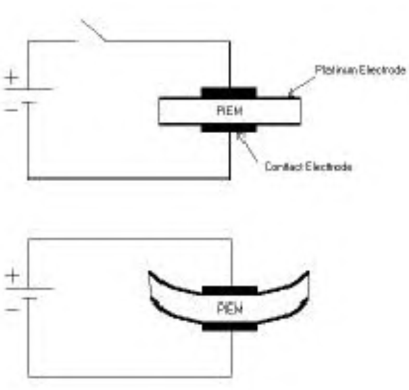


Figure 6. Mechanism of bending in EAP.

In order to generate an electrode in the polymer, metal ions (platinum/gold) are dispersed on the polymer surface and the ions are then reduced to the metal atoms which form the electrode film. Au, when used for electrode formation gives better results due to higher electrical conductivity. However platinum electrodes are preferred, since platinum can be easily reduced.

When the voltage is alternately increased and decreased, the IPMC EAP bends and straightens alternately, similar to a car-wiper action. At low voltages (1–10 V) when frequencies are low, say below 1 Hz, it induces large bending. The amplitude of bending decreases with increasing frequency.

Applications

Owing to the ability of the IPMC to work under extremely harsh environments of low temperatures and vacuum conditions, it can be used in space applications. They are also light, compact and driven by low power, which are very advantageous in space applications. These polymers exhibit excellent chemical and thermal stability and a relatively low voltage is required.

Dust wipers: It was found that certain space environments cause accumulation of dust on hardware surfaces. This hampers the long-term operation of optical instruments and also degrades the efficiency of solar cells to produce power. To remove this dust, one can use a similar mechanism as that of automobile windshield wipers. As we have already seen, IPMC, when activated by means of an AC voltage, undergoes alternate bending and straightening. Thus when IPMC is applied with signals of about 0.3 Hz, it is seen to bend through angles which exceed 90º.

For dust cleaning of windows, it is necessary to place the wiper outside the viewing area and move it inward while cleaning (Figure 7). Thus by means of two wipers placed on opposite sides of the window, one can efficiently wipe the dust from the window. In this way IPMC can be used as a dust wiper[9].

Gripper: The bending action of IPMC is used to grip a rock sample. As shown in Figure 8, the gripper holds onto the sample, when it is made to bend. The sample is released when the gripper is straightened[10]. Experiments have shown that the gripper can lift rocks weighing up to 10 g. It is envisaged to use this arrangement on a land rover, so that the gripper can pick up rock samples and place them on the rover. Since IPMCs are light-weight and require low voltage, they act as excellent gripping devices on the land rover, where power conservation and low weight are critical.

Shortcomings of IPMC

There are a few shortcomings of the applications of IPMC[6,9].

Protection from drying: The actuation ability of the IPMC depends to a large extent on the moisture content in the polymer. This is because most of the deflection produced in the polymer is due to the movement of the hydrated ions. Thus, it becomes important to maintain the moisture content in the polymer for a long time. It was seen that using an etching procedure and silicon coating, an IPMC film could operate efficiently for

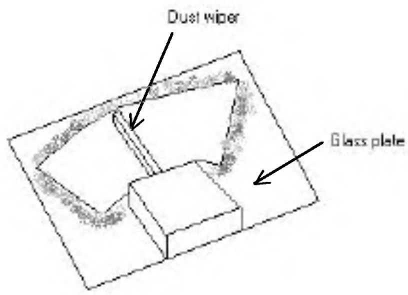


Figure 7. Action of dust wiper.

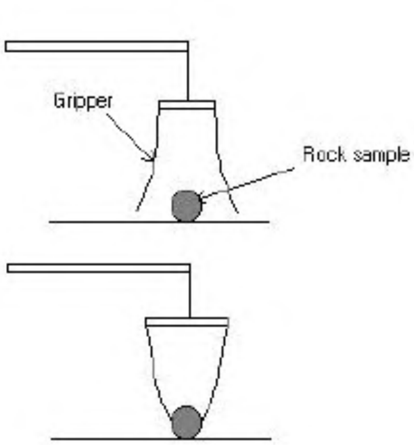


Figure 8. Bending action of IPMC.

about four months without drying. But this does not work in the case of space applications where moisture content has to be maintained in the polymer for longer periods under testing conditions of low temperature and low pressure. This is a serious drawback and various other coating techniques are being considered to obtain the desired results.

Electrolysis: Due to the wetness of the IPMC polymer, voltages greater than 1.03 V involve electrolysis during electro-activation causing degradation, heat and release of gases like hydrogen. These emitted gases accumulate under the protective coating and generate blisters that rupture the protective coating. The use of tetra-*n*-butylammonium cations shows greater actuation efficiency in applications where the frequency of the applied signal is high and the voltage is low.

Permanent deformation under DC activation: Under an AC activation, IPMC is found to operate efficiently, having alternate bending and straightening, depending largely on the applied voltage and the frequency of the applied AC voltage. However on application of DC, IPMC does not maintain the induced bending for long and retracts after several seconds. Further, on removing the DC voltage, IPMC undergoes recoiling, wherein an overshoot bending occurs in the direction opposite to the activating voltage. This leads to a permanent deformation.

In general, EAP have found application in the fields of medicine, robotics, research and development, space technology and this list is fast growing. In fact, it is envisaged that EAP will eventually work as a bionic arm, thus providing a new lease of life to the handicapped. Thus EAP are truly materials of the future!

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Identification of a gene associated with *Bt* resistance in the lepidopteran pest, *Heliothis virescens* and its implications in *Bt* transgenic-based pest control

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Agriculture feeds 6 billion humans everyday, and within 50 years will have to feed a population of approximately 9 billion (UN forecast). It is estimated that 1/3 of the world's agricultural production is lost to insect pests, pathogens and weeds. Among the insect pests, the order Lepidoptera represents a diverse and important group, since it embraces most agronomically important insects which include the world's most damaging crop pests that belong to Noctuidae. The Lepidoptera also includes economically important silk-secreting insects that belong to Bombycidae and Saturniidae. The noctuids encompass the heliothines, *Helicoverpa armigera* in Africa, Southern Europe, Asia, Australia and the Pacific, *H. zea* and *Heliothis virescens* in the Americas, which are three of the world's major crop pests. The heliothines are commonly referred to as cotton bollworm, tobacco bollworm, corn earworm, etc. depending upon their host crop. The lepidopteran pest larvae cause extensive damage to cotton, potato, tobacco, tomato, maize, sunflower, beans, citrus and other crops. The control of agriculture pest populations is achieved mainly by the application of chemical insecticides. Biological control methods (parasites, parasitoids and entomopathogens such as bacteria and viruses) are also part of integrated crop protection strategies. Genetically engineered crops producing their own built-in insecticides are emerging as an increasingly popular tool for controlling lepidopteran pests, while reducing the need for potentially dangerous chemical pesticides. The common soil bacterium, *Bacillus thuringiensis* (*Bt*) produces crystal-containing proteins that are toxic to certain insects, but are harmless to most other organisms, including beneficial insects[1]. Genes encoding *Bt* toxins have been incorporated and expressed in crop plants, thus providing environmentally benign control of insect pests[2]. The lepidopteran pest larvae are the primary targets of more than 99% of the currently deployed *Bt*-producing transgenic plants[3]. The risk of resistance development by the lepidopteran pest larvae is the most