Artificial Muscles, Biosensors and Drug Delivery Systems Based on Conducting Polymers: A Review

Ali Akbar Entezami¹* and Bakhshali Massoumi²

(1) Polymer Laboratory, Faculty of Chemistry, Tabriz University, Tabriz-51664, I.R. Iran
(2) Department of Chemistry, Payame Noor University, Tabriz Branch, Tabriz, I.R. Iran

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ABSTRACT

Polymer (PPy) and polyaniline (PANI) are of the most promising materials for multifunctionalized applications. The application of conducting polymers for the direct conversion of electrical energy to mechanical energy in electro-mechanical actuators is analyzed using theoretical and experimental results. Electrically conducting organic polymers and a novel class of "synthetic metals" that combine the chemical and mechanical properties of polymers with the electronic properties of metals and semiconductors. These polymers become conductive upon partial oxidation or reduction, a process commonly referred to as doping. One of the unique aspects for conducting polymers is controlled-release devices, as well as biologically active ions and drugs such as adenosine 5-triphosphate, heparin, dexamethasone phosphate, glutamate and sulphosalicylic acid as a model of sulphonic drugs. During the last decade, polymers have gained tremendous recognition in the field of artificial sensor in the goal of mimicking natural sense organs. Better selectivity and rapid measurements have been achieved by replacing classical sensor materials with polymers involving nano-technology and exploiting either the intrinsic functions of polymers. In this review, application of conducting polymers such as PPy and PANI in drug delivery systems, biosensors and preparation of artificial muscle such as robots, artificial limbs are discussed.
INTRODUCTION

Applications of conducting polymers were essentially extended during last years and include now such different fields of science and technology as corrosion protection and antistatic coatings [1-5], applications in biosensors for coupling of electron transfer [6-7], for immobilization of biomolecules or as selective filters, preparation of pH or reference electrodes, development of ion-exchangers and catalysts, fabrication of electrochemical windows and gas sensors [8-9], development of individual electronic devices and whole integrated circuits [10-13]. Many of these applications are based on electrical properties of these polymers or on modification of these properties. A molecular swelling has been proposed to allow the incorporation of counter ions during anodic oxidation. Counteraction of the structure occurs during reduction. Burgmayer and Murray, using polypyrrole membrane [15], showed that the membrane permeability of certain ion could be changed by two orders of magnitude under polarization at different potentials. It has attempted to prove the presence of this change in volume by building a mechanical device, controlled by electric currents or potentials, able to transform molecular movement into a macroscopic movement [16-18]. The interest in these systems is connected with the fact that muscles can be considered the optimum system able to transform chemical energy into mechanical energy, triggered by an electric signal. Foremost among the current commercial ventures are applications of conducting polymers in energy storage devices such as rechargeable batteries [19-21] and capacitors. Some of the conducting polymers can change their optical properties an application of current or voltage and therefore may find useful application as heat shutters and light emitting diodes [22]. Conducting polymers have also been tried as drug-delivering systems and release drugs and biomolecules [23]. L.L. Miller reported the controlled release of a neurotransmitter from polymer-coated electrode [24]. A polymer bilayer represents a polymer-modified electrode consisting of two physically segregated layers of electroactive materials with different redox potentials. This review introduces the application of conducting polymers in drug delivery system and artificial muscles.

PHARMACEUTICAL APPLICATIONS

Biosensor

A biosensor may be considered as a combination of a bioreceptor, the biological component, and a transducer, the detection method. The total effect of a biosensor is to transform a biological event into an electrical signal. Biosensors have found extensive applications in medical diagnostics, environmental pollution control for measuring toxic gases in the atmosphere and toxic soluble compounds in river water. Tables 1-3 show the conductance measurement of polyaniline (PANI) blends, which were affected by different concentrations of toxic gases and vapours. The conductivity of PANI blends increases upon exposure to tested samples. The conductivity changes upon exposure to these relatively small concentrations, are gases and vapours almost reversible. When higher concentrations of samples were used, the conductivity changes become smaller and partly irreversible [8].

Table 1. Conductance changes of PVAC-PANI blend, so = 0.08 s/cm for different of toxic gases and vapours.

<table>
<thead>
<tr>
<th>Rel. Concentration (ppm)</th>
<th>200</th>
<th>500</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂</td>
<td>0.08</td>
<td>0.086</td>
<td>0.12</td>
</tr>
<tr>
<td>Br₂</td>
<td>0.086</td>
<td>0.11</td>
<td>0.14</td>
</tr>
<tr>
<td>I₂</td>
<td>0.099</td>
<td>0.15</td>
<td>0.22</td>
</tr>
<tr>
<td>HCl</td>
<td>0.09</td>
<td>0.16</td>
<td>0.23</td>
</tr>
<tr>
<td>HBr</td>
<td>0.16</td>
<td>0.24</td>
<td>0.36</td>
</tr>
<tr>
<td>HI</td>
<td>0.36</td>
<td>0.61</td>
<td>0.62</td>
</tr>
<tr>
<td>HCN</td>
<td>0.2</td>
<td>0.22</td>
<td>0.3</td>
</tr>
<tr>
<td>MCAA¹</td>
<td>0.13</td>
<td>0.17</td>
<td>0.29</td>
</tr>
<tr>
<td>TCMB²</td>
<td>0.15</td>
<td>0.22</td>
<td>0.35</td>
</tr>
<tr>
<td>BA³</td>
<td>0.082</td>
<td>0.082</td>
<td>0.083</td>
</tr>
<tr>
<td>MBB⁴</td>
<td>0.12</td>
<td>0.15</td>
<td>0.24</td>
</tr>
</tbody>
</table>

(1) Monochloroacetic acid, (2) 1, 3, 5 trichloromethylbenzene (TCMB).
(3) Bromobenzene, (4) methyl benzyl bromide (MBB).
Applications of different conducting polymers as sensors also are summarized in Table 4. These pollutants include heavy metals, nitrates, nitrites, and herbicides. Pesticides such as: polychlorinated biphenyls, polyaromatic hydrocarbons, trichloroethylene, etc. Pollutant sensitive biocomponents have been used with a variety of detection modes for their quantitative estimation [25-27]. The use of enzyme sensors can help in the direct measurement of organic compounds, including organic pollutants for environmental controls. Since hydrogen peroxide, used in food textile and dye industries for bleaching and sterilization purposes, can be directly measured by enzyme sensors as the following equation, with the liberated oxygen detected by oxygen electrode.

\[
\text{H}_2\text{O}_2 \xrightarrow{\text{Catalase}} \text{H}_2\text{O} + \frac{1}{2} \text{O}_2
\]

This technique is faster and more convenient than the classical colorimetric and volumetric methods. Figure 1 shows the principle of the operation of a biosensor [28], which starting from the analyte can provide all the information needed for its evaluation.

By far the largest group of direct electron-transfer biosensors is based on co-immobilization of the enzyme in a conducting polymer, namely polypyrrrole [28,29], and polyaniline [30]. Various epoxy cements are somewhat similar [30-32].

**Table 2.** Conductance changes of PS-PANI blend, \(s_0 = 0.03\) s/cm for different toxic gases and vapours.

<table>
<thead>
<tr>
<th>Rel. Concentration (ppm)</th>
<th>200</th>
<th>500</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.03</td>
<td>0.034</td>
<td>0.045</td>
</tr>
<tr>
<td>Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.033</td>
<td>0.038</td>
<td>0.058</td>
</tr>
<tr>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.04</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>HCl</td>
<td>0.04</td>
<td>0.054</td>
<td>0.056</td>
</tr>
<tr>
<td>HBr</td>
<td>0.059</td>
<td>0.075</td>
<td>0.079</td>
</tr>
<tr>
<td>HI</td>
<td>0.075</td>
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<td>0.25</td>
</tr>
<tr>
<td>HCN</td>
<td>0.065</td>
<td>0.08</td>
<td>0.092</td>
</tr>
<tr>
<td>MCAA</td>
<td>0.045</td>
<td>0.058</td>
<td>0.078</td>
</tr>
<tr>
<td>TCMB</td>
<td>0.08</td>
<td>0.1</td>
<td>0.15</td>
</tr>
<tr>
<td>BA</td>
<td>0.032</td>
<td>0.036</td>
<td>0.038</td>
</tr>
<tr>
<td>MBB</td>
<td>0.05</td>
<td>0.06</td>
<td>0.09</td>
</tr>
</tbody>
</table>

**Table 3.** Conductance changes of PVC-PANI blend, \(s_0 = 1\) s/cm for different toxic gases and vapours.

<table>
<thead>
<tr>
<th>Rel. Concentration (ppm)</th>
<th>200</th>
<th>500</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.2</td>
<td>1.4</td>
<td>1.6</td>
</tr>
<tr>
<td>Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.4</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.8</td>
<td>1.9</td>
<td>2.3</td>
</tr>
<tr>
<td>HCl</td>
<td>1.9</td>
<td>2.9</td>
<td>3.3</td>
</tr>
<tr>
<td>HBr</td>
<td>3.1</td>
<td>4.2</td>
<td>5.0</td>
</tr>
<tr>
<td>HI</td>
<td>2.4</td>
<td>5.1</td>
<td>10</td>
</tr>
<tr>
<td>HCN</td>
<td>2.2</td>
<td>3.1</td>
<td>4.0</td>
</tr>
<tr>
<td>MCAA</td>
<td>1.2</td>
<td>2.5</td>
<td>4.3</td>
</tr>
<tr>
<td>TCMB</td>
<td>5.3</td>
<td>6.5</td>
<td>7.0</td>
</tr>
<tr>
<td>BA</td>
<td>1.5</td>
<td>1.8</td>
<td>2.2</td>
</tr>
<tr>
<td>MBB</td>
<td>2.7</td>
<td>2.5</td>
<td>4.4</td>
</tr>
</tbody>
</table>

**Figure 1.** Major stages of measurements of analytes with a biosensor.
A novel reagents direct electrochemical DNA sensor has been developed using ultra thin films of the conducting polymer polypryrole doped with an oligonucleotide probe [38]. It was to develop a prototype electrochemical DNA sensor for detection of a bio warfare pathogen variola major virus. The sensor has been optimized for higher specificity and sensitivity. It was possible to detect 1.6 fmol of complementary oligonucleotide target in 0.1 mL in seconds by using chronoamperometry. Polyaniline synthesized in the presence of various acids were used to label the monoclonal Bovine viral diarrhea virus (BVDV) antibody and further used to test the biosensor performance for BVDV detection [39]. The biosensor was tested in BVDV pure culture ranging in concentrations from $10^1$ to $10^5$ cell culture infective dose per milliliter (CCID/mL). The detection limit of the biosensor consisting of polyaniline polymerized in 4-hydroxy benzenesulphonic acid (HBSA), sulphobenzoic acid (SBA), and phenylphosphonic acid (PPA) was $10^5$ CCID/mL of samples [40].

The analytical curve of a biosensor prepared by the immobilization of the enzyme oxalate oxidase (OOX) onto a prussian blue (PB) is shown in Figure 2. The current response to oxalate was recorded in a succinate buffer solution (pH=3.8) at 0.00 V in the 0.05-0.45 mmol L$^{-1}$ concentration range, which covers levels of oxalate in medical analysis [40,41].

Amperometric choline biosensors immobilized by enzyme of choline oxidase (ChO) and a bi-enzyme of cho/horseradish peroxidase (ChO/HRP), separately, on the conducting polymer film appending a carboxyl group coated on a GC electrode were successfully fabricated and their performances to choline detection were compared [42]. The use of conducting polymer film for the immobilization of enzymes through covalent bonding resulted to a very stable sensor system. The amounts of enzymes on the polymer film were determined from QCM (quartz crystal microbalance) studies.

Electronic nose technology could be useful as well in discriminating pre-dialysis forms post-dialysis blood

Table 4. Polymers used in different enzyme biosensors.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Polymer</th>
<th>Sensing elements</th>
<th>Sensor properties</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>Polypyrrole</td>
<td>Glucose oxidase</td>
<td>Long-term stability is 7 days.</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>Poly-N-methylpyrrole</td>
<td></td>
<td>Detect analyte with in the concentration range 0-0.22 mol/dm$^3$</td>
<td></td>
</tr>
<tr>
<td>L-Amino acids</td>
<td>Polytyramine</td>
<td>L-Aminoacid oxidase</td>
<td>Lower limit of detection is 0.07 mM. Stability is more than 1 month</td>
<td></td>
</tr>
<tr>
<td>Peroxides</td>
<td>Poly(aminomethylferrocene)</td>
<td>Horseradish</td>
<td></td>
<td>[36]</td>
</tr>
<tr>
<td>Glucose, Urea,</td>
<td>Polyaniline</td>
<td>Peroxidase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triglycerides</td>
<td></td>
<td>GOD, Urease, Lipase</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. Analytical curve (mean of three determinations) obtained at 0.00 V vs. Ag/AgCl with PB/OOX biosensor in succinate buffer (0.10 mol L$^{-1}$, pH 3.8).
as well as control blood [43]. Together with an appropriate classification model, it might be possible to build an on-line monitoring system for the management of renal failure. It might also be possible to improve and modify currently used sensor arrays towards specific volatile markers or marker groups, which would simplify the optimization of such applications. Complexation of Cu ions in a terthiophene carboxylic acid (TTCA) polymer film resulted an enhanced anodic current for acacetaminophen oxidation when compared to polymer coated and bare glassy carbon electrodes in human blood and buffer media [44]. Scanning electron microscopy (SEM) and ESCA experiments indicate the involvement of copper in the electrocatalytic oxidation of acetaminophen. No interference was observed from other biologically important and phenolic compounds used with this modified electrode. Especially, the non-interference from N-acetyl cysteine, an antidote for the treatment of acetaminophen poisoning, reveals the proposed method’s superiority in medicinal applications.

**Function of Conducting Polymers in Drug Delivery System**

Ion movement to maintain charge neutrality with the mobile species accompanies electrochemical switching of conducting polymers and the direction of ion flux is controlled by polymer-ion interaction [45]. Conducting polymers with immobile high molecular weight or multianionic dopant (polyelectrolyte incorporated during electropolymerization) exhibit cation-dominated transport. Recently there has been a significant effort directed to finding new drug release systems in which bioactive molecules contained in a reservoir can be supplied to a host system while controlling the rate and period of delivery [46]. The optimum mode of administration would be achieved if the drug was delivered to a precise region of the body where it is physiologically required. Polymers have proven especially useful materials for drug carriers since they can be easily processed and their physical and chemical properties turned via molecular architecture. Conducting electroactive polymers have been considered for drug delivery due to their unique redox properties, which allow controlled ionic transport through the polymer membrane. Electrochemical switching of the polymer is accompanied by the movement of counter ions, so-called dopant ions, in and out of the membrane for charge balance.

The electrochemical behaviour of polypyrrole/adenosine triphosphate (PPy/ATP) has been reported and shows varied features according to the synthesis conditions and cycling electrolyte [46]. On the basis of these properties, a variety of anions including salicylate and ferrocyanide, glutamate, have been electrostatically entrapped into conducting polymer membranes and released during reduction. Furthermore, by entrapping large anionic dopants inside the membrane, cations have been released during oxidation of the polymer; such processes included the release of protonated dopamine [47]. These systems, however, may exhibit spontaneous drug release, which has hampered development of drug release devices. A polymer bilayer represents a polymer-modified electrode consisting of two physically segregated layers of electroactive materials with different redox potentials [48]. It has been shown that the bilayer, which consists of a high redox potential inner film and a low redox potential outer film possesses interesting properties when subjected to electrochemical switching, including charge trapping for energy storage [49,50]. The bilayer concept is outlined in Figure 3. By constructing a bilayer of PPy-ATP (or possibly other anionic biological molecules which can be electrochemically released) and poly(N-methyl pyrrole) chloride (PNMP-Cl) (or possibly other anionic biological molecules as dopants), a single polymer modified electrode can be used to absorb or emit bioactive anions by controlling the redox state of the films [45,51,52].

Recently the electrochemically stimulated release of sulpho-salicylic acid (SSA), as a model of sulphonic drugs, from conducting polymer bilayer films has been reported [53]. Conducting polymer bilayers containing PPy/SSA as inner film and PNMP/polystyrene sulphonic acid (PSS) or PANI/PSS as outer films were prepared by electrochemical methods. The controlled releasing of SSA from inner film was carried out by applying cathodic potential. The amount of SSA released has been investigated by UV spectrophotometry and shown in Figure 4. SSA was reincorporated to inner film by applying anodic potential, then releasing of SSA has been performed at the above conditions.

A drawback to the sequential electropolymerization method is that, after the initial formation of swollen inner film conducting polymer layer, the second monomer penetrated the film and could be partially
Figure 3. Schematic diagram showing the control of ion flux and electrochemically stimulated ATP release from PPy-ATP bilayers.
electropolymerized with in the first layer. This led to an ill-defined and difficult characterization interface between the two-polymer [55]. The utilization and high molecular weight conducting or electroactive polymer film (solution cast over the inner film) could provide a more definitive interface. In order to achieve a definitive interface in the bilayer structure, self-doped polyaniline (SPANI) (a broad class of soluble conducting polymer) is used [56]. It has been synthesized by the reaction between leuco polyaniline with fuming sulphuric acid [57]. 2-Ethyl hexyl phosphate (EHP) as a model of phosphate drugs and dexamethasone sodium phosphate (DMP) released from PPy-EHP and PPy-DMP were investigated at open circuit and compared with electrochemically stimulated release during potential cycling. It was found that the fast EHP and DMP release from the PPy-EHP and PPy-DMP single layer is substantially retarded and that amounts of spontaneously and electrochemically released EHP and DMP can be reduced by constructing bilayers, consisting of a PPy-EHP or PPy-DMP inner layer and a PNMP-PSS or SPANI as the outer films. The presence of outer film over the PPy-EHP or PPy-DMP allowed surface-property modification, as well as the control of the rate of EHP and DMP release, while electrochemically stimulated EHP and DMP release from inner films was not substantially hampered by the outer layer. The quantity of the EHP and DMP was investigated using UV-Vis spectrophotometry and an electrochemical quartz-crys-

Figure 4. The amounts of SSA released from PP/SSA-PNMP/PSS vs time (UV absorbance at 297 nm).

Figure 5. UV Absorbance of changes EHP (at 206 nm) released by electrochemical stimulation in the solution of 0.1 M aqueous, LiClO₄ from (●) PPy-EHP single layer, (▲) ppy-EHP: bilayer, (●) PPy-EHP: SPANI bilayer, (●) PPy-EHP: PNMP/PSS bilayer after redischarge, (─) spontaneous release from PPy-EHP singler layer.

Figure 6. Frequency changes during preparation of PPy/DMP film in 20 mM DMP and 0.1 M pyrrole aqueous solution at + 0.85 V versus time.
the outer film could act as a barrier to ion-and solvent transport between the inner film and electrolyte, yielding a more balanced counter-directional movement of anions \[58,59\].

Physical entrapment or covalent binding are methods that have been previously used to immobilize proteins such as enzymes \[60,61\] or antibodies \[62,63\] and even whole living cells \[58\] into conducting polymers. As discussed in some detail for enzymes \[64\] electrochemical entrapment methods indeed by polymerization of the bioactive moiety are simple and can be used to localize the bioactive component. However, as the biological component is randomly oriented within the polymer matrix it is often inaccessible to the target analyte \[65,66\]. Co-immobilization techniques often involve with the biological component. This provides a more effective usually smaller more highly charged an ionic dopant which in turn results in a polymer with improved electronic and electrochemical switching properties. This approach has been used for incorporation of glucose oxidase \[67,68\] as well as urease \[69\] and sulphite oxidase \[70\]. Mousty et al. \[71\] introduced novel hydrophilic cross-linked polymers using dipyrrolic derivatives as starting materials and showed this to be effective in immobilization of glucose oxidase. The covalent attachment method chosen required the completion of four steps as shown in Figure 7 \[72\].

The physical entrapment of the antibody into a conducting polymer matrix was the simplest method of immobilization used in this study.

The polypyrrole-anti-listeria (PPy-alis) polymer film was prepared galvanostatically according to the following reaction:

Where: Ab⁻ is the counter ion, in this case the listeria antibody.

**MEDICAL APPLICATIONS OF CONDUCTING POLYMERS**

**Preparation of Artificial Muscles**

Conducting polymers such as polypyrrole can be electrochemically oxidized and reduced in a continuous and reversible way (Scheme I). Simultaneously varia-

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**Scheme I.** Scheme of electrochemical switching of polypyrrole film in (ClO₄⁻) solutions.

**Figure 7.** Schematic diagram of the steps involved in the attachment of the antibody fragment to the polypyrrole backbone.
tion in the oxidation depth changes in conductivity, volume, colours, etc. is observed. All these properties are linked to movements of ions and solvents inside and outside the conducting polymer.

These movements are accompanied by conformational changes along the polymeric chains, driving the opening and closure of the polymer entanglement. Artificial muscles based on reversible stress gradient linked to these reverse conformational changes were developed by construction of (non-conducting polymer/conducting polymer) bilayers [73-76]. These bilayers bend reversibly more than 360 degrees when the conducting film is electrochemically oxidized or reduced in an electrolytic solution (Scheme II).

These devices based on intrinsically conducting polymers can be considered as the second generation of artificial muscles. This expression was used for the first time by Katchalsky, and it is related to electrochemical devices based on ionically conducting polymer gels [77,78]. Those devices can be considered a first generation of artificial muscles [79,80]. The second generation of artificial muscles based on intrinsically conducting polymers (both electronically and ionically) is closer to natural muscles. The contraction of a natural muscle is triggered by a nervous pulse which promotes an increase of Ca\(^{2+}\) concentration in the vicinity of muscles fibres from \(10^{-7}\) M to \(10^{-3}\) M. That concentration change is enough to promote conformational changes in the troponin-tropomyosin to allow the muscle contraction. This process consumes chemical energy, which comes from the transformation of ATP to ADP, and converts it into mechanical energy through conformational changes [81,82]. In conducting polymers an electric pulse arriving from the electrochemical equipment promotes a chemical reaction involving a flow of ions from the solvent and new chemical (ionic) interactions between the polymer and those ions (Scheme I).

These interactions promote the opening of the polymer chains with the penetrations of counterions (Scheme III). Conformational changes are transformed through a

**Scheme III.** Conformational changes and subsequent volume changes occurring during electrochemical doping in polypyrrole films.
Artificial Muscles, Biosensors and Drug Delivery Systems...

Entezami A.A. et al.

Iranian Polymer Journal / Volume 15 Number 1 (2006)

A bilayer device to macroscopic circular movements.

Important difference from natural muscles is the reversibility of the electrochemical reactions: artificial muscle works under contraction (reduction) as well as under expansion (oxidation).

In natural muscles electric pulses arrive at 100-200 mV. In conducting polymers important movements are obtained using over potentials between 100 and 500 mV. However, response times are of some seconds in conducting polymers in contrast to milliseconds observed in natural muscles. This is a short response time, taking into account the difference in dimensions between bilayers (10-50 µm thickness) and a fibre myosin. Until now, bilayer and multilayer systems have been manufactured from polypyrrole, polyaniline and thiophene derivatives [76-80]. A technological point of view artificial muscles are suitable for microrobotics, micromachinery, actuator, etc. At the present state the developments are far away from the possible use of natural muscles or from compatibility (physiologically) with natural muscles. The development of muscle actuators is involved with an interdisciplinary effort using expertise in materials science, chemistry, electronics and robotics. In macroscopic actuators, the electrical resistance of a PPy film can produce significant IR drop along its length, which can reduce the actuator performance. This effect is illustrated in Figure 8 [83].

The availability of electroactive polymers (EAP) actuators that can bend or extend/contract allows producing unique robotic devices that emulate human hands. The authors investigated several potential applications including gripper, robotic arm and surface wiper. Ion-exchange membrane platinum (IEMP) composite films are demonstrating a remarkable bending strain under a relatively low voltage drive, using a very low power [84]. However, these ionomers are demonstrating a relatively low force actuation capability. Since IEMPs are made of a relatively strong materials with a large strain capability, they were employed similar to the function of human fingers, in Figure 9, a gripper is shown using IEMP fingers in the form of an end-effector of miniature low mass robotics arms.

The fingers move back and forth to allow opening similar to human hand, embracing the desired object and gripping on it. The hooks at the end of the fingers are function similar to fingernails to secure the gripped object. The structure and properties of the IEMP have been the subject of numerous investigations [84-85]. One of the interesting properties of this material is its ability to absorb large amounts of polar solvents, i.e. water. IEMP Bending actuator has the ideal characteristics of surface wiper. As shown in Figure 10 a simple, small, light weight, low power consuming surface wiper can be constructed using an ionomer film. The ionomer responds to activation signals at the millisecond range and the angle of bending can exceed 180 degrees span and can cover 1.0-1.5 inch diameter of a circular area using about 1.5-2.0 inch long wiper. The wiper element can be set straight in the middle of the desired area and activated to sweep left and right by

Figure 8. Stress generated by unplatinized and platinized PPy film and a schematic diagram showing the effect of IR drop on the actuations of the polymer.
switching the electric field polarity.

**Effect of Doping Anions on the Force of Bilayer Artificial Muscles**

Force variations with respect to the film thickness for the PPy muscles with different anions prepared. It was cleared that the force produced by the muscle made with small inorganic anions (ClO$_4^-$) is very small.

Furthermore, the force produced when medium sized anions sodium tosylate (NaOTS) is involved is larger than that produced with polymeric anions poly-styrene sulfonate (PSS$^-$) and polyvinyl sulphonate (PVS$^-$). However, the force produced by the muscles made with surfactant anions seems to be larger. Maximum force was observed with the muscle fabricated with largest surfactant anions 4-(6-dodecyl) benzene sulphonate [86]. It has been reported that the type and size of the dopant anion used during the polymerization change the morphology of the film [87]. It has also been found that PPy films made with small inorganic anions exchange anions during the redox process [88].

But Yong and Kwake have reported that anion movement does not make significant volume changes in the PPy matrix and that the anions do not drag much sol-

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**Figure 9.** A 4-finger IEMP end-effector lifting 10.3-g rock.

**Figure 10.** A view of a surface wiper with a simulated window, where ionomer is bending back and forth next to a glass plate.
vent with them [89]. Semla and Dadegaard have reported that the cation movement makes large volume changes in PPy film [90]. Furthermore, cations carry huge amount of solvent with them [91]. The solvent movement is also partially responsible for the large volume changes observed with the cation movement. So it is clear that the force obtainable with cation movement should be higher. Anions used during polymerization of PPy films have a greater effect on the force produced by artificial muscles made with such films. Higher forces can be obtained with large surfactant anions. The type of cations in the cycling electrolyte is very important in optimizing the force of PPy/DBS muscles. More force can be obtained from PPy/DBS artificial muscles when they are cycled in electrolytes containing smaller cations. The PPy film can be grown along one side of the poly(tetrafluoroethylene) (PTFE) walls and exhibits morphological anisotropy of the PPy packing density along the thickness direction. A piece bends in a regular direction (the surface in contact with the PTFE wall) and reverts during a redox cycle without the use of any additional processes such as lamination. The actuation property of the anisotropic PPy actuator strongly depends on the size of the cation in the driving electrolyte and the bending behaviour of this actuator at room temperature becomes slower for larger cations. Such behaviour based on electrochemical stimulus not only provides information related to ionic transfer and storage but also suggest that the anisotropic PPy film can be put to practical use as an electrochemical actuator for artificial muscle which directly converts electrical energy to mechanical energy [92].

**Tactile Muscles**

Considering the sensing abilities of the artificial muscles was related to one of the most almost human sensing abilities that researchers are looking for from long time ago: touching and tactile sensitivity [93]. That means an actuator is being able to detect the moment when the device touches an obstacle being able, at the same time to detect the resistance of the obstacle to be shifted. This should be an initial step to develop in the future tactile actuators being able to distinguish between different fabrics: nylon, polyester, silk, cotton, velvet, etc, just by touching its surface [94]. Figure 11 shows the movement of a muscle meeting and shifting an obstacle, and shows the chronopotentiometric responses under flow of a constant current of 5mA when the muscle moves through an angle of 90 degrees.

**Polymer Gels**

Conducting electroactive polymer (CEP)/hydrogel (HG) composites are interesting structures combining the properties of both classes of materials [95,96] with potential application as electrically stimulated controlled release devices or artificial muscles. That is, they are electronic conductors but also are capable of swelling to contain large quantities of water and expelling this water under conditions that encourage dehydration. Previously such structures have been formed by electropolymerization of pyrrole or aniline inside a performed gel or by doping the conducting polymer with an appropriate polyelectrolyte. Application of these materials e.g., in the area of sensors, membranes, biomaterial or actuators [97,98] requires that they would be produced in different shapes and sizes as required. While is achievable to a limited extent with the in-gel polymerization method even this is limited in terms of subsequent processability.

**Liquid Crystal Elastomer (LCE) Materials**

Liquid crystal elastomers were pioneered at Albert Ludwings Universität [99]. These materials can be used to form an EAP actuator that has piezoelectric characteristics as well as electrically activated by inducing Joule heating. LCE is composite materials that consist of monodomain nematic liquid crystal elastomers and conductive polymers that are distributed within their network structure [100]. The actuation mechanism of these materials involves phase transition between nematic and isotropic phases over a period of less than a second. The reverse process is slower, taking about 10 s, and it requires cooling to cause expansion of the elastomer to its original length. The mechanical properties of LCE materials can be controlled and optimized by effective selection of the liquid crystalline phase, density of cross-linking, flexibility of the polymer backbone, coupling between the backbone and liquid crystal group and the external stimuli [96], where a rapid contraction appears when the phase transition occurs and the thermo-mechanical behaviour is by steric.

**Need for EAP Technology Infrastructure**

As polymers, EAP materials can be easily formed in various shapes, their properties can be engineered and they can potentially be integrated with sensors to produce smart actuators. As mentioned earlier, their most attractive feature is their ability to emulate the operation of biological muscles.
with high fracture toughness, large actuation strain and inherent vibration damping.

Unfortunately, the EAP materials that have been developed so far still exhibit low force, are far below their efficiency limits and not robust, and there is no standard commercial material available for consideration in practical applications. The documented EAP materials that induce large strains are driven by many different phenomena [97,100-101]. Each of these materials requires adequate attention to their unique properties and constraints in order to be able to take these materials from the development phase to use as effective actuators; there is a need to establish an adequate EAP infrastructure. The requirements of the EAP infrastructure involves developing adequate understanding of EAP materials behaviour, as well as processing and characterization techniques. Enhancement of the actuation force requires understanding the basic principles using computational chemistry models, comprehensive materials science, electro-mechanics analytical tools and improved materials processing techniques. Efforts are needed to gain a better understanding of the parameters that control the EAP electro-actuations force and deformation. The processes of synthesizing-fabricating, electroding, shaping and handling will need to be refined to maximize the EAP materials actuation capability and robustness. Methods of reliably characterizing the response of these materials are required to establish data-base with documented materials properties in order to support design engineers considering use of these materials and towards making EAP as actuators of choice. Various configurations of EAP actuators and sensors will need to be studied.

Figure 11. Movement of 90° of the free end of an artificial muscle under flow of 5 mA at 25°C in 1M LiClO₄ aqueous solution, touching an obstacle of 3000 mg after 10 s of movement starts and sliding it later. The dimension of the device was: 2 cm × 1 cm and each polypyrrole film weights 6 mg, being 13 µm thick.
and modelled to produce an arsenal of effective smart EAP driven system. The development of the infrastructure is a multi-disciplinary task and it requires international collaborations.

CONCLUSION

The results summarized in this review clearly establish the fact that the initial expectation of a large number of applications for conducting polymers such as polyaniline and polypyrrole has become a reality. Now, conducting polymers base biomedical devices which likely find specific therapeutic applications as bioanalytical, microelectrods, for in-vivo drug delivery and detection of toxic gas and vapour. The results of conductivity measurement of conducting polymers exposed to the toxic gases and vapours show that conductivity increase with increasing the samples concentration. Therefore, PANi is good candidate for sensing toxic gases and vapours.

One important point to be considered in a drug delivery system is its biocompatibility. Conducting polymers based on PPy have low cytotoxicity and are stable to a broad selection of redox and acid/base conditions. The field of conducting polymers have now attained a level of maturity consistent with a new set of opportunities to develop a wide range of applications based on conducting polyaniline as material for industrial products. Conducting polymers can be electrochemically oxidized and reduced in a continuous and reversible way. Simultaneously variation in the oxidation some abrupt changes in conductivity, volume, colours, etc. are observed. All these properties are linked to movements of ions, which are accompanied by conformational changes along the polymeric chains, driving the opening and closure of the polymer entanglements. Artificial muscles based on reversible stress gradient linked to these reverse conformational changes were developed by construction of (non-conducting polymer/conducting polymer) bilayers

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