# **Chapter 2: Conducting Polymer Actuators**

Conducting polymer actuators make use of bulk material deformations that result from changes in oxidation state to perform work. Oxidation state of the polymer is altered chemically or electrochemically. In the electrochemical case the polymer acts as one or both electrodes in the cell, and is charged and discharged as a battery or capacitor. A flow of ions to and from the polymer serves to balance charge as electrons are added and removed from the backbone. The accompanying dilatation may be due to ion and solvent fluxes, electrostatic interactions between chains, or conformational changes.

Limitations to the application of these actuators have included relatively slow response and low power (<  $0.5 \text{ W}\cdot\text{kg}^{-1}$ ), low number of cycles (< 10 000), low electrical to mechanical efficiencies (< 1%), and difficulties in encapsulating the polymer for use in dry environments. Developments during the course of this work, and described in detail in later chapters, overcome some of these limitations, and demonstrate how others will be surmounted.

This chapter includes some introductory information on conducting polymers and their applications. This is followed by a chronological review of developments in conducting polymer actuator technology. The possible mechanisms of actuation in polyacetylene, polyaniline and polypyrrole are discussed. Finally, a brief review is provided of achievements in conducting polymer actuator figures of merit, including strain, load, strain rate, power to mass ratio, efficiency and lifetime.

# 2.1 Conducting Polymers: Background

Conducting polymers are also known as conjugated polymers due to their conjugated backbone structure, represented by alternating single and double bonds. The structures of some of the most common conducting polymers are shown in Figure 1. Of these, polyaniline and polypyrrole have been studied as actuators.



Figure 1: Schematic showing bond structure of four conducting polymers.

The conjugation allows the delocalization of electrons along the backbone and hence some degree of conductivity. In the state shown in Figure 1 these molecules are semiconductors, as delocalization is incomplete (Roth 1995). The polymer is doped by changing its oxidation state, which, when performed electrochemically, leads to the migration of ions into the bulk polymer, balancing charge. These ions are known as dopants, in analogy to traditional semiconductors. In the doped form, conductivities equaling that of copper have been reported (Kohlman and Epstein 1998). Doping is typically reversible, and hence properties that change with doping level, such as conductivity and volume are also reversible.

The range of devices constructed using conjugated polymers (listed in Figure 2) spans the



Figure 2: Devices made using conducting polymers.

range of sub-systems needed for autonomous micro-mechanical devices. Polymers can be used in energy storage, actuators, sensors, computation, and communications. By changing the doping level, which in turn changes the oxidation state of the polymer, conductivity can be switched by up to 13 orders of magnitude (Baughman, Shacklette and Elsenbaumer 1991b). The switching of conductivity is employed in making kilohertz frequency transistors (Jones, Chao and Wrighton 1987). High efficiency photosensors and photoemitters are constructed from conducting polymer blends. High energy density batteries (1 MJ/kg) and supercapacitors (0.4 MJ·kg<sup>-1</sup>) make use of the dense charge storage properties of conducting polymers. Finally, several of these materials are biocompatible. Polypyrrole, for example, is used to guide nerve regeneration (Schmidt, Shastri, Vacanti and Langer AUG 19 1997).

# 2.2 History of Conducting Polymer Actuators

Baughman, Shacklette and Elsenbaumer were the first to propose conducting polymerbased actuators (Baughman and others 1991b). A few more than thirty articles from ten research groups have been written on the subject of conducting polymer actuators (Baughman 1996; Baughman and others 1991b; Che, Fisher and Martin 1999; Chiarelli and Genuini 1987; Della Santa, De Rossi and Mazzoldi 1997; Della Santa, DeRossi and Mazzoldi 1997; Della Santa, Mazzoldi, Tonci and De Rossi 1997; Gandhi, Murray, Spinks and Wallace 1995; Herod and Schlenoff 1993b; Hunter and Lafontaine 1992a; Jager, Smela and Inganas 1999; Kaneto, Kaneko, Min and MacDiarmid 1995b; Kaneto, Kaneko and Takashima 1995b; Lee, Hong, Trevino and Northrup 1994b; Lewis, Spinks, Wallace, De Rossi and Pachetti 1997; Lopez, Mendes Viegas, Bidan and Vieil 1994b; Madden, Brenan and Dubow 1997; Madden, Lafontaine and Hunter 1995b; Madden, Cush, Kanigan, Brenan and Hunter 1999b; Mazzoldi, Degl'Innocenti, Michelucci and De Rossi 1998b; Mazzoldi, Della Santa and De Rossi 1999b; Otero, Angulo, Rodriguez and Santamaria 1992b; Otero, Rodriguez, Angulo and Santamaria 1993b; Otero and Sansinena 1998; Otero 1997; Pei and Inganas 1993b; Pei and Inganas 1992b; Pei and

Inganas 1993b; Pei and Inganas 1993f; Sansinena, Olazabal, Otero, Fonseca and De Paoli 1997b; Smela and Gadegaard 1999; Smela, Inganas and Lundstrom 1993b; Smela, Inganas, Pei and Lundstrom 1993b; Takashima, Fukui, Kaneko and Kaneto 1995b), including four reviews (Baughman 1996; Madden and others 1997; Mazzoldi and others 1999b; Otero 1997) and four issued patents (Hunter, Lafontaine and Madden 2000; Kaneto, Keiichi , Min, Yonggang, MacDiarmid and Alan G. 1996; Otero, Angulo, Rodriguez and Santamaria 1992a; Otero, Rodriguez and Santamaria 1992). Research began with the demonstration of bilayer actuators, qualitatively demonstrating the deformation, but providing little quantitative data about performance. The introduction of linear actuators has allowed tensile strength, stress, strain, power to mass, efficiency and other properties to be determined. A key technological development is the use of encapsulation techniques, enabling actuators to be used outside a liquid environment. No products have yet been reported that employ conducting polymer-based actuators.

Volume changes associated with the change in oxidation state of conducting polymers have long been observed, mostly as a source of annoyance to makers of electrochromic devices, transistors and batteries. Baughman of Allied Signal was the first to fully express the tremendous potential of these volume changes when employed in actuators. In his seminal paper entitled "Micro electromechanical actuators based on conducting polymers" (Baughman, Shacklette and Elsenbaumer 1991a) he explores the underlying mechanisms of electrical and chemical to mechanical transduction and proposes upper bounds on actuator performance. These predictions include the generation of 10 % strains, 460 MPa active stresses, and bandwidths of 10 kHz, which would result in the highest power to mass ratio of any actuator technology (Hunter and Lafontaine 1992b).

Baughman's proposal led to a series of papers in the early 1990s demonstrating polypyrrole beam-bending actuators, in which a differential degree of expansion between two or more laminated layers leads to beam bending, similar to the response of a bimetallic strip upon change in temperature. In 1992 and 1993 Qibing Pei and Olle Inganäs reported bilayers responding to both chemical and electrochemical stimuli, explored actuation mechanisms, and proposed the use of these beams as chemical and electrochemical detectors (Pei and Inganas 1993a; Pei and Inganas 1992a; Pei and Inganas 1992c; Pei and Inganas 1993a; Pei and Inganas 1993c; Pei and Inganas 1993e). Elizabeth Smela joined Pei and Inganäs at the Linkoping Institute in Sweden, demonstrating micro-machined bilayers that responded in 5 seconds, rather than taking the minutes observed in larger actuators (Smela, Inganas and Lundstrom 1993a; Smela, Inganas and Lundstrom 1995; Smela, Inganas, Pei and Lundstrom 1993a). Lee and colleagues at Lawrence Livermore National Labs also employed silicon micromachining techniques, demonstrating 1.2 Hz bandwidth (Lee, Hong, Trevino and Northrup 1994a). Otero et al and Lopez et al also demonstrated early polypyrrole bilayers (Lopez, Mendes Viegas, Bidan and Vieil 1994a; Otero, Rodriguez, Angulo and Santamaria 1993a).

In 1993 Herod and Schlenoff reported the first polyaniline actuator, and also the first linear actuator, consisting of a polyaniline film clamped at each end, which was both chemically and electrochemically activated (Herod and Schlenoff 1993a). Kaneto's group at the Kyushu Institute of Technology subsequently reported a number of bilayer and linear polyaniline actuators (Kaneko, Fukui, Takashima and Kaneto 1997a; Kaneto and others 1996; Kaneto, Kaneko, Min and MacDiarmid 1995a; Kaneto, Kaneko and Takashima, Fukui, Kaneko and Kaneto 1995a; Takashima, Uesugi,

Fukui, Kaneko and Kaneto FEB 15 1997). Danilo De Rossi, Alberto Mazzoldi and their colleagues at the University of Pisa recently pioneered the use of polyaniline fibers (Mazzoldi, Degl'Innocenti, Michelucci and De Rossi 1998a), being the first to report using fibers as opposed to films.

Conducting polymer actuators are generally operated in a liquid environment. Pei et. al. described one of the first actuators out of solution by demonstrating the contraction of a bilayer in response to ammonia gas (Pei and Inganas 1993a). Madden and colleagues (Madden, Lafontaine and Hunter 1995a) and Kaneto and colleagues (Kaneto and others 1995a) reported the first polypyrrole and polyaniline bilayers, respectively, operating outside liquid environments. Other bilayers operating in air were reported by Sansinena et al (Sansinena, Olazabal, Otero, Fonseca and De Paoli 1997a). Linear actuators employing solid or gel electrolytes were reported by Mazzoldi et al (Mazzoldi and others 1998a) in polyaniline and Madden et al in polypyrrole (Madden, Cush, Kanigan, Brenan and Hunter 1999a), the latter being described in Chapter 6.

Recent work has shown that power to mass can equal that of mammalian skeletal muscle (Madden, Cush, Kanigan and Hunter 2000) as is described in Chapter 7. This thesis explores the mechanisms limiting strain rate, power to mass, and efficiency.

## **2.3** Polyacetylene, Polyaniline and Polypyrrole Actuators

In this section, properties of conducting polymers are reviewed polymer by polymer. All but one of the conducting polymer actuators reported to date are constructed from one of these three polymers. The mechanisms appear to be somewhat different, depending on the polymer employed.

A key question in analyzing the literature on conducting polymers is: How do conducting polymer actuators convert electrical energy to mechanical work? Baughman proposed two primary mechanisms for producing deformations resulting from polymer oxidation or reduction: (1) conformational changes in the polymer (2) flux of ions and molecules to and from the material (Baughman and others 1991a). Kaneto suggested a third mechanism: (3) change in the degree of electrostatic repulsion between chains (Kaneko and others 1997a). The extent to which these mechanisms are important depends on several factors, including which polymer is employed, how it is grown, the nature of the solvent, and the doping ions used, as is now discussed. Also described are the maximum strains achieved, as reported in the literature and in Chapter 5. As is discussed, the maximum reported strains are typically in the range of 1 - 2%, and reach 11 % in chemically doped polyaniline.

### 2.3.1 Polyacetylene

Polyacetylene actuators are the best understood because their highly ordered structure is easily investigated by x-ray diffraction. They are also the least practical, because polyacetylene is highly unstable. Nevertheless, the observed mechanisms of strain provide some insight into what may be occurring in polyaniline and polypyrrole. In polyacetylene both changes in chain length and ion insertion between chains are important in explaining observed dimensional changes. X-ray diffraction measurements are employed to show that the chain length of polyacetylene increases by between 1.0 to 1.6% upon doping with lithium, sodium or potassium (Baughman and others 1991a). Doping with iodine leads to a contraction of 0.4%. X-ray diffraction studies are also employed to study the insertion of ions between chains, demonstrating that the addition of new columns of alkali atoms between parallel polyacetylene backbones leads to a volume increase of 6.6 % (Baughman and others 1991a). The insertion of alkali ions leads to expansion perpendicular to the chain direction, and thus strains are anisotropic in stretch aligned samples.

In polyacetylene, polypyrrole and polyaniline, the degree of expansion is proportional to the amount of charge transferred over a certain range of oxidation states. The charge transferred is also proportional to the number of bonds on the backbone whose state has been altered. The number of altered bonds and the number of ions transferred might reasonably be expected to result in a proportional change in volume. This proportionality,  $\alpha$ , is defined in terms of strain,  $\varepsilon$ , per unit charge density,  $\rho$ :

$$\alpha_{i} = \frac{\partial \varepsilon_{i}}{\partial \rho} \Big|_{\frac{\partial \sigma}{\partial t} = 0} , \qquad 1$$

under isotonic conditions (constant stress,  $\sigma$ ). For sodium doped polyacetylene  $\alpha = 25 \times 10^{-12} \text{ m}^3 \cdot \text{C}^{-1}$  along the chain direction. This applies for doping levels of between 0.08 and 0.15 sodium ions per monomer. Polyacetylene that has not been stretch aligned produces volume changes of up to 6.6 % when doped with sodium or potassium, generating an isotropic  $\alpha = 40 \times 10^{-12} \text{ m}^3 \cdot \text{C}^{-1}$  between doping levels of 0.0625 and 0.125.

X-ray diffraction measurements indicate that in this range the number of alkali metal columns per polymer chain changes from two to four, while beyond this range the ions simply fill the columns and little expansion is observed (Baughman and others 1991a). The extent of expansion perpendicular to the chain orientation appears to be related to the size of the doping ion. The effect of stress level on  $\alpha$  is unclear.

While strains and volumetric changes in polyacetylene are relatively high, especially when compared with piezo-electrics, the material rapidly degrades, and therefore is not suitable for use in actuators.

## 2.3.2 Polyaniline

Polyaniline exists in a variety of states, as shown in Figure 3. Switching between these states is achieved either by changing the oxidation state chemically or electrochemically, or by changing pH and thereby protonating or deprotonating the polymer backbone (Chiang and MacDiarmid 1986; Maron, Winokur and Mattes 1995). Note that many intermediate states or doping levels exist between each of the states depicted in Figure 3.

A number of polyaniline actuators have been reported (De Rossi, Della Santa and Mazzoldi 1999; Herod and Schlenoff 1993a; Kaneto and others 1995a; Kaneto and others 1995a; Mazzoldi and others 1998a; Mazzoldi, Della Santa and De Rossi 1999a; Takashima and others 1995a), all of which start with material in the emeraldine salt form, identifiable by its emerald color and relatively high conductivity (typically ~100 S·m<sup>-1</sup> unstretched, ~10 000 S·m<sup>-1</sup> stretched).

Herod and Schlenoff (Herod and Schlenoff 1993a) were the first to demonstrate polyaniline actuators. They placed emeraldine salt films in 1 M aqueous NaOH solution,



switching the polymer to the emeraldine base form. The deprotonation was reversed using 1 M aqueous HCl, HF, or HClO<sub>4</sub>. Electrochemical activation in 0.5 M aqueous  $H_2SO_4$  was also employed, with polyaniline films first reduced, towards the leucoemeraldine form, and then oxidized. Both stretched (3×) and unstretched films were tested under isotonic conditions (~0.1 MPa).

#### 2.3.2.1 Chemical Activation

Conversion to the emeraldine base form by immersion in 1 M NaOH leads to a film contraction, which may then be reversed by immersion in 1 M HCl, HF, or HClO<sub>4</sub>.

Strains are 1.7 % along the stretched direction, 11.2 % perpendicular to the stretch direction, and 7.2 % in unstretched films, independent of the acid employed. Note that the percentage increases in volume in the stretched and unstretched cases are roughly equal (21.6 % unstretched, 24.1 % stretched). Herod and Schlenoff attribute the strain parallel to the orientation direction to imperfect alignment of chains, citing x-ray diffraction data. They conclude that strain occurs normal to the chain axis. The nature of the acid affected strain rate but not the magnitude of strain. The fact that the magnitude of strain is independent of the acid employed suggests that the size of anion (A<sup>-</sup> in Figure 3) is not important for the range of anion sizes employed (Cl<sup>-</sup> 0.362 nm diameter, F<sup>-</sup> 0.272 nm (Kittel 1966), ClO<sub>4</sub><sup>-</sup> 0.58 nm estimated from specific density of HClO<sub>4</sub><sup>&</sup>). The expected volume change if expansion is due to ionic volume alone is roughly 6.5 % for the transition between emeraldine base and emeraldine salt in HCl<sup>#</sup>, which, in a perfectly stretch aligned film, results in a strain perpendicular to the orientation direction of 3.3 %.

There are several possible reasons why the expansion is independent of anion size: (1) solvent flux occurs, leading to additional swelling, (2) electrostatic repulsion is responsible for expansion, or (3) the orientation of the backbone changes. Polyaniline x-

<sup>&</sup>lt;sup>&</sup> The numbers for Cl<sup>-</sup> and F<sup>-</sup> are derived from ionic crystals having coordination numbers of 6. When in tetrahedral covalent bonds the diameters are 0.198 for Cl and 0.124 for F. The volume consumed by a bonded ion or molecule is primarily determined by the balance between attractive forces (Van der Waal's, coulombic) and the repulsive exchange interaction (Pauli exclusion). Thus the effective "diameter" is context dependent. For example, effective diameters in aqueous solution are 0.6 nm for Cl<sup>-</sup>, 0.7 nm for ClO<sub>4</sub><sup>-</sup>, 0.8 nm for SO<sub>4</sub><sup>2-</sup> (Dean 1999).

<sup>&</sup>lt;sup>#</sup> Herod and Schlenoff provide mass and dimensions of the film in the emeraldine salt form. Assuming no solvent is present (giving the upper bound), the density divided by the monomer  $+ \frac{1}{2}$  dopant per monomer molecular weight, all times Avagadro's number, gives the number of moles per unit volume. This is then multiplied by the volume of one ion and the ions per monomer (1/2) to give the volume change due purely to ion insertion.

ray diffraction studies and associated structural models reported to date are not able to discriminate between these possibilities (Maron and others 1995; Winokur 1998).

#### **2.3.2.2** Electrochemical Activation

Herod and Schlenoff place their emeraldine salt films in 1.0 M H<sub>2</sub>SO<sub>4</sub> and electrochemically drive polyaniline films towards the leuco-emeraldine state under galvanostatic conditions (constant current) (Herod and Schlenoff 1993b). They measure strains of 0.9 % parallel and 4.0 % perpendicular to the orientation direction. Strains of 1.35 % strain are observed in an unoriented film. All measurements are performed under isotonic conditions (0.1 MPa). In these experiments the charge transferred per monomer was -0.13 in all cases. The strain to charge density ratios<sup>--</sup> are  $\alpha_{\perp} = 3.010^{-10} \text{ m}^3 \cdot \text{C}^{-1}$ ,  $\alpha_{\parallel} = 0.68 \times 10^{-10} \text{ m}^3 \cdot \text{C}^{-1}$  and  $\alpha_{unstretched} = 1.0 \times 10^{-10} \text{ m}^3 \cdot \text{C}^{-1}$ . Once again the strain perpendicular to the direction of chain orientation is largest. In the unstretched case, the change in volume per electron transferred is  $4.8 \times 10^{-29} \text{ C}^{-1} \cdot \text{m}^3$ , corresponding to the addition of a 0.46 nm diameter sphere per charge. Figure 3 suggests that in switching between the emeraldine and leuco-emeraldine states, protons are transferred. However, the observed volume change is much larger than can be accounted for simply by the transfer of a proton.

Kaneto and his colleagues have continued the work of Herod and Schlenoff by examining the effects of electrochemically oxidizing similarly polymerized,  $3-4 \times$  stretched polyaniline from the emeraldine salt form towards the leuco-emeraldine state using 1 M

 $<sup>\</sup>sim$  Herod and Schlenoff report the total charge transferred, the strain, and the film dimensions. The strain to charge ratio is calculated by dividing strain by the charge transferred and multiplying by volume.

aqueous HCl, H<sub>2</sub>SO<sub>4</sub>, HBF<sub>4</sub> and HClO<sub>4</sub> (Kaneto and others 1995a). The emeraldine salt is reduced by between 0.19 and 0.24 electrons per monomer, resulting in contractions of up to 3.4 %. The strain to charge ratios along the stretched orientation are  $3.0 \times 10^{-10}$  C<sup>-1</sup>·m<sup>3</sup> (HCl),  $2.6 \times 10^{-10}$  C<sup>-1</sup>·m<sup>3</sup> (H<sub>2</sub>SO<sub>4</sub>),  $4.4 \times 10^{-10}$  C<sup>-1</sup>·m<sup>3</sup> (HBF<sub>4</sub>), and  $4.4 \times 10^{-10}$  C<sup>-1</sup>·m<sup>3</sup> (HClO<sub>4</sub>). No clear correlation with ion size is observed, although the authors claim otherwise (Kaneko and others 1997a).

De Rossi and colleagues employ elongated polyaniline fiber actuators (Mazzoldi and others 1998a; Mazzoldi and others 1999a) in 1 M aqueous HCl and HClO<sub>4</sub>, achieving isotonic (near zero load) strains of up to 0.6 % (HClO<sub>4</sub>) and 1.25 % (HCl). The strain to charge density ratios are 0.8 and  $1.0 \times 10^{-10}$  C<sup>-1</sup>·m<sup>3</sup>, for HClO<sub>4</sub> and HCl, respectively. Once again, the material contracts as it is being reduced.

In summary, the largest strains in polyaniline (11 %) occur perpendicular to the direction of chain orientation. Nevertheless, strains of up to 3.4 % are observed parallel to orientation, perhaps due to the still imperfect degree of alignment. Strain to charge ratios range from 0.68 to  $4.4 \times 10^{-10} \text{ C}^{-1} \cdot \text{m}^3$ . The magnitude of strain appears to be independent of ion size for the relatively small dopant ions employed (F<sup>-</sup>, Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>). All results to date involve either chemically transforming the emeraldine salt form into the emeraldine base state, or electrochemically switching between the emeraldine salt and leuco-emeraldine salt states. The emeraldine salt contracts as it is deprotonated and as it is reduced. Dimensional changes are independent of anion size.

## 2.3.3 Polypyrrole Synthesis, Conductivity and Actuation

The properties of polypyrrole actuators have been reported by a number of authors. Before reviewing their findings, synthesis and conductivity are discussed. Conductivity is very sensitive to polymer structure. The structural information found from a combination of x-ray diffraction measurements and the investigations of electronic state may eventually help determine the mechanisms responsible for charge induced actuation in polypyrrole. The structure is very sensitive to synthesis conditions.

#### 2.3.3.1 Synthesis

All of the polypyrrole actuators reported in the literature are electrochemically synthesized. Electrochemical synthesis leads to the highest conductivity and the best mechanical properties. As synthesized, polypyrrole has a backbone configuration shown at the bottom of Figure 4, where roughly  $1/3^{rd}$  of the monomers are charged (Baker and Reynolds 1988; Sato, Yamaura and Hagiwara 1991; Yamaura, Hagiwara and Iwata 1988; Yamaura, Sato and Hagiwara 1990; Yamaura, Sato and Iwata 1992). The backbone charge is balanced by the presence of anions. In this state, polypyrrole is shiny black in appearance, and has typical conductivities of up to ~ $10^4$  S·m<sup>-1</sup>, reaching  $10^5$  S·m<sup>-1</sup> when stretch aligned (Yamaura and others 1988). Reduction leads to a semiconducting state, as shown in Figure 5.

The steps involved in electrochemical synthesis have been proposed by Baker and Reynolds (Baker and Reynolds 1988), and are shown in Figure 4.

In bulk, the monomer costs ~US\$1.00 per kilogram. The estimated minimum cost of electrodeposited polypyrrole is ~\$1.50 per kilogram.



Figure 4: Mechanisms of Polypyrrole polymerization.

#### 2.3.3.2 Conductivity

Before discussing the mechanisms of strain, it is worth discussing the mechanisms of conduction in conducting polymers, and polypyrrole in particular. Electronic properties, including the temperature dependence of conductivity, the dielectric response, reflectivity and absorption, are all sensitive to polymer structure. As a result they provide clues that may ultimately help in understanding the molecular origins of the coupling between strain and oxidation state.

Changes in synthesis conditions, such as the dopant employed and the temperature at which synthesis takes place, result in major changes in the temperature dependence of conductivity in conducting polymers (Kohlman and Epstein 1998). For example, polypyrrole (PPy) doped with  $PF_6^-$  and grown at  $-30^{\circ}C$  shows a drop in conductivity by a factor of two between 300°C and 1.5 K, whereas when doped with methylsulfonate (MS), a slightly larger anion, the ratio is ~30, and when doped with a large polyanion (PA), the decrease is over nine orders of magnitude. The differences appear to be structure related, with the PPy(PF\_6^-) having a crystallinity of ~50%, and the PPy(MS) ~25 %. The PPy(PA) has a very different, and highly amorphous structure. Given the great sensitivity to structure, the form of the conductivity provides insight into the relative order of the material. Interestingly, while the nature of the dopant used during synthesis has an enormous effect on conductivity, exchanging dopants after synthesis has little effect (Yamaura and others 1990).

A number of models have been proposed to describe macroscopic conductivity in conducting polymers. The choice of model, and the form of the temperature dependence of conductivity, reflect assumptions about the nature of disorder within the material,

35

because it is the disorder that limits the propagation of charge carriers by providing energy barriers, inducing scattering, or preventing charge transfer between chains. Disorder may be homogeneous and isotropic, or inhomogeneous, with relatively crystalline domains being surrounded by incoherent regions.

Measurements and modeling of highly conductive  $PPy(PF_6)$  indicate that an inhomogeneous model applies, with crystalline domains that are ~ 2 nm comprising approximately 50 % of the material (Kohlman and Epstein 1998). The ordered regions appear to be numerous enough that charge is able to percolate through the entire polymer. For  $PPy(PF_6)$ , the resulting conductivity is described as metallic in the sense that the resistivity is finite at temperatures close to absolute zero, the change in resistivity with



temperature is small, and in fact increases with temperature below 15 K, and the magnetic susceptibility is temperature independent, among other indications. However, the application of magnetic fields and pressure can significantly affect conductivity, as



can slight changes in structure, suggesting that  $Ppy(PF_6)$  is very close to being in an insulating state, wherein the conductivity drops to zero as temperature tends to zero.



## 2.3.3.3 Actuation

Pei and Inganas performed a series of studies using a bilayer actuator in 0.1 M aqueous solutions of a number of salts in which he was able to relate strain to the direction of ion flux (Pei and Inganas 1992d; Pei and Inganas 1993d). Figure 6 and 7 depict the structures of many of the ions they and others have employed in studies of polypyrrole actuators. In particular, Pei and Inganas showed that if the polymer is doped with bulky anions such as Dodecylbenzenesulfonate (DBS<sup>-</sup>) and reduced in a solution containing small cations such as Na<sup>+</sup>, the polymer expands reversibly upon reduction, as depicted in Figure 8. Alternatively, if small anions, e.g.  $ClO_4$ , and relatively large cations, e.g.  $(C_2H_5)_4N^+$ , are employed the polymer contracts upon reduction, as shown in Figure 5. If the doping anion is larger than the cation but still mobile, e.g. Li<sup>+</sup> and pmethylbenzenesulfonate, the polymer initially swells upon reduction, followed by a contraction of larger magnitude as depicted in Figure 9. The extent of swelling is initially proportional to charge. However, during the contraction period, the current is nearly This observation suggests that Li<sup>+</sup> and p-methylbenzenesulfonate are zero. simultaneously exiting the polymer (salt draining).

Interestingly, using  $ClO_4^-$  doped polypyrrole in 0.1 M LiClO<sub>4</sub> it is found that the polymer contracts upon reduction, suggesting that the lithium ion is less mobile than the perchlorate within the polymer, perhaps due to an entrained solvation sphere. The opposite response is observed when the same experiment is performed in acetonitrile.

When the polymer is in its undoped state, in the presence of large anions and small cations in the electrolyte (e.g. NaDBS), the polymer becomes electrically inactive. The anions are unable to penetrate into the polymer, preventing doping.

In summary, Pei and Inganas observe that polypyrrole contracts if ions are expelled, and expands if they are incorporated. The relative magnitudes of anion versus cation flux during redox cycling are a function of the relative sizes (including solvation spheres) and therefore mobilities of the ions. It is not clear whether strain is directly proportional to ion size. The interpretation of ion flux is consistent with quartz crystal microbalance studies, in which polymer mass is observed as a function of oxidation state in a variety of electrolytes (Baker and Reynolds 1988).

![](_page_21_Figure_1.jpeg)

Pei's work, subsequently confirmed by others as shown in Table 1, indicates that ions play a key role in polypyrrole dimensional changes. The net transport of ions determines whether polypyrrole contracts or expands as it changes oxidation state. These results lead to a key question: does size matter? Will the transport of larger ions lead to larger strains, albeit at the expense of rate?

![](_page_22_Figure_0.jpeg)

X-ray diffraction studies of oxidized polypyrrole suggest that in the crystalline regions chains are aligned such that neighboring rings face each other, with dopants sitting above and below (Nogami, Pouget and Ishiguro 1994; Pouget, Oblakowski, Nogami, Albouy, Laridjani, Oh, Min, MacDiarmid, Tsukamoto, Ishiguro and Epstein 1994). Yamaura, and colleagues, and Wernet et al employ x-ray diffraction to demonstrate that the spacing between polypyrrole chains is proportional to dopant ion size as grown, where the dopant size is taken to be the longest axis (Wernet, Monkenbusch and Wegner 1984; Yamaura and others 1988). It appears that the long hydrophobic tails of ions such as DBS form separate, lipid bilayer like phases between conducting planes.

Actuator	Dopant	Solution	Potential	Reduce	Strain/	Strain
			(V)		Charge	
					$(m^3 \cdot C^{-1})$	
					×10 <sup>-12</sup>	
Bilayers						
Pei 1992c	ClO <sub>4</sub>	LiClO <sub>4</sub> (aq)	-0.85 V to	С		
Ppy(TsO)	$DS^{-}$	NaDS	0.25 V vs.	None		
	ClO <sub>4</sub>	$(C_2H_5)_4NClO_4$	Ag/AgCl	С		
	DBS	NaDBS		E		
	MBS	LiClO <sub>4</sub>		E/C		
		NaDS		E/C		
		$(C_2H_5)_4NClO_4$		С		
Otero	ClO <sub>4</sub>	0.1-3 M LiClO <sub>4</sub>	-2 V to 2 V	С		
1993a						
Otero	ClO <sub>4</sub>	0.1M LiClO <sub>4</sub> (aq)	-0.7 to	С		
1993b		in PC	+0.2V vs.	None		
		in AC	SCE	None		
Lopez	ClO <sub>4</sub>	0.5 M LiClO <sub>4</sub> (aq)	-1.2 ti +0.2	С		
1994			VS.			
			Ag/AgCl			
Linear Actuators						
Madden	DBS	M NaDBS (aq)		E	170	0.01
1997	$PF_6$	$0.05 \text{ M} (C_2H_5)_4\text{NPF}_6$		C	530	0.01
		(aq)	0.5 to $-1.0$	0		
	$PF_6$	$0.05 \text{ M} (C_2H_5)_4\text{NPF}_6$	VS.	C	130	0.06
		(PC)	Ag/AgClO <sub>4</sub>			
Della	BS	0.01 M NaBS (AN)	+1 V to -	E	30	0.01
Santa			1V vs. SCE			
1997						
Gandhi	pMS	1 M NaPVS (aq)	+0.3 V to -	E		
1995		$1 \text{ M NaNO}_3(aq)$	0.8 V vs.	E		
		$1 \text{ M Mg(NO_3)}_2$ (aq)	Ag/AgCl	C		
	PVS <sup>-</sup>	1 M NaPVS (aq)		E		
		1 M NaNO <sub>3</sub> (aq)		E		
		$1 M Mg(NO_3)_2$ (aq)		E		

 Table 1: Summary of polypyrrole actuator properties.

DBS = Dodecylbenzene sulfonate, PE = Polyethylene, PPy = Polypyrrole, MS = methanesulfonate, DS = dodecyl sulfonate, BS=benzenesulfonate, pMS=paramethylbenzene sulfonate, PVS=polyvinylsulfate, PC=propylene carbonate, AN=acetonitrile – refer to Figure 6 for structure of these ions and molecules.

## **2.4** Polymer Actuator Performance

Thus far the discussion of actuators has focused on mechanisms. How do conducting polymers perform in basic figures of merit such as the strain that can be produced, the load they can born, the strain rate achievable, the power to mass that can be generated, the efficiency with which electrical energy is converted to mechanical work, and the number of cycles that can be performed?

## 2.4.1 Strain

The maximum strain achieved is 14 % by Herod and Schlenoff, induced in polyaniline perpendicular to the stretch direction by changing the degree of protonation (Herod and Schlenoff 1993b). Otherwise, strains reported in polyaniline and polypyrrole are in the range of 1-2% (Baughman and others 1991b; Kaneko, Fukui, Takashima and Kaneto 1997b; Madden and others 1997; Madden and others 1999b; Madden and others 2000; Mazzoldi and others 1999b). Most studies have been done on bilayer actuators, where determining strain can be problematic, and hence there reports of strain and other figures of merit are relatively few.

#### 2.4.2 Load

The highest reported load applied to polypyrrole actuators is 5 MPa (Madden and others 1997). Polyaniline fibers are actuated at stresses as high as 20 MPa (Mazzoldi and others 1998b). These fibers however produce strains of only 0.2 %. This is probably due to their high degree of stretch alignment along the fiber direction, which Herod and Schlenoff found to reduce stain (Herod and Schlenoff 1993b).

#### 2.4.3 Strain Rate

The highest strain rate achieved is 3  $\% \cdot s^{-1}$  is achieved in polypyrrole films, using a shaped voltage technique described in Chapter 7 (Madden and others 2000). The strain rate is 30× faster than any reported in the literature.

## 2.4.4 Power to Mass

The highest power to mass ratio is 39 W·kg<sup>-1</sup>, again achieved in polypyrrole using a shaped voltage technique (Madden and others 2000). As discussed in Chapters 8-10, much higher strain rates and power to mass ratios should be attained by using thinner films and fibers, in which the time constants associated with mass transport are greatly reduced.

#### 2.4.5 Efficiency

Measured electrical to mechanical conversion efficiency is only reported once (Madden and others 1997). This dearth of reports may be related to the fact that efficiencies are invariably less than 1 %, as can be calculated from measurements in which current, voltage, force and displacement are all given (Della Santa and others 1997; Mazzoldi and others 1999b). As discussed in Chapters 5, 8 and 10, efficiencies are maximized by using large loads at small strains. Also discussed is the fact that more than 90 % of the electrical energy input to the polymer is typically stored, and can be recovered. Energy recovery will enable efficiencies of at least 10 %, and likely higher, to be achieved.

## 2.4.6 Lifetime

The largest number of cycles yet reported in conducting polymer actuators is  $10^5$ , achieved in a bilayer activated at 3 Hz and estimated to have been undergoing a 0.3 % strain (Madden and others 2000). Otherwise, where reported, cycle number ranges from 5 to 3000 (Lee and others 1994b; Otero 1997; Pei and Inganas 1993b; Smela and others 1993b). These numbers are for bilayer actuators, which often fail due to delamination. One thousand cycles are reported in a linear actuator (Madden and others 2000). No systematic study of cycle life has been reported. The numbers of cycles reported are not always associated with failure at the end of cycling, and thus relatively long lifetimes may be possible.

Conducting polymer-based electrochromic devices, electrochemical transistors, capacitors and batteries are cycled through similar changes in oxidation state. Cycle numbers reach  $10^6$  (Baughman 1996; Baughman and others 1991b). Such a lifetime amounts to 10 days of operation at a 1 Hz. Oxygen has been found to limit life by replacing dopants during cycling (Tourillon and Garnier 1983).

## **2.5 Reference List**

- Baker, Charles K. and Reynolds, John R. A Quartz Microbalance Study of the Electrosynthesis of Polypyrrole. Journal of Electroanalytical Chemistry, 1988, 251, 307-322.
- Baughman, R. H. Conducting Polymer Artificial Muscles. Synthetic Metals, 1996, 78(3), 339-353.
- Baughman, R. H.; Shacklette, R. L., and Elsenbaumer, R. L. Micro electromechanical actuators based on conducting polymers. Lazarev, P. I., Editor. Topics in Molecular Organization and Engineering, Vol. 7: Molecular Electronics. Dordrecht: Kluwer; 1991; 267.
- Che, Guangli, Fisher, Ellen R. and Martin, Charles R. An Electrochemically Driven Actuator Based on a Nanostructured Carbon Material. Analytical Chemistry, 1999, 71(15), 3187-3191.
- Chiang, Jin-Chih and MacDiarmid, Alan G. 'Polyaniline': Protonic Acid Doping of the Emeraldine Form to the Metallic Regime. Synthetic Metals, 1986, 13, 193-205.
- Chiarelli, P., Genuini, G. and De Rossi D. Electrochemically Driven Muscle-like Actuators. Ninth annual conference of the Engineering in Medicine and biology Society: IEEE; 1987; 1089-1091.
- De Rossi, D., Della Santa, A. and Mazzoldi, A. Dressware: Wearable Hardware. Materials Science and Engineering C, 1999, 7(1), 31-35.
- Dean, John A. Lange's Handbook of Chemistry. 15th ed. New York: McGraw Hill; 1999.
- Della Santa, A., De Rossi, D. and Mazzoldi, A. Performance and Work Capacity of Polypyrrole Conducting Polymer Linear Actuator. Synthetic Metals, 1997, 90, 93-100.
- Della Santa, A., DeRossi, D. and Mazzoldi, A. Characterization and Modeling of a Conducting Polymer Mucle-Like Linear Actuator. Smart Materials and Structures, 1997, 6, 23-34.
- Della Santa, A., Mazzoldi, A., Tonci, C. and De Rossi, D. Passive Mechanical Properties of Polypyrrole Films: A Continuum Poroelastic Model. Materials Science and Engineering C, 1997, 5, 101-109.
- Gandhi, M. R., Murray, P., Spinks, G. M. and Wallace, G. G. Mechanism of Electromechanical Actuation in Polypyrrole. Synthetic Metals, 1995, 73, 247-256.
- Herod, Timothy E. and Schlenoff, Joseph B. Doping Induced Strain in Polyaniline: Stretchoelectrochemistry. Chemistry of Materials, 1993, 5, 951-955.
- Hunter, I. W. and Lafontaine, S. A Comparison of Muscle with Artificial Actuators. Technical Digest IEEE Solid State Sensors and Actuators Workshop: IEEE; 1992: 178-185.
- Hunter, Ian W.; Lafontaine, Serge R., and Madden, John D., inventors. Conducting

Polymer Driven Rotary Motor . Massachusetts Institute of Technology, United States Navy, assignee. United States of America US6084321. 2000 Jul 4.

- Jager, Edwin W. H., Smela, Elisabeth and Inganas, Olle. On-Chip Microelectrodes for Electrochemisty with Moveable PPy Bilayer Actuators as Working Electrodes. Sensors and Actuators B, 1999, 56, 73-78.
- Jones, E. T., Chao, E. and Wrighton, M. J. Preparation and Characterization of Molecule-Based Transistors With a 50 Nm Separation. Journal of the American Chemical Society, 1987, 109, 5526-5529.
- Kaneko, Masamitsu, Fukui, M., Takashima, W. and Kaneto, K. Electrolyte and Strain Dependences of Chemomechanical Deformation of Polyaniline Film. *Synthetic Metals*, 1997a, 84, 795-796.
- ---. Electrolyte and Strain Dependences of Chemomechanical Deformation of Polyaniline Film. *Synthetic Metals*, 1997b, 84, 795-796.
- Kaneto; Keiichi ; Min; Yonggang; MacDiarmid, and Alan G. inventors. Conductive Polyaniline Laminates . US5556700. 1996 Sep 17.
- Kaneto, K., Kaneko, M., Min, Y. and MacDiarmid, Alan G. "Artificial Muscle": Electromechanical Actuators using Polyaniline Films. Synthetic Metals, 1995, 71, 2211-2212.
- Kaneto, Keiichi, Kaneko, Masamitsu and Takashima, Wataru. Response of Chemomechanical Deformation in Polyaniline Film on Variety of Anions. Japanese Journal of Applied Physics, 1995, 34, Part 2(7A), L837-L840.
- Kittel, Charles. Introduction to Solid State Physcis. 3 ed. New York: John Wiley & Sons; 1966.
- Kohlman, R. S. and Epstein, Arthur J. Insulator-Metal Transistion and Inhomogeneous Metallic State in Conducting Polymers. Skotheim, Terje A.; Elsenbaumer, Ronald L., and Reynolds, John R., Editors. Handbook of Conducting Polymers. 2nd ed. New York: Marcel Dekker; 1998; 85-122.
- Lee, Abraham P.; Hong, Keith C.; Trevino, James, and Northrup, M. Allen. Thin Film Conductive Polymer for Microactuator and Micromuscle Applications. Dynamic Systems and Control: ASME; 1994: 725-732.
- Lewis, T. W., Spinks, G. M., Wallace, G. G., De Rossi, D. and Pachetti, M. Development of an All Polymer Electromechanical Actuator. Polymer Preprints, 1997, 38, 520-521.
- Lopez, C., Mendes Viegas, M. F., Bidan, G. and Vieil, E. Comparison of Ion Exchange Porperties of Polypyrrole With and Wihtout Immobilized Dopants by Optical Beam Deflection. Synthetic Metals, 1994, 63, 73-78.
- Madden, J. D., Brenan, C. J., and Dubow, J. Progress Towards An Automatic, Microfabricated Polymer Air -Fluid Sampling Inlet. Springfield,VA: NTIS; 1997; Accession Number AD-A332 030/6/XAB.
- Madden, J. D., Lafontaine, S. R., and Hunter, I. W. Fabrication by Electrodeposition:

Building 3D Structures and Polymer Actuators. Proceedings - Micro Machine and Human Science 95; Nagoya, Japan. 1995a.

- Madden, John D., Cush, Ryan A., Kanigan, Tanya S., Brenan, Colin J. and Hunter, Ian W. Encapsulated Polypyrrole Actuators. Synthetic Metals, 1999, 105, 61-64.
- Madden, John D., Cush, Ryan A., Kanigan, Tanya S. and Hunter, Ian W. Fast Contracting Polypyrrole Actuators. Synthetic Metals, 2000 May, (113), 185-193.
- Maron, J., Winokur, M. J. and Mattes, B. R. Processing-Induced Changes in the Local Structure of Amorphous Polyaniline by Radial Distribution Function Analysis of X-Ray Scattering Data. Macromolecules, 1995, 28, 4475-4486.
- Mazzoldi, A., Degl'Innocenti, C., Michelucci, M. and De Rossi, D. Actuative Properties of Polyaniline Fibers Under Electrochemical Stimulation. Materials Science and Engineering C, 1998, 6, 65-72.
- Mazzoldi, A.; Della Santa, A., and De Rossi, D. Conducting polymer actuators: Properties and modeling. Osada, Yoshihito and De Rossi, Danilo E., editors. Polymer Sensors and Actuators. Heidelberg: Springer Verlag; 1999.
- Nogami, Yoshio, Pouget, Jean-Paul and Ishiguro, Takehiro. Structure of Highly Conducting PF<sub>6</sub>-Doped Polypyrrole. Synthetic Metals, 1994, 62, 257-263.
- Otero, T. F.; Angulo, E.; Rodriguez, J, and Santamaria, C., inventors. EP9200095. 1992a.
- ---. EP9200095. 1992b.
- Otero, T. F., Rodriguez, J., Angulo, E. and Santamaria, C. Artificial Muscles From Bilayer Structures. Synthetic Metals, 1993a, 55-57, 3713-3717.
- Otero, T. F.; Rodriguez, J., and Santamaria, C., inventors. EP9202628. 1992.
- Otero, Toribio F. and Sansinena, Jose M. Soft and Wet Conducting Polymers for Artificial Muscles. Advanced Materials, 1998, 10(6), 491-494.
- Otero, Toribio Fernandez. Artificial Muscles, Electrodissolutoin and Redox Processes in Conducting Polymers. Nalwa, Hari Singh, Editor. Handbook of Organic and Conductive Molecules and Polymers. Chichester: John Wiley & Sons; 1997; pp. 517-594.
- Pei, Qibing and Inganas, O. Electrochemical Muscles: Bending Strips Built From Conjugated Polymers. Synthetic Metals, 1993, 55-57, 3718-3723.
- Pei, Qibing and Inganas, Olle. Conjugated Polymers and the Bending Cantilever Method: Electrical Muscles and Smart Devices. Advanced Materials, 1992a, 4(4), 277-278.
- ---. Electrochemical Application of the Bending Beam Method. 1. Mass Transport and Volume Changes in Polypyrrole During Redox. Journal of Physical Chemistry, 1992c, 96(25), 10507-10514.
- ---. Conjugated Polymers As Smart Materials, Gas Sensors and Actuators Using Bending Beams. Synthetic Metals, 1993a, 55-57, 3730-3735.
- ---. Electrochemical Applications of the Beam Bending Method; a Novel Way to Study Ion Transport in Electroactive Polymers. Solid State Ionics, 1993c, 60, 161-166.

- ---. Electroelastomers: Conjugated Poly(3-Octylthiophene) Gels With Controlled Crosslinking. Synthetic Metals, 1993e, 55-57, 3724-3729.
- Pouget, J. P., Oblakowski, Z., Nogami, Y., Albouy, P. A., Laridjani, M., Oh, E. J., Min, Y., MacDiarmid, A. G., Tsukamoto, J., Ishiguro, T. and Epstein, A. J. Recent Structural Investigations of Metallic Polymers. Synthetic Metals, 1994, 65, 131-140.
- Roth, Siegmar. One-dimensional Metals. New York: Springer-Verlag; 1995.
- Sansinena, J. M., Olazabal, V., Otero, T. F., Fonseca, N. P. and De Paoli, M. A Solid State Artificial Muscle Based on Polypyrrole and a Solid Polymeric Electrolyte Working in Air. Chemical Communications, 1997, 7, 2217-2219.
- Sato, K., Yamaura, M. and Hagiwara, T. Study on the Electrical Conduction Mechanism of Polypyrrole Films. Synthetic Metals, 1991, 40, 35-48.
- Schmidt, C. E., Shastri, V. R., Vacanti, J. P. and Langer, R. Stimulation of Neurite Outgrowth Using an Electrically Conducting Polymer. Proceedings of the National Academy of Sciences of the United States of America, AUG 19 1997, 94(17), 8948-8953.
- Smela, Elisabeth and Gadegaard, Nikolaj. Surprising Volume Change in PPy(DBS): An Atomic Force Microscopy Study. Advanced Materials, 1999, 11(11), 953-957.
- Smela, Elisabeth, Inganas, Olle and Lundstrom, Ingemar. Conducting Polymers As Artificial Muscles: Challenges and Possibilities. Journal of Micromechanics & Microengineering, 1993a Dec, 3(4), 203-205.
- ---. Controlled Folding of Micrometer-Size Structures. Science, 1995 Jun 23, 268, 1735-1738.
- Smela, Elisabeth, Inganas, Olle, Pei, Qibing and Lundstrom, Ingemar. Electrochemical Muscles: Micromachining Fingers and Corkscrews. Advanced Materials, 1993a, 5(9), 630-632.
- Takashima, Wataru, Fukui, Masanori, Kaneko, Masamitsu and Kaneto, Keiichi. Electrochemomechanical Deformation of Polyaniline Films. Japanese Journal of Applied Physics, 1995a, 34, Part 1(7B), 3786-3789.
- Takashima, Wataru, Uesugi, Tomohiro, Fukui, Masanori, Kaneko, Masamitsu and Kaneto, Keiichi. Mechanochemoelectrical Effect of Polyaniline Film. SYNTHETIC METALS, FEB 15 1997, 85(1-3), 1395-1396.
- Tourillon, G. and Garnier, F. Journal of the Electrochemical Society, 1983, 130, 2042.
- Wernet, Wolfgang, Monkenbusch, Michael and Wegner, Gerhard. A New Series of Conducting Polymers With Layered Structure: Polypyrrole N-Alkylsulfates and N-Allkylsulfonates. Makromolekular Chemie: Rapid Communications, 1984, 5, 157-164.
- Winokur, Michael J. Structural Studies of Conducting Polymers. Skotheim, Terje A.; Elsenbaumer, Ronald L., and Reynolds, John R., Editors. Handbook of Conducting Polymers. 2nd ed. New York: Marcel Dekker; 1998; pp. 707-726.

- Yamaura, M., Hagiwara, T. and Iwata, K. Enhancement of Electrical Conductivity of Polypyrrole Film by Stretching: Counter Ion Effect. Synthetic Metals, 1988, 26, 209-224.
- Yamaura, M., Sato, K. and Hagiwara, T. Effect of Counter-Anion Exchange on Electrical Conductivity of Polypyrrole Films. Synthetic Metals, 1990, 39, 43-60.
- Yamaura, M, Sato, K and Iwata, K. Memory Effect of Electrical Conductivity Upon the Counter-Anion Exchange of Polypyrrole Films. Synthetic Metals, 1992, 48, 337-354.