Chapter 1: Introduction

1.1 Conducting Polymers

Conducting polymers exhibit electronic conductivity, making them unusual amongst organic materials, as depicted in Figure 1 (Elias 1987; Kohlman and Epstein 1998). Organic materials tend to form strong covalent bonds in which electrons are highly

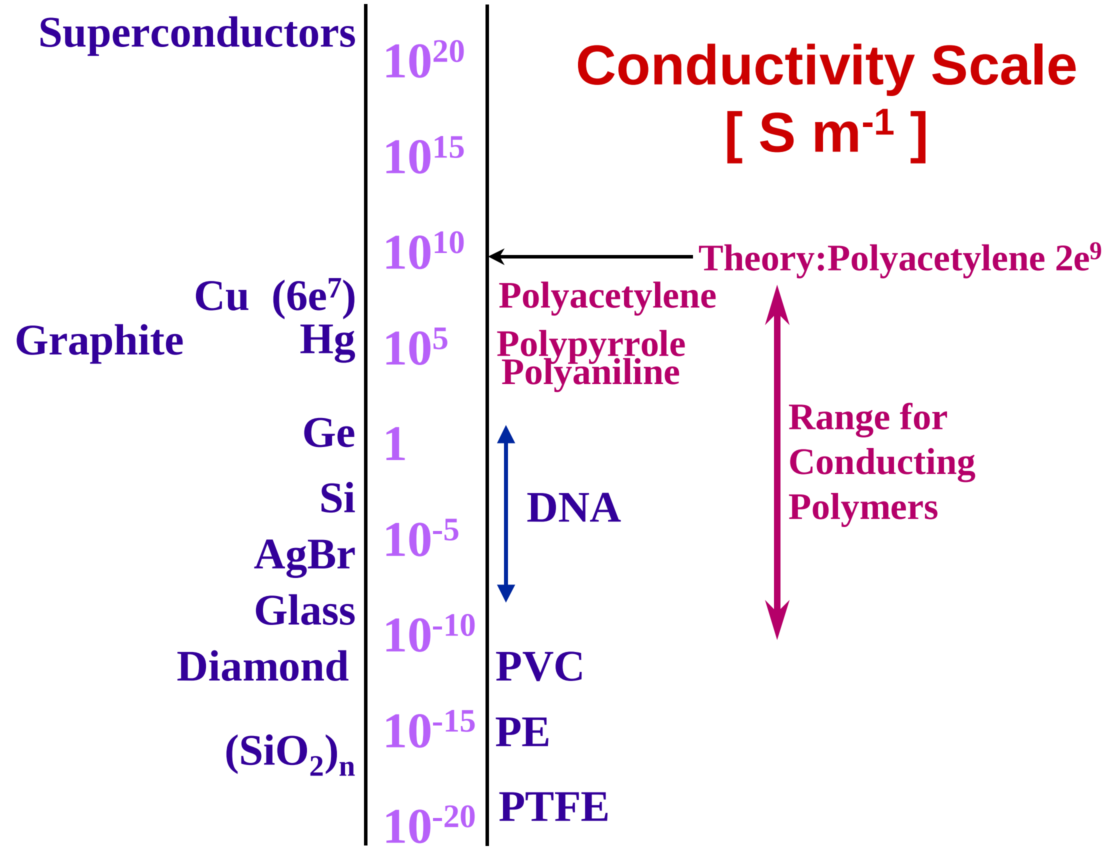

Figure 1: Conductivities of conducting polymers relative to other common polymers and inorganic materials. PE is polyethylene, PVC is polyvinylchloride and PTFE is polytetrafluoroethylene, also known as Teflon©. The upper limits in conductivity for the conducting polymers polyaninline, polypyrrole and polyacetylene are shown.

localized, thereby limiting conductivity. However, electron delocalization can occur in conjugated structures, such as benzene and graphite (Atkins 1990). A defining feature of conducting polymers is their conjugated backbone, as shown in Figure 2, enabling some degree of electron delocalization and hence electronic conduction.

The polymers shown in Figure 2 are semiconductors. Charge carriers must overcome a band gap in order to become delocalized and enable conduction (Kittel 1966). The band gap in polyacetylene is 1.7 eV[*] (Roth 1995). Conductivity decreases with temperature, as the number of carriers with sufficient thermal energy to reach the conduction band is reduced.

The band gap is reduced in a process known as doping (Roth 1995). Doping involves the addition or removal of charges from the polymer chain, resulting in structural changes and the creation of states in the band gap. These changes in polymer oxidation state are generally performed chemically or electrochemically. In the chemical doping process electrons or protons are effectively donated to or withdrawn from the polymer backbone via chemical reactions with 'dopant' molecules. In electrochemical doping the conducting polymer is in electrical contact with an electrode in an electrochemical cell, as shown in Figure 3. Electrons are added to or removed from the polymer via the electrode, thereby changing oxidation state. The oxidation process leads to a change in the polymer charge state, which is balanced by the flux of ions to or from the electrolyte. These ions are referred to as dopants.

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[*] An eV is an electron volt, equal to 1.60×10^{-19} Joules. Silicon has a bandgap of 1.14 eV and diamond a bandgap of 5.4 eV.

The doping process is analogous to doping in silicon and other crystalline semiconductors. There are some notable differences. Doping levels in conducting polymers are much higher, reaching 1 dopant for every two or three monomer units on the polymer backbone. The dopant need not be a donor or an acceptor in conducting polymers, often being present simply to maintain charge balance. Charge carriers in the polymer are not simply electrons or holes, but are coupled with local conformational distortions in the polymer chain, among other differences (Skotheim, Elsenbaumer and Reynolds 1998). In the doped state, conductivities can be appreciable, as shown in Figure 1.

In general, doping is chemically or electrochemically reversible. Conductivity can be switched chemically or electrochemically by 13 orders of magnitude, an effect used in electrochemical transistors (Jones, Chao and Wrighton 1987). The reversible doping is made use of in many applications including batteries, electrochromic devices, supercapacitors, and chemical sensors. The doping process also produces volume changes. These dimensional changes are used to perform mechanical work. Thus, actuation in conducting polymers is derived from dimensional changes associated with changes in polymer oxidation state.

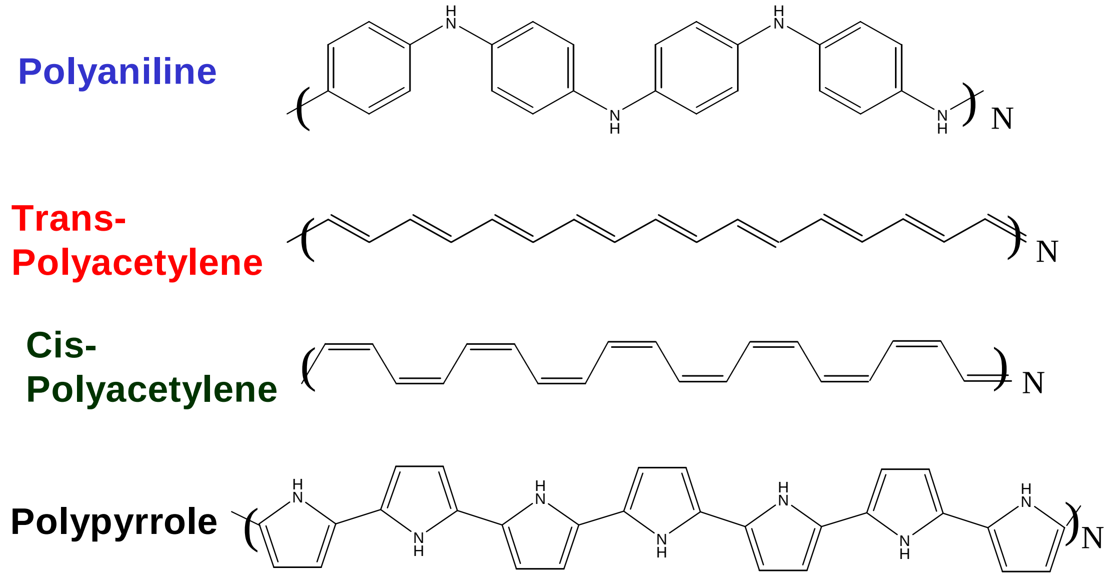

Figure 2: The chemical structures of some common conducting polymers.

1.2 Conducting Polymer Actuators

The study of conducting polymer actuators is motivated by high expectations of their performance relative to other actuator technologies. In particular, the high tensile strengths attainable in conducting polymer fibers may eventually allow actuators to be loaded at forces of greater than 200 MPa (200 MN·m^{-2}), almost 1000 × greater than is achieved in mammalian skeletal muscle, and matching shape memory alloys, as shown in Figure 4 (Hunter and Lafontaine 1992). In combination with the strain rates of 3 %·s^{-1} already achieved (Chapter 7), the power to mass ratio of conducting polymer actuators reaches 4 kW·kg^{-1}, exceeding that of the internal combustion engine by a factor of 4. It has been predicted that strain rates can be further improved by a factor of 100 or more, leading to power to mass ratios that match or exceed those of all other actuator technologies (Baughman 1996).

Conducting polymers are extremely versatile materials, which have been employed to make high energy density storage devices, sensors, generators, computational elements, display technologies, conductive wires, strong fibers and actuators (Skotheim and others 1998). This diversity, combined with techniques for processing and patterning, make conceivable the fabrication of entire, multifunctional, and autonomous devices from a single material, as is currently being done with silicon micro-electro-mechanical systems. Conducting polymers have a number of advantages over silicon, including much higher energy storage capability, and, as will be seen, a superior actuator technology.

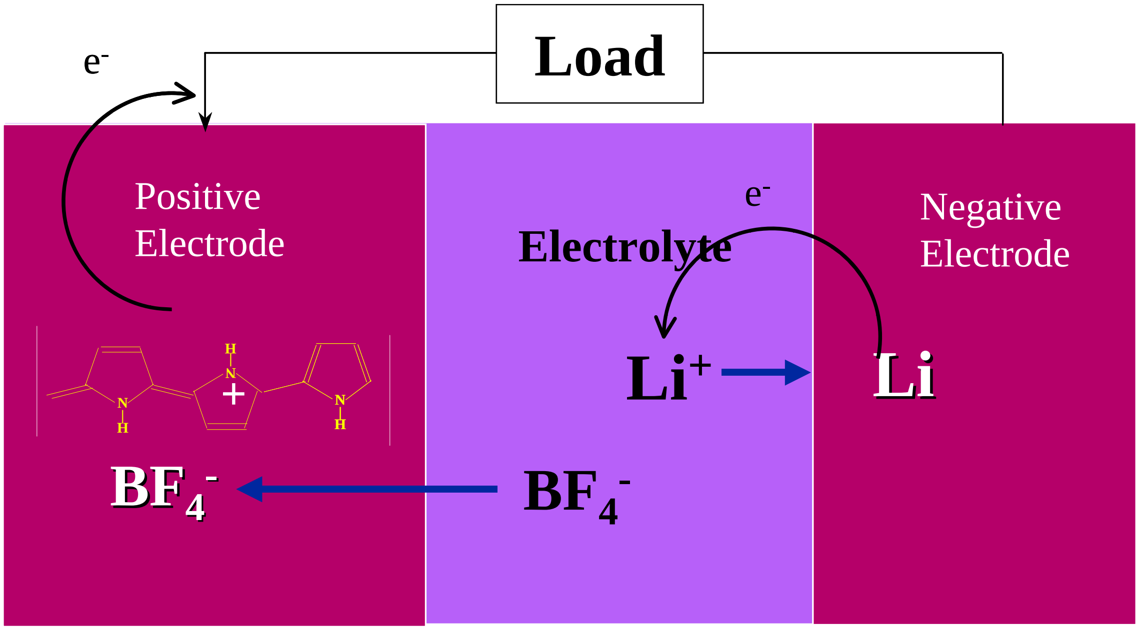

Figure 3: Lithium/polypyrrole battery. Discharge involves the doping of polypyrrole, Py + BF_4^- → $Py^+BF_4^-$ + e^-, at one electrode, and the deposition of lithium at the other.

In conducting polymers, actuation is the result of molecular level interactions. Polypyrrole, polyaniline and other known conducting polymers may or may not live up to their promise. However, the ability to tailor material properties by molecular design creates the potential of rationally designing polymers that will achieve required mechanical properties. Ultimately, it may be possible to develop molecular stepping motors akin to muscle.

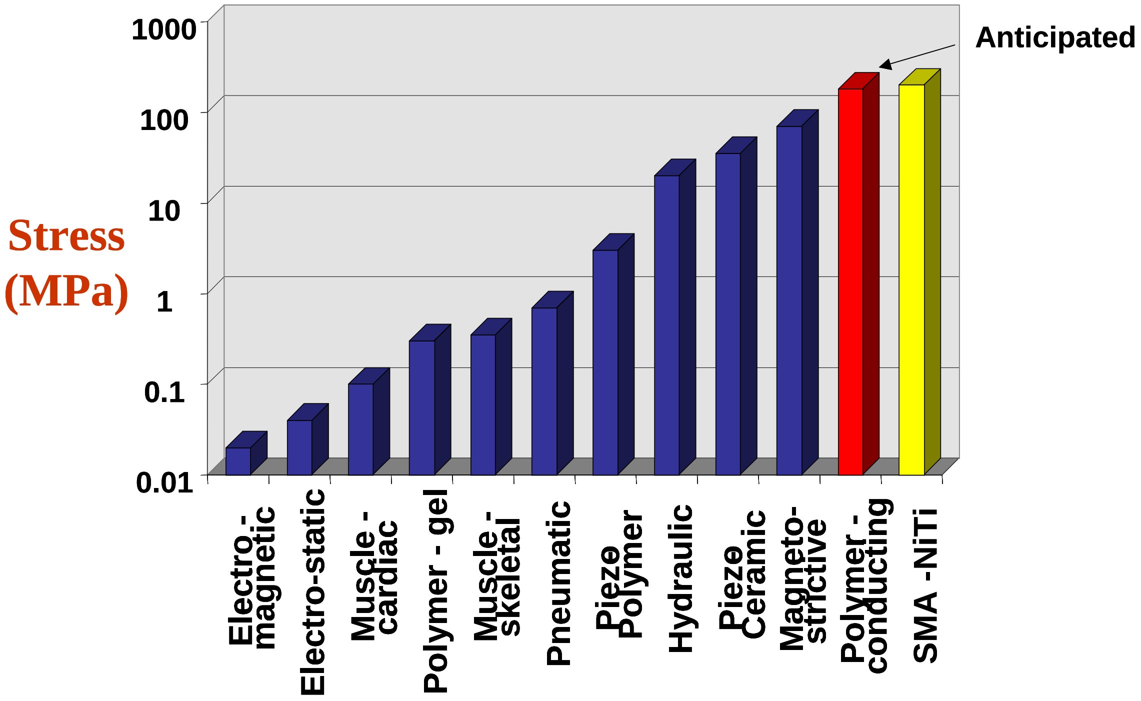

Figure 3: Forces per cross-sectional area achieved in a number of actuator technologies (Hunter and Lafontaine 1992).

1.3 Aims

Important figures of merit for muscle-like actuators (i.e. involving length and volume changes) are force per cross-sectional area (stress), strain, strain rate, energy density, power density, cycle life, and efficiency. Also relevant is the actuator's ability the convert mechanical energy back into potential energy, electrical or otherwise (i.e. a generator). Finally, for design and control purposes it is desirable to have the ability to

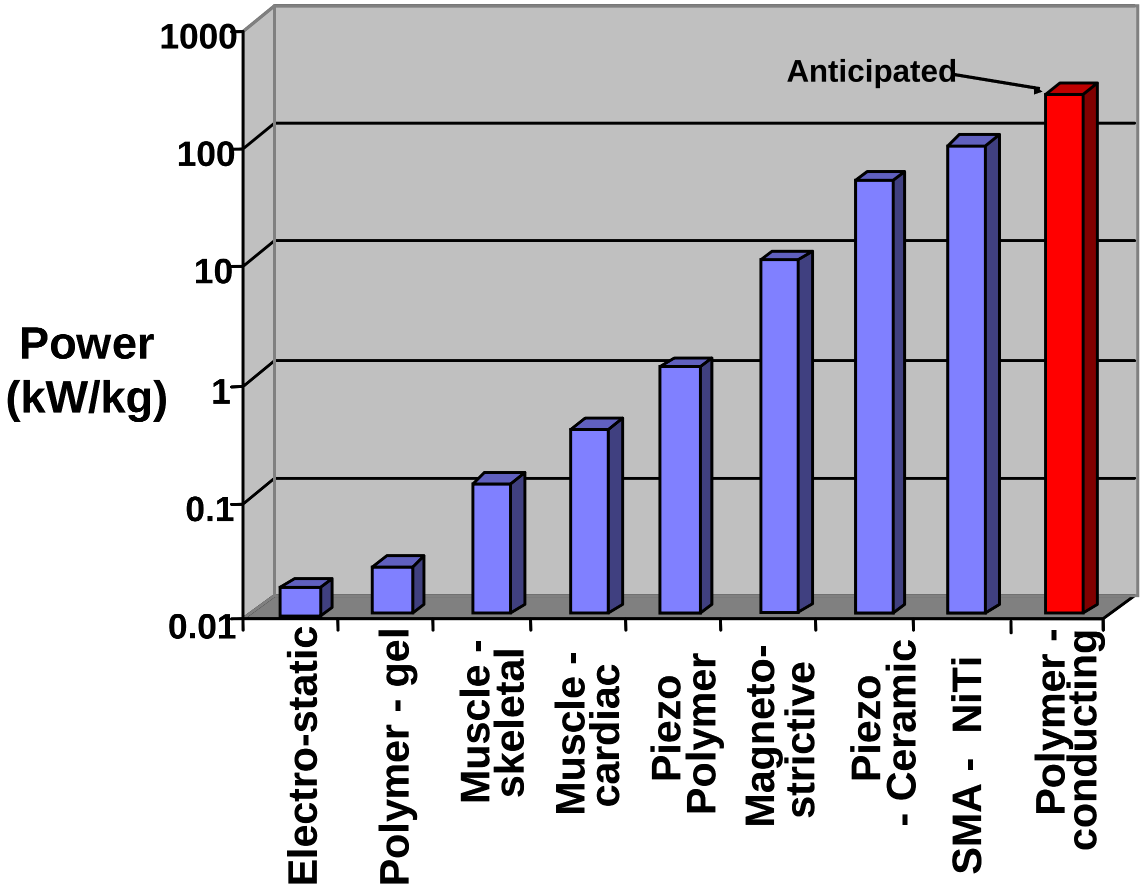

Figure 4: Power to mass ratios achieved in a number of actuator technologies (Hunter and Lafontaine, 1992).

model actuator behavior. The primary goal of this thesis is to measure and model these characteristics in polypyrrole, thereby determining current performance, and anticipate future potential.

1.4 Scope of the Work

Strain, strain rate, power to mass, and efficiency of polypyrrole actuators are all measured and modeled, making this work most comprehensive study of conducting polymer actuator properties to date. The polypyrrole actuators are electrochemically activated. Their electrical and mechanical response to step current inputs, and to step and sinusoidal voltage inputs is observed. These results are presented in Chapters 5 and 10, with the experimental methods being described in the early part of Chapter 5 and in Chapter 9. A model is developed in Chapter 8, which relates the electrical and mechanical actuator response. Chapter 7 describes a method for maximizing strain rate and power to mass, achieving values that are 30× greater than any previously reported. In Chapter 6 and 7, linear and bilayer actuators employing gel electrolytes are demonstrated. The use of gels enables the actuators to be run outside of a liquid environment. Chapter 4 describes the polymer electrochemical synthesis techniques employed. Chapter 3 is a review of electrochemical theory, and Chapter 2 is a review of the literature on conducting polymer actuators. Chapter 11 summarizes the finding of this work, emphasizing the strengths and weaknesses of polypyrrole actuator performance.

1.5 Reference List

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