To my parents for their endless love and encouragement.

To my husband Hongbin Ren and my daughter Silvia Ren for their support and patience.
CERTIFICATION

I, Binbin Xi, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Department of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Binbin Xi

August 2005
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ABSTRACT

Electrochemical actuators based on conducting polymers and conducting polymer/carbon nanotube composites have been constructed and characterised. The actuation performance was optimised in terms of the actuation strain, cycle life, stability and work-per-cycle.

Different conducting polymers, such as polypyrrole, polythiophene, and polyaniline were investigated as actuator materials. More reproducible and stable strain response from polypyrrole actuators has been achieved by the combination of current pulsing control for electrochemical stimulation and ionic liquid for the electrolyte. Current pulsing ensures that the oxidation and reduction processes are equal in their magnitude and prevents the slow net oxidation (or reduction) that typically occurs during symmetrical voltage cycling. Ionic liquid electrolytes permit higher current densities to be applied to the polymer because the polymer can endure a wider potential window in ionic liquids. Also, operation of polypyrrole actuators in ionic liquids produces much smaller changes in elastic modulus, thus resulting in a more stable isotonic strain with increasing applied loads and a higher work-per-cycle. The effect of dopants, potential scan rate and electrolyte temperature on actuation performance is also investigated for polypyrrole actuators. For polythiophene actuators, an increasing strain response was observed under increasing applied loads when operated in ionic liquids as electrolytes. This is the first time that conducting polymer actuators have been reported to exhibit an increasing strain with increasing applied loads.

Using the phase inversion technique, polyaniline actuators were prepared in different geometrical configurations such as films, tubes and tubes with a platinum wire as helix. The actuation strain of the polyaniline actuator was
significantly increased by incorporating a platinum wire as helix configuration into the polymer in acid solution electrolyte. However, the porous nature and subsequent brittleness of the polyaniline actuators prepared using the phase inversion technique has restricted their actuation performance and limited practical application.

The use of carbon nanotubes as reinforcement fillers and electrical conductors in polyaniline was investigated due to the remarkable properties of carbon nanotubes such as high tensile strength, Young’s modulus, and electrical conductivity. Polyaniline/carbon nanotube composite actuators were fabricated aiming to improve the actuation behaviour. Layered composite actuators consisting of polypyrrole, polyaniline and carbon nanotubes were fabricated by coating a polyaniline/carbon nanotube solution onto the polypyrrole tube and drying on a hotplate. Polyaniline/carbon nanotube composite fibre actuators were prepared using a wet-spinning process. The presence of carbon nanotubes allowed high stresses to be applied to the composite actuators. The actuation performance of the composite actuators is enhanced by the carbon nanotubes as reinforcement fillers in conducting polymers.
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<th>Definition</th>
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<tbody>
<tr>
<td>3MT</td>
<td>3-methylthiophene</td>
</tr>
<tr>
<td>A</td>
<td>cross-section area</td>
</tr>
<tr>
<td>A⁻</td>
<td>doping anion</td>
</tr>
<tr>
<td>Ag/AgCl</td>
<td>silver/silver chloride reference electrode</td>
</tr>
<tr>
<td>Ag/Ag⁺</td>
<td>silver/silver ion reference electrode</td>
</tr>
<tr>
<td>BS⁻</td>
<td>benzenesulfonate</td>
</tr>
<tr>
<td>C</td>
<td>coulomb</td>
</tr>
<tr>
<td>°C</td>
<td>degree Celsius</td>
</tr>
<tr>
<td>CEP</td>
<td>conducting electroactive polymer(s)</td>
</tr>
<tr>
<td>cm</td>
<td>centimetre</td>
</tr>
<tr>
<td>CNT</td>
<td>carbon nanotube(s)</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>DBS⁻</td>
<td>dodecylbenzene sulfonate</td>
</tr>
<tr>
<td>DMPU</td>
<td>N,N’-dimethylpropylene urea</td>
</tr>
<tr>
<td>ΔE</td>
<td>potential difference</td>
</tr>
<tr>
<td>E</td>
<td>potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;app&lt;/sub&gt;</td>
<td>applied potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;p(a)&lt;/sub&gt;</td>
<td>anodic peak potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;p(c)&lt;/sub&gt;</td>
<td>cathodic peak potential</td>
</tr>
<tr>
<td>EB</td>
<td>emeraldine base</td>
</tr>
<tr>
<td>EMI.Br</td>
<td>1-ethyl-3-methylimidazolium bromide</td>
</tr>
<tr>
<td>EMI.TFSI</td>
<td>ethylmethylimidazolium bistrifluoromethanesulfonimide</td>
</tr>
<tr>
<td>ES</td>
<td>emeraldine salt</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>F</td>
<td>load</td>
</tr>
<tr>
<td>G</td>
<td>gram</td>
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</tbody>
</table>
HCSA  camphorsulfonic acid
HDBSA  dodecyl benzenesulfonic acid
HFSI− bis(heptafluorobutane-sulfonyl)imide
i  current
i_{p,a}  anodic peak current
i_{p,c}  cathodic peak current
Δl  actuator length change
IL  ionic liquid
LEB  leucoemeraldine base
LiTFSI  Lithium bistri fluoromethanesulfonimide
M  molar
mA  milliampere(s)
mC  millicoulomb
MPa  mega Pascal
MSA  methanesulfonic acid
mV  millivolt
MW  molecular weight
MWNT  multi-walled carbon nanotube(s)
n  number of electron
NFSI− bis(nonafluorobutanesulfonyl)imide
NMP  N-methyl-2-pyrrolidinone
ox  oxidation process
PAn  polyaniline
PC  propylene carbonate
PF_6^−  hexafluorophosphate
PFSI− bis(pentafluorobutanesulfonyl)imide
PmPV  poly(m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene)
PPS^−  p-phenolsulfonic
PPy  polypyrrole
Pt   platinum
PTh  polythiophene
P3MT poly(3-methylthiophene)
Q    charge
Q_{ox} charge consumed during oxidation process
O_{red} charge consumed during reduction process
R    resistance
R_T  total resistance
R_p  polymer resistance
red  reduction process
S    siemens
s    second
SEM  scanning electron microscopy
T    temperature
TBA.BF_4 tetrabutylammonium tetrafluoroborate
TBA.PF_6 tetrabutylammonium hexafluorophosphate
TFSI^- bis(trifluoromethanesulfonyl)imide
µm   micrometre
V    volt
W    work-per-cycle
W_G  gravimetric work
W_V  volumetric work
Y    Young’s modulus
Y_d  Young’s modules at expanded state
Y_o  Young’s modules at contracted state
X^+  cation
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Chapter 1 General Introduction

1.1 MOTIVATIONS OF THIS PROJECT

Electrochemical actuators are devices based on materials that can expand and contract when given an electrochemical stimulus. For conducting polymer actuators, the design of actuators is based on the fascinating electrochemical switching properties that lead to changes in polymer volume. The expansion and contraction are derived from the polymer backbone conformational changes and ion and solvent flows in and out of the polymer during the switching of redox states of the polymer. The ability that conducting polymer actuators could function more analogously to natural muscles has allured research efforts and gained them the name of artificial muscles. The lightweight nature, low operating potential and large dimensional changes make conducting polymer actuators applicable for robots, medical implants and human assist devices. The development of conducting polymer actuators has turned into a novel technology during the last decade with continuing development on the actuator designs, material selections and performance improvements.

This project aims to construct conducting polymer actuators and optimize the actuation performance in terms of the actuator strain, work-per-cycle, energy efficiency and stability when the actuators are operated at different applied stress levels. Different conducting polymers, such as polypyrrole, polythiophene and polyaniline are investigated as actuator materials. Composite actuators are fabricated by introducing carbon nanotubes into the polymers as reinforcement fillers aiming to improve the actuation behaviours.
1.2 BACKGROUND OF THIS PROJECT

1.2.1 CONDUCTING ELECTROACTIVE POLYMERS

The Nobel Prize in Chemistry for 2000 was awarded to MacDiarmid, Shirakawa and Heeger for their revolutionary discovery of the electrical conductivity of certain doped polymers, before which time polymers were considered to be insulators. For the first time in 1977 they demonstrated a significant increase (10^9 times) in the electrical conductivity of polyacetylene when it was exposed to halogen vapors and other oxidizing agents [1]. The high conductivity (10^3 S/cm) gained it the name “organic metal”. Following this discovery, in 1979 Diaz et al [2] reported conducting polypyrrole films synthesised from a new approach: electrochemical polymerisation. They showed that polypyrrole could be deposited on the surface of the anode by electrochemical oxidation of pyrrole monomer. Later in 1980, conducting polyaniline films were prepared by Diaz et al [3] in the same way and another conjugated conducting polymer, polythiophene, was also reported [4]. Since then, a new branch of material science has been developed to investigate conducting electroactive polymers (CEPs).

Unlike metal, a polymer does not possess free electrons that can move through the lattice in an electric field. These free electrons are considered as charge carriers for electrical conduction in metals. For a polymer to be able to conduct electric current, it must contain overlapping $\pi$ molecular orbitals through a high degree of $\pi$-bond conjugation. Polymers are insulating materials in their neutral state. When a $\pi$ electron is removed from the polymer backbone, it becomes a radical cation (polaron) that is delocalised...
over 3-4 monomer units. When a second electron is removed from the polymer, two individual polarons or bipolaron can form. Because the formation of bipolarons is energetically more favourable than the separated polaronic states, bipolarons are spread over the polymer [5]. Polarons and bipolarons are mobile in an electric field and are the charge carriers responsible for electrical conduction in polymer chains.

In recent years conducting polymers have drawn considerable attention as a new class of advanced functional materials. Many applications have been developed based on the unique properties of electroactivity, conductivity and other physical or chemical properties. The potential applications include polymeric batteries [6], photovoltaics [7], electrochromic devices [8], ion selective membranes [9], electromagnetic interference shielding [10], radar absorption [11], electrical wires [12], corrosion inhibitors [13] sensors [14] and electromechanical actuators [15], also referred to as artificial muscles.

Although polyacetylene showed high conductivity of between $10^3$ S/cm and $10^5$ S/cm [16], its poor environmental stability has limited its further development potential. Among the wide range of conducting organic polymers, polypyrrole, polyaniline and polythiophene are all relatively stable in air and moisture. These three types of conducting polymers are most attractive and have been extensively studied during the last two decades.
1.2.1.1 Polypyrrole

Polypyrrole and derivatives thereof are the most attractive and interesting polymers due to their high electrical conductivity and electroactivity both in aqueous and organic media. Together with their environmental stability and high mechanical strength, it has made polypyrrole and its derivatives the leading material among conducting polymers.

1.2.1.1.1 Synthesis of Polypyrroles

Polypyrrole and its derivatives can be easily synthesised either chemically [17] or electrochemically [18]. Chemical polymerisation is carried out by reacting pyrrole monomer with an oxidant in a suitable solvent whereas electrochemical polymerisation is formed by the oxidation of pyrrole monomer at a suitable anode upon the application of a positive potential. The polymerisation process in both cases involves the incorporation of certain charged anionic species into the polymer. A simplistic representation of the polymerisation process can be expressed as:

\[
\begin{align*}
\text{m} \cdot \text{n} \quad \text{H}_2\text{C}==\text{CH}==\text{CH}_2 + \text{m} \cdot \text{A}^- & \rightarrow \quad \left[ \begin{array}{c} \text{H}_2\text{C}==\text{CH}==\text{CH}_2 \text{H}^+ \\
\text{N} \end{array} \right]^{n+ \text{A}^-} \quad \text{m} \\
\end{align*}
\]

where \( \text{A}^- \) represents the counterion incorporated into the polymer to balance the charge, \( n \) is the number of pyrrole monomers per positive charge (usually 2~3), and \( m \) is the number of the counterion incorporated into the polymer.
The overall polymerisation process involves several discrete steps as shown in Schematic 1.1 [19]. The first step is the oxidation of the monomer A to form a delocalized radical cation B. This radical cation can possibly exist in resonance forms C, D and E. The next step involves the dimerization of the radical cation, which occurs via radical-radical coupling at the $\alpha$-position. The coupling is accompanied by the expulsion of two protons to form the neutral dimer F which can be further oxidised to form dimer radical. This can then combine with other monomeric, dimeric, or oligomeric radicals in a similar sequence of events to extend the polymer chains.

It is generally agreed that for preparation of free-standing conducting polymer actuators, electrochemical polymerisation is an optimal technique compared to chemical polymerisation. The electrochemical method allows the insertion of a wide range of anions into the polymer to form different anion doped polymer species. Also by controlling the electrochemical polymerisation parameters, such as applied current, potential, time, electrolytes, temperature and substrates etc, polypyrrole can be varied with different morphology and hence mechanical and electrical properties.

In this work, polypyrrole and polythiophene actuators were all synthesised electrochemically.
1. Monomer oxidation

\[
\text{[A]} \xrightarrow{\text{E}_{\text{app}} \text{ (ox)}} \text{[B]}
\]

2. Resonance forms

\[
\begin{align*}
\text{N}^+ & \leftrightarrow \text{N}^+ \\
\text{N} & \leftrightarrow \text{N}^+ \cdot \text{A}^- \\
\text{N}^+ \cdot \text{A}^- & \leftrightarrow \text{N}^+ \cdot \text{A}^-
\end{align*}
\]

3. Radical-radical coupling

\[
\text{N}^+ \cdot \text{A}^- \xrightarrow{} \text{N}^+ \cdot \text{H} \xrightarrow{} \text{N}^+ \cdot \text{N} + 2 \text{H}^+
\]

4. Chain propagation

\[
\text{N} \xrightarrow{\text{E}_{\text{app}} \text{ (ox)}} \text{N}^+ \cdot \text{N} + 2 \text{H}^+
\]

**Scheme 1.1:** Mechanism of polymerisation of pyrrole [19].
1.2.1.1.2 Switching Properties of Polypyrrole

After polymerisation, polypyrroles exist in their oxidised states. By applying electrochemical stimulation, polypyrroles are capable of switching between their oxidised and reduced states. The switching processes are often described as below:

\[
\begin{align*}
\text{N} \quad (n) \quad +e & \quad \text{N} \quad (n) \\
\text{A}^- \quad m & \quad \text{A}^- \quad m
\end{align*}
\]

where \( A^- \) represents the counterion incorporated into the polypyrrole, \( X^+ \) represents the cation from the electrolyte, \( n \) is the number of pyrrole monomers for each \( A^- \) incorporated, \( m \) is the number of polypyrrole repeat unit to determine molecular weight of polymer.

The changes in polypyrrole redox states are usually accompanied by ion exchange between the polymer and electrolyte. As the polymer is reduced, anions are detached and leave the polymer backbone to maintain the neutral state (Equation 1-2). However, in the case of bulky anions, such as dodecyl benzene sulfonate (DBS\(^-\)), which are immobile due to their large size, the charge compensation may be achieved by incorporation of cations from the electrolyte (Equation 1-3). When the polymer is oxidised again, it is possible for the charge to be balanced by either incorporating further anions or
releasing newly incorporated cations. In some cases, there is mixture of both cation and anion movement during the redox process [20]. The dominating ion movements at oxidation and reduction are affected by a series of factors, such as counterion size, mobility, charge density, electrolyte and temperature.

The ion exchange processes occurring during polymer oxidation/reduction causes significant mass and volume changes in the polymer. These polymer volume changes form the basis of conducting polymer electrochemical actuators.

1.2.1.2 Polythiophene

The advantageous properties of polythiophene have been reviewed by a number of workers [21-24]. The main advantages include high conductivity (10^2 S/cm), stability both in air and moisture, structural versatility and wide electrochemical potential windows, which can make it less susceptible to over-oxidation and therefore degradation.

1.2.1.2.1 Synthesis of Polythiophene

Like polypyrrole, polythiophene and its derivatives are essentially prepared by chemical and electrochemical syntheses through oxidation of the thiophene monomer, resulting in the doped form of polythiophene. This process can be expressed as:

\[
\text{S}_n + m\text{A}^- \xrightarrow{\text{Oxidation}} \left[\text{S}_n \right]^{+m\text{A}^-}_{-m}\]

(1.4)
As with polypyrrole, \( n \) is the number of thiophene monomers per positive charge, usually between 2 and 4; \( A^- \) is a counterion incorporated into the polymer to balance the charge, \( m \) is the number of the counterions incorporated into the polymer. The polymerisation of thiophene (Schematic 1.2) occurs via the formation of radical cations that react with each other or with the starting monomer to develop the polymeric structure.

**Scheme 1.2:** Mechanism of polymerisation of thiophene [25].
1.2.1.2.2 Switching Properties of Polythiophene

Similar to polypyrrole, the redox states of polythiophene can be modulated by applying electrochemical stimulation as follows:

\[
\begin{align*}
\text{[Polythiophene]}_n^+ + A^- & \xleftrightarrow{+ e} \text{[Polythiophene]}_n^0 + m.A^- \\
& \text{[Polythiophene]}_n^- - e \\
\end{align*}
\]

The ion exchange processes occurring during the redox process are also determined by the counterion and electrolyte.

1.2.1.3 Polyaniline

Polyaniline has many similarities with polypyrrole and other conducting polymers, however other attributes differ markedly and can generate advantages in certain applications. Its solubility (and hence high processability), environmental stability, electroactivity, and pH switching properties have made it one of the most promising organic conducting polymers for commercialisation.
1.2.1.3.1 Synthesis of Polyaniline

Polyaniline can be synthesised by chemical [26] or electrochemical methods [27]. Electrochemical polymerisation is routinely conducted in an acidic aqueous solution of aniline under an applied potential between 0.8V and 1.1V (vs Ag/AgCl). Chemical polymerisation is usually carried out in an acidic aqueous solution of aniline and oxidant. The mechanism of chemical and electrochemical polymerisation are depicted in Scheme 1.3 and 1.4, respectively.
1. Oxidation of monomer

\[
\text{Ph-NH}_2 + \text{HA} \rightarrow \text{Ph-N}^+ + \text{H}^- + \text{A}^- \quad \text{and} \quad \text{Ph-N}^+ + \text{H}^+ \rightarrow \text{Ph-NH}_2^+ + \text{A}^- 
\]

2. Radical coupling and oxidation to the diradical dication

\[
\text{Ph-N}^+ + \text{Ph-N}^+ \rightarrow \text{Ph-N}^+\text{Ph-N}^+ + \text{A}^- \rightarrow \text{Ph-N}^+\text{Ph-N}^+ + \text{H}^- \rightarrow \text{Ph-N}^+\text{Ph-NH}_2^+ + \text{A}^- 
\]

3. Propagation of chain

\[
\text{Ph-N}^+\text{Ph-NH}_2^+ + \text{Ph-N}^+\text{H}^- \rightarrow \text{Ph-N}^+\text{Ph-N}^+\text{Ph-N}^+\text{H}^- + \text{A}^- 
\]

4. Reduction of Pernigraniline Salt to Emeraldine Salt

\[
\left[ \text{Ph-N}^+\text{Ph-NH}_2^+ \right]_n + \text{Ph-NH}_2 \rightarrow \left[ \text{Ph-N}^+\text{Ph-N}^+\text{Ph-N}^+\text{H}^- \right]_n + \text{A}^- 
\]

**Scheme 1.3:** Chemical polymerisation of aniline [28].
1. Oxidation of monomer

\[ \text{NH}_2 \text{N} \overset{\text{HA}}{-\text{e}^-} \text{NH}_2 \text{N} \]

2. Radical coupling and rearomatization

\[ \text{A}^+ \text{NH}_2 + \text{A}^+ \text{NH}_2 \rightarrow \text{A}^+ \text{NH}_2 \text{NH}_2 \text{NH}_2 \text{A}^- \]
\[ \text{A}^+ \text{NH}_2 \text{NH}_2 \text{NH}_2 \text{A}^- \rightarrow \text{A}^- \text{NH}_2 \text{NH}_2 \text{NH}_2 \text{A}^- \]

3. Chain propagation

\[ \text{A}^- \text{NH}_2 \text{NH}_2 \text{NH}_2 \text{A}^- \rightarrow \text{A}^- \text{NH}_2 \text{NH}_2 \text{NH}_2 \text{A}^- \]
\[ \text{A}^- \text{NH}_2 \text{NH}_2 \text{NH}_2 \text{A}^- \rightarrow \text{A}^- \text{NH}_2 \text{NH}_2 \text{NH}_2 \text{A}^- \]

4. Oxidation and doping of the polymer

\[ \text{A}^- \text{NH}_2 \text{NH}_2 \text{NH}_2 \text{A}^- \rightarrow \text{A}^- \text{NH}_2 \text{NH}_2 \text{NH}_2 \text{A}^- \]

**Scheme 1.4:** Mechanism of the electrochemical polymerisation of aniline [29].
1.2.1.3.2 Switching Properties of Polyaniline

Unlike polypyrrole and polythiophene, polyaniline undergoes two major redox processes and exists in a variety of protonation and oxidation forms [28], as shown in Scheme 1.5.

![Scheme 1.5: The protonation of redox reactions between the various forms of polyaniline.](image)

These processes are clearly observed using cyclic voltammetry when the potential is swept between −0.2 V to 1.0 V (vs Ag/AgCl) at a 50 mV/s scan rate (Figure 1.1). Three redox pairs are observed namely A/A', B/B' and C/C'.
The first peak A (at ~0.2V) corresponds to the first step of oxidation of neutral polyaniline from polyleucoemeraldine base to polyemeraldine salt. Peak B (at ~0.7 V) corresponds to the further oxidation of polyaniline from polyemeraldine salt to polypernigraniline base. Redox pair C/C' is from the presence of ortho-coupled polymer or the degradation of polyaniline. It is also very interesting that the polyaniline can be switched between base and salt forms by the addition of acids or bases that protonate and deprotonate the base sites within the polymers [30, 31]. The conductive form of polyaniline is the polyemeraldine salt form which can be derived by controlling the potential between approximately +0.20V and +0.60V (vs. Ag/AgCl), or by chemically doping the emeraldine base form in acidic solution of pH < 4 [31].

Figure 1.1: Cyclic voltammogram of PAn/HCl film in 1M HNO₃, potential scan rates: 50mV/s.

When polyaniline emeraldine base is doped in acid solution, the anions from the acid solution are incorporated into the polymer backbone, converting the
polymer into the polyaniline emeraldine salt form which is conductive. When it is exposed to electrochemical stimulation (negative or positive potential), the dopant anions are able to leave the polymer or move back again. Like polypyrrole and polythiophene, dopant movement leads to volume changes that generates an expansion or contraction in the polymer structure.

1.2.1.3.3 Processing of Polyaniline

The processability of conducting polymers is limited by the fact that most of the conducting polymers are insoluble in common organic and aqueous solvents. Polyaniline, however, is distinctive due to its solubility in the non-conducting base form. The solubility of the emeraldine base makes polyaniline the production of stable free-standing films and fibres feasible. These can be easily converted to the emeraldine salt form with exposure to an acidic solution.

The first report on solubility of polyaniline was in 1910 [32] when Green et al reported that it was soluble in 80% acetic acid, 60% formic acid, pyridine and concentrated sulphuric acid. In 1987, Angelopoulos et al [33] reported that polyaniline emeraldine base was partially soluble in N-methyl-2-pyrrolidinone (NMP), benzene and chloroform. Later in 1991 Heeger and co workers [34, 35] reported that by doping emeraldine base with a surfactant-like acid such as camphorsulfonic acid (HCSA) or dodecyl benzenesulfonic acid (HDBSA), even the emeraldine salt form can be made soluble in NMP, dimethylsulfoxide (DMSO), m-cresol and xylene. During the last decade, most of the work related to processing polyaniline into films or fibres has been done by
dissolving polyaniline emeraldine base in NMP or \(N,N'\)-dimethylpropylene urea (DMPU) [36-48].

NMP is a commonly used solvent for polyaniline emeraldine base. There are many reports about polyaniline free-standing films prepared from polyaniline emeraldine base in NMP solution [36-42, 47]. However, when the emeraldine base concentration is above 5\% (w/w), the solution will be unstable and rapid gelation takes place at room temperature [45]. The poor stability of polyaniline emeraldine base/NMP solution has limited the development of processability. Later Gregory and co-workers [45, 46] reported that compared with NMP as solvent, DMPU is significantly better with regard to solution stability. Emeraldine base can be dissolved up to 10\% (w/w) in DMPU with minimal solution viscosity change for at least 3000 minutes. They also reported [43] that when the oxidation state of emeraldine base is changed to the reduced state of leucoemeraldine base form (by adding a reducing agent such as phenyl hydrazine), the formation of an elastic and gel structure is inhibited thus the ease of processing can be improved.

Polyaniline free-standing films can be easily prepared by a conventional approach that involves three steps: dissolving of polyaniline emeraldine base in a solvent; casting solution on a substrate; and drying the films at high temperature. This method is employed by Kaneto et al [37] to prepare polyaniline films from emeraldine base in NMP solution. Similar work has been reported by Herod [40], Bormashenko [49], Li [50] and their co-workers.
Although the conventional approach is a useful way to process polyaniline, it is hard to fabricate polyaniline in configurations other than films and to obtain desirable microstructures. The phase inversion technique, which is controllable by means of solvent/non-solvent choice, is an alternative procedure to overcome the drawback of the conventional approach.

The phase inversion technique is a process whereby a polymer is transformed in a controlled manner from solution to a solid state by coagulation [51]. Phase inversion techniques involve four steps: dissolution of polyaniline emeraldine base in a solvent; casting solution onto a substrate or spinning solution into fibres; coagulating the polymer in a non-solvent bath, and drying the films or fibres. Polyaniline films and fibres prepared by this procedure were reported by Sansinena [47], Zhang [52], Yang [42] and their co-workers. The main advantage of the phase inversion technique is that the micro-porosity of the polymer can be controlled by appropriate choice of solvent and non-solvent.

Since polyaniline emeraldine base has good solubility in organic solvents, it is possible to fabricate polyaniline/carbon nanotubes composites by dispersing carbon nanotubes in the solution. This is a part of polymer/carbon nanotubes composites which have been extensively studied in recent years and will be discussed in detail later in this chapter.

1.2.2 CARBON NANOTUBES AND CONDUCTING POLYMERS

Carbon nanotubes (CNTs) were first discovered in 1991 by Iijima [53] with their novel carbon structures consisting of multi-layer concentric hollow fibres
with nanometer scale diameters. Since then, carbon nanotubes have been proven to possess extraordinary properties, such as high tensile strength (100 GPa), high Young’s modulus (0.6TPa) [54], and exceptional electrical conductivity (5000 S/cm) [55]. These properties have led to the use of carbon nanotubes as sensors [56], super capacitors [57], actuators [58] and conductive yarns [59].

The remarkable properties of carbon nanotubes not only make them a new class of functional materials, but also make them potentially useful as reinforcement fillers within a host polymer matrix. The formation of carbon nanotubes/polymer composites is considered as an approach for fabricating promising polymer based devices [60-64].

The first composite was prepared by Ajayan et al [65] through mechanically mixing the multi-walled carbon nanotubes (MWNTs) and epoxy resin. Curran et al [63] reported that carbon nanotube powder was mixed with poly(m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene) (PmPV) to get CNT/PmPV composite. It has been reported that the incorporation of carbon nanotubes into a polymer matrix improves the electrical conductivity as well as the mechanical properties of the original polymer [66-70].

As described earlier in this chapter, among the wide range of conducting polymers, polyaniline is a unique and promising material due to its good processability, environmental stability and switching properties by both charge-transfer doping and protonation. Consequently CNT/PAn composites have drawn more attention and have been reported on by several groups of researchers [71-73]. CNT/PAn composites can be formed by both in-situ
chemical [72, 74-76] or electrochemical polymerisation [77, 78] of aniline in presence of carbon nanotubes and ex-situ dispersion of carbon nanotubes into the polyaniline solution [79-83]. These various methods have been used in this thesis to prepare novel actuator materials.

1.2.3 ELECTROCHEMICAL ACTUATORS BASED ON CONDUCTING POLYMERS

As described above, the ability to switch the redox states in conducting polymers is intriguing. The reduction and oxidation of conducting polymers can be operated through a variation of electrochemical stimulations. The switching properties of conducting polymers have formed the main mechanism of electrochemical actuators.

Conducting polymer actuators were first proposed in 1990 by Baughman et al [84] who underlined the great interests in developing material technologies based on conducting polymers suitable for the construction of electrochemical actuators. They demonstrated a simple cantilever actuator based on the electrochemical doping and dedoping of a conducting polymer. Since then, many research efforts have focused on the analysis of actuator mechanisms and the construction of practical conducting polymer actuator devices.

1.2.3.1 Mechanism of Conducting Polymer Actuators

Actuators are made of materials that expand and contract when given a voltage stimulus [85]. The actuator system works in the similar way as natural muscles; however, the mechanism of actuation is the polymer volume change
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driven by the electrochemical switching of the polymer redox states. The polymer volume change arises from polymer backbone conformational change, ion exchange process between the polymers and electrolytes, and the electrolyte solvent flux accompanying the ion exchanges.

1.2.3.1.1 Natural Muscles and Artificial Muscles

Natural muscles and artificial muscles were reviewed in detail by Nalwa [86]. Natural muscles are elegant devices that have developed over millions of years of evolution in order to transfer chemical energy to mechanical energy. Mechanical work is conducted by the muscular fibres that can change their volumes under the control of electrical pulses sent from brain through the nervous system. This approach can be described in Figure 1-2 below.

**Figure 1.2:** Muscle: a nervous stimulus (ionic pulse) arriving from the brain through the nervous system triggers ionic and water transport, chemical reactions of volume change in a muscle with the production of mechanical energy and heat.

It can be seen from the above that in order to mimic natural muscles, artificial muscles need to be able to conduct both electrons and ions. Conducting
polymers, which can be electronic and ionic conductors [87, 88], can receive electrochemical stimulus and perform redox reactions in a reversible way in ionic media. Similar to natural muscles, conducting polymer actuators work as an electrochemical system consisting of electronic equipment (producing electrochemical stimulus), metal wires (transporting stimulus) and polymers surrounded by electrolyte (conducting electrochemical reactions). Metal wires conduct electron flow to the surface of polymer actuator where ions from electrolyte exist. The ion exchange processes occurring between the polymer and electrolyte occur in order to maintain electroneutrality. This system is described in Figure 1-3 below.

![Electrochemical system of a conducting polymer actuator](image)

**Figure 1.3:** Electrochemical system of a conducting polymer actuator

### 1.2.3.1.2 Volume Changes in Conducting Polymers

It is generally agreed that volume changes in conducting polymers under electrochemical stimulation arise from the conformational change of the polymer backbone and the insertion/ejection of ions and solvent molecules. When the electrical stimulus is applied to the polymer, the only way to maintain electroneutrality is to allow the penetration of ions. To do so, the
polymeric structure has to be opened by the formation of channels which allow the passage of ions [89, 90]. According to Otero’s analysis [91], when positive charge is applied along the chains at the polymer-solution interface, cumbic repulsion between those chains leads to the conformational changes which increases the polymer radius of gyration, or volume occupied by a single chain. These conformational changes open enough space between the chains to allow the penetration of ions and electrolyte solvent molecules.

After the conformational change of the polymer structure, the ion exchange occurs between the polymer and electrolyte. Ion exchange during polymer redox processes has been studied by several researchers [20, 86, 92-101]. Electrochemical changing of redox states leads to the addition or removal of charge from the polymer backbone and a flux of ions to balance charge. It is generally agreed that the redox processes occur according to the following processes:

\[
\begin{align*}
N^+ & \rightarrow N^- + e^- \\
A^- & \rightarrow A^+ \\
N^+ & \rightarrow N^- + e^- \\
A^- & \rightarrow A^+ \\
\end{align*}
\]

where \(A^-\) is a counterion incorporated during polymer growth; \(X^+\) is a cation from the supporting electrolyte.
It is also generally agreed that the dopant anions have a strong influence on the ion exchange processes. According to the extensive research work carried on polypyrrole actuators, dopant anion size is a critical factor that determines the dominating reaction [20, 102-106]. In the case of polypyrrole doped with small anions, such as NO$_3^-$, Cl$^-$, ClO$_4^-$, when polypyrrole is reduced, electrons are injected into the polymer chains and small anions will be ejected from the polypyrrole [102]. The polymer will then shrink. In contrast, during oxidation of the polymer, the electrons are extracted from the polymer chains, positive charges are stored along the chains, the counter anions are incorporated into the polymer and the polymer will swell [103, 104]. In this case, the polymer redox process is dominated according to Equation 1.6. Contrary to small dopant anions, when polypyrrole is doped with large anions, such as dodecylbenzene sulfonate, polyvinylsulphate or poly(4-styrenesulphonate), these are trapped inside the polymer chains and remain immobile. As a result, the charge will be balanced by cations from electrolyte [105]. When the polymer is reduced, cations will be injected into the polymer to neutralise the negative charge and lead to the polymer expansion, while during oxidation cations will be expelled from the polymer and result in polymer contraction. In this case, the polymer redox process is dominated according to Equation 1.7. Based on this opposite mechanism, Han et al [106] reported a three-layer composite films consisting of polythiophene film sandwiched between two polypyrrole films: one doped with the large anion dodecylbenzene sulfonate anion and the other doped with the small anion perchlorate anion. The bending actuation behaviour of the layered film confirmed the anion influence on the polymer redox process.
Although anodic contractions are observed for many cases of polypyrrole doped with large anion, a bulky dopant called di-2-butoxy-2-ethoxy-ethyl-ester of sulfosuccinic acid (DBEEESSA) showed a contrary performance. Takashima et al [107] reported that DBEEESSA-doped polyaniline exhibited anodic expansion in HCl aqueous solution electrolyte. In this case, the anodic expansion is possibly caused by the large conformational changes of polymer, and this conformational change can overcome the anodic contraction due to the ejection of small proton. Thus, the net volume changes observed during actuation are usually the result of a number of molecular mechanisms occurring simultaneously.

In addition to the anion size effect, the electrolyte in which the conducting polymer actuators are operated plays an important role in the redox process. Ding [108] reported that polypyrrole actuators doped with hexafluorophosphate anion (PF$_6^-$) exhibit different actuation behaviours in different electrolytes. In propylene carbonate (PC) containing 0.25 M tetrabutylammonium hexafluorophosphate (TBA.PF$_6$) as electrolyte, anion migration dominates the redox process, whereas in the ionic liquid ethylmethylimidazolium bistrifluoromethanesulfonimide (EMI.TFSI) as electrolyte, cation movement is the dominant mechanism. Khalkhali et al [20] also reported that the changing of the electrolyte temperature could affect the mobility of the counterion and the ion exchange properties of polypyrrole.

The solvent flux that usually accompanies ion exchange also contributes to the volume change in the conducting polymers. The solvent molecules that enter the polymer can be driven either by specific solvation effects or by entropic effects linked to the changes in the number of free ionic carriers in the
polymer [109]. Bay et al [95] observed that solvent molecules moving into the polymer resulted in a large volume change; the polymer expansion decreased as the electrolyte concentration increased. This indicates that a considerable part of the total expansion is due to this so-called osmotic effect. Careem and co-workers [100] also reported that different cations from electrolytes such as Li$^+$ and Na$^+$ were incorporated into the polymer and were accompanied by different amounts of water molecules and resulted in relative actuator force generation which was directly related to volume change. 15 water molecules accompanying with each Li$^+$ and only 10 with Na$^+$ resulted in forces of 40 µN and 35 µN, respectively.

It can be concluded that insertion of ions between polymer chains is primarily responsible for the polymer volume changes during redox reactions, however, conformational change of the polymer backbone and solvent flux may also play a role [110]. In most cases, the conformational change is expected to be much smaller than the ionic contribution [15].

### 1.2.3.2 Electrochemical Actuators Based on Polypyrrole

Polypyrrole actuators are usually fabricated electrochemically from solutions containing pyrrole monomer and a dopant. The most extensively employed dopants include hexafluorophosphate (PF$_6^-$) [108, 111-116], dodecylbenzene sulfonate (DBS$^-$) [95, 100, 117], tetrafluoroborate (BF$_4^-$) [115, 118], benzenesulfonate (BS$^-$) [119], p-phenolsulfonate (PPS$^-$) [120], perchlorate (ClO$_4^-$) [121] and bis(trifluoromethanesulfonyl)imide (TFSI$^-$) [115, 122]. The polymerisation solution solvents vary from aqueous [106, 120] to organic such as propylene carbonate [108, 111-116, 123], methyl benzoate [115, 118, 122,
124] and acetonitrile [121]. The polymer conductivity and morphology are related to dopant, solvent, temperature and the electrode material onto which the polymer is deposited [115].

To achieve good actuation performance, efficient electrical connection to all parts of the actuator is essential. The polymer redox reactions are determined by the electrical potential achieved at the polymer working electrode [116]. The potential is reduced by cell resistance as:

\[ E = E_{app} - iR_T, \quad R_T = R_s + R_p \]  \hspace{1cm} (1.8)

where \( R_T \) is the total resistance, \( R_s \) is the solution resistance, \( R_p \) is the polymer resistance, \( E_{app} \) is the potential applied by the external power source and \( i \) is the current flow along the polymer. \( R_p \) can be increased during the redox cycling. Lewis et al [125] showed that this change is exacerbated by using non-potentiostated two electrode systems. This effect will slow down the response and decrease the efficiency unless the actuators have high conductivity or are combined with a good electrical conductor that can minimize the \( iR \) drop.

Madden et al [126] used the resistance compensation technique to reduce \( iR \) drop so that the actuation strain rate was maximized with minimal polymer degradation. In their work, a shaped potential was applied which was initially large in magnitude then tapered as \( iR \) drop was diminished. In this process, the potential was adjusted so that the difference between the applied potential and the solution potential drop was less than or equal to a threshold voltage. This threshold voltage was chosen to be in a range at which polymer degradation
was minimal. Using this technique, the strain rate reached 1.3%/s which was about 10 times higher than other reported rates at that time.

To prevent and reduce the $iR$ drop along the actuators, some efforts have been made to improve the polymer inner electrical connection by introducing metal conductor into polymer actuators. A novel interconnect system with platinum (Pt) wire embedded in polypyrrole actuators was developed by Zhou et al [127]. A hollow polypyrrole tube with a thin helical platinum wire interconnect embedded in the inner wall was demonstrated and enabled the improvement of polypyrrole actuators [116] especially in terms of switching speed so that a maximum strain rate of 13%/s was achieved. Bay and co-workers [109] fabricated a polypyrrole actuator with a compliant gold (Au) electrode and proved that the additional gold electrode increased the actuation strain (12%). Hara et al [118] reported that polypyrrole was deposited on tungsten (W) micro-coil and formed a muscle fibre like actuator with 11.6% strain. Recently an electroactive paper actuator was also prepared by depositing polypyrrole onto a gold-coated cellophane paper and exhibited a maximum displacement of 9.1 mm and over 1000 life cycles [128]. These systems are all based on earlier work by Hutchison et al [129] with the effort to apply a platinum coating on one side of polypyrrole films. All these designs are aimed at reducing actuator $iR$ drop and hence improving the actuation performance.

Actuation strain is the most important factor to value in actuation performance. Conventional conducting polymer actuators produce 1-3% strain [15, 37, 119, 130]. However, actuation strain is remarkably increased by incorporation of metal inner connectors as described above. Recently an extremely large strain
(26%) produced by a TFSI-doped polypyrrole actuator using low potential scan rate (0.2 mV/s) was reported [131]. The large strain was due presumably to the large TFSI anion which could easily move in and out of the polymer. Further investigation on TFSI derivatives ((C_{n}F_{2n+1}SO_{2})_{2}N^-) as dopants conducted by the same group [122] revealed that the larger the size of the anion, the larger the strain is observed in the order of bis(nonafluorobutanesulfonylimide) > bis(heptafluorobutane-sulfonylimide) > bis(pentafluorobutanesulfonylimide) > bis(trifluorobutanesulfonylimide), i.e. NFSI (n=4) > HFSI (n=3) > PFSI (n=2) > TFSI (n=1). NFSI-doped polypyrrole exhibited 40% strain which is the largest strain reported to date. The reason was that the polymer films had gel like properties that enabled the polymer to swell enough for giant anion penetration. A large expansion of the film thickness was reported by Smela et al [132] with 35% strain for DBS-doped polypyrrole film. Even though extremely high strain was achieved, the fact that the actuators were operated under very low potential scan rate (0.2 mV/s ~ 10 mV/s) should be noticed because low strain rate is a limitation for practical applications.

Although large strains (> 10%) have been reported by a number of groups, the stability and life cycle are limited. For example, a TFSI-doped polypyrrole actuator produced 23% strain on the first cycle, but only about 14% strain was observed on the second cycle [131]. The instability of conducting polymer actuators is always a challenge for practical application. It has been shown that the operating cycle life of electrochemical devices, including conducting polymer actuators, was greatly increased by operating the devices in ionic liquid electrolytes [108, 133]. Up to 6000 operating cycles have been reported for polypyrrole actuators with only a 20% decrease in actuation strain. In
comparison, the same polypyrrole actuators operated in propylene carbonate electrolytes show a 75% decrease in strain after 3500 cycles [108]. Furthermore, when the actuators are operated under isotonic load, the strain decreases significantly at higher loads in propylene carbonate electrolyte but changes little in ionic liquid electrolyte [108]. This was later explained by the observation where changes of elastic modulus occur during electrochemical cycling in propylene carbonate [111] and ionic liquid [113].

In conclusion, the actuation performances of polypyrrole actuators are closely related to the dopant anion species, polymerisation conditions, actuator design and actuation operating conditions. A number of performance parameters need to be considered for practical applications, including strain, strain rate, force and stability. It is not yet known how all these properties are affected by all the causal factors.

1.2.3.3 Electrochemical Actuators Based on Polythiophene

Polythiophene and its derivatives are not as extensively employed for actuator materials as polypyrrole, however, some works have been carried out on the fabrication and characterisation of polythiophene based actuators. Fuchiwaki et al [134] reported a electrochemical actuator based on poly(3-alkyl thiophene). A strain of 3% with obvious creep was produced by the poly(3-alkylthiophene) film when tested in 0.2 M tetrabutylammonium tetrafluoroborate (TBA.BF₄) in acetonitrile electrolyte. Other than electrochemical actuators, Anquetil and co-workers [135] have developed polythiophene-based molecular actuators which are not driven by the mechanism of ion intercalation but by the molecular force to change the shape
of the polymer backbone. The bilayer beam bending test showed 21% strain produced by this poly(quarterthiophene) actuator.

Electrochemical polymerisation and characterisation of polythiophene from different thiophene monomers, namely thiophene, 3-methylthiophene, 3-ethylthio-phenone, were conducted by Sato et al [136]. Poly(3-methylthiophene) films were the most conductive among the as-grown films with a conductivity of 510 S/cm. The high conductivity and stability of poly(3-methylthiophene) are attractive properties for electrochemical devices such as actuators.

1.2.3.4 Electrochemical Actuators Based on Polyaniline and Polyaniline/Carbon Nanotubes

Polyaniline actuators are usually prepared by casting and drying polyaniline emeraldine base in NMP solution [36-40, 44, 47, 93, 107, 137, 138] and exhibit 1-3% linear strain. Dichloroacetic acid is also reported as polyaniline emeraldine base solvent to prepare polyaniline-graphite composite actuators [50]. Electrochemical polymerisation of aniline in acid solution is another technique used to fabricate polyaniline films that can perform swelling and shrinking changes upon redox switching [139]. However, using electrochemical polymerisation it is difficult to form free-standing films given that the polyaniline produced is powder-like and cannot be peeled off from the electrode.

The use of phase inversion techniques to prepare polyaniline films and fibres as chemical or electrochemical actuators has been reported [44, 47, 140]. Mazzoldi et al [140] reported that by using DMPU as polyaniline emeraldine
base solvent, polyaniline fibres could be spun into a water coagulation bath. The as-spun fibres could produce 0.3% strain. Gao et al [44] prepared polyaniline films by dissolving polyaniline emeraldine base in NMP then coagulating in a water bath. The resulting films showed bending-recovery movement when exposed to organic vapors. Instead of using water as the coagulation bath, hexane was employed to produce polyaniline films that possessed good electrochemically driven bending performance [47].

The actuation strains produced by polyaniline actuators have proved to be closely related to the size of the dopant anion used. Kaneto and co-workers [48] reported that an approximately linear increase in strain was observed for polyaniline films with the increasing of anion size. A detailed investigation on the relationship of actuation strain and anion size was conducted by Qi et al [141]. Their work indicates that for anions smaller than Br⁻, a large strain was obtained for a large anion; when the anion was larger than Br⁻, a large strain was produced by a smaller anion. As a result, the linear strain changes significantly but not linearly with the anion volume.

As described earlier in this chapter, the beneficial properties of carbon nanotubes have been utilised in constructing polymer/carbon nanotube composites. Several research groups [72, 74, 75, 77, 81, 83] have reported significant improvements in conductivity by incorporation of carbon nanotubes into polymers. Cadek et al [142] reported that the Young’s modulus of free-standing composite films of poly(vinyl alcohol) and carbon nanotubes were greatly increased with increased level of carbon nanotubes. The enhanced electrical and mechanical properties of polymer/carbon nanotube
composites suggests they should be promising materials for electrochemical actuators.

Polyaniline/carbon nanotube composite actuators were reported by Tahhan et al [79]. In their studies, the actuation of the composite film was dominated by polyaniline while carbon nanotubes provide a reinforcing effect that allows high strains to be maintained at high-applied stress. This was due to the incorporation of carbon nanotubes that reduced the Young’s modulus changes of the composites at their expansion and contraction states. These changes, theoretically, can result in the reduction of actuation strain under applied load [15, 111]. Since the practical applications often require the actuators to be operated under loads, the stability of strain is especially important for actuator development.

1.2.3.5 Modeling Conducting Polymer Actuator Performance

Conducting polymer actuator performance has been investigated both by experimental characterisation and by theoretically modeling. Based on the experimental results, the modeling approaches of the dependence of actuation strain on charge transferred [110] and on ion movements in polymer [95] were developed.

1.2.3.5.1 Strain vs Charge Modeling

The actuation strain produced by conducting polymer electrochemical actuators can be separated into two parts: the displacement due to the tensile force and the displacement from voltage stimulation. Madden et al [110, 143]
reported that the actuation strain $\varepsilon$ is proportional to the density of charge $\rho$ transferred according to:

$$\varepsilon = \frac{\sigma}{E} + \alpha \rho$$  \hspace{1cm} (1-9)

where $\sigma$ is the applied stress, $E$ is the elastic modulus, $\alpha$ is an empirically derived constant of proportionality referred to as the strain to charge ratio which is approximately $\pm 1\sim 5 \times 10^{-10}$ m$^3$·C$^{-1}$ [110]. In the case of cations dominating the ion transfer, the sign of strain to charge ratio is negative. When anions dominate the ion movement, however, the sign of strain to charge ratio will be positive [92]. The dominating ions are usually the smallest of the available cations and anions due to their higher mobility.

The strain to charge model is only effective when the stresses are less than 4 MPa [143]. When stress exceeds 4 MPa, the effects of creep and stress relaxation begin to become significant, so the strain is no longer linearly related to the stress and elastic modulus.

### 1.2.3.5.2 Osmotic Expansion Modeling

The expansion and contraction of conducting polymer actuators can also be separated into two parts according to the analysis by Bay et al [95]: one part from the changes of polymer backbone on reduction/oxidation and another part due to the osmotic expansion of the polymer phase. The osmotic effect causes solvent molecules to move into the polymer resulting in polymer volume changes. Under the external applied force, the polymer dimensional
change \( l \) will be a function of the redox state of the polymer determined by the potential \((E_p)\), the osmotic pressure difference \(\pi\) between the polymer and electrolyte and the mechanical pressure \(P\) from external applied force:

\[
l = f(\pi, P, E_p)
\]  

(1-10)

The osmotic pressure difference \(\pi\) can be given as

\[
\pi = RT \Phi_p c_p - RT \Phi_1 c_1
\]  

(1-11)

where \(\Phi_p\) and \(\Phi_1\) is the osmotic coefficient in the polymer and electrolyte, respectively, \(c_p\) and \(c_1\) is the concentration of free ions in the polymer and electrolyte, respectively.

This osmotic expansion model has been confirmed by the measurements of PPy/DBS films when tested in electrolytes with different concentrations [95]. The experiments clearly show that the expansion decreases with increasing electrolyte concentration. The osmotic expansion modeling suggests that the osmotic effect should be taken into account for actuator design and characterisation.

### 1.2.3.6 Demonstration Devices Using Conducting Polymer Actuators

More than a decade of research work into conducting polymer actuators has led to many application proposals. Some devices have been developed,
including a few leading demonstrations, such as micro-robots, Braille cells and propellers. These are described in the following.

**Micro-robots**

Several types of microactuators based on polypyrrole-gold bilayer have been developed by Lundstrom and co-workers [144, 145] from simple paddles to self-assembling and disassembling cubes. These conducting bilayers are used as hinges to connect rigid plates to a silicon substrate. By controlling the bending of the hinges, the position of the plates can be precisely controlled. These microactuator techniques are then extended to micro-robots [145] which can perform a series of actions, such as picking up, lifting, moving and placing micrometer sized objects in an aqueous medium. This micro-robot device can be operated not only in aqueous salt solution, but also in biological environments, such as blood plasma, urine and cell culture medium. Therefore, the micro-robot techniques have the potential to be developed for biomedical applications. For example they can be used for multistation single-cell diagnostics. Firstly the robot arm could catch certain biological entities (single cells, bacteria, multi-cellular organism, etc.) from a sample, and then the robot arm could transfer the entities to a certain area for diagnosing or checking.

**Braille cells**

A multi-dot Braille cell using conducting polymer actuators was developed by Wallace et al [146]. Based on this Braille cell, a two-dimensional Braille screen is possible to be constructed for visually impaired people to use with computers. The Braille cell consists of an array of pins that are each connected
with a polypyrrole hollow tube actuator with a platinum helix. These pins can be lowered or raised by the contraction and expanding of the actuators. By controlling the actuation of each actuator, the lowering or raising of pins can form the different patterned dots that visually impaired people can read. The use of ionic liquid electrolytes and the platinum helix wire have provided significant improvements in terms of the actuator cycle lifetime and strain rate, respectively, and have brought the electronic Braille screen a big step closer to reality.

**Propellers**

Madden et al [147] developed conducting polymer driven propellers that are used to drive hydrodynamic control surfaces and in particular to change the camber of a foil. The foil is intended for used in the propeller blade of an autonomous underwater vehicle. A trilayered actuator consisting of two thin sheets of polypyrrole sandwiching a layer of gel electrolyte is embedded within the blade. Application of a potential difference between the two polypyrrole sheets causes one sheet to expand and the other to contract, thus producing bending. The camber can be varied by the bending performance of the actuators.

**1.3 CONDUCTING POLYMER ACTUATORS – REMAINING CHALLENGES**

Challenges still remain in developing actuators with ideal performance. These are related to cycle life, performance under loads and low tensile strength.
1.3.1 CYCLE LIFE

Instability is common for conducting polymer actuators. For practical applications, the actuator should provide repeatable movement for many cycles with only occasional calibration. It is usual for the actuators to exhibit very large strain in the first few operating cycles but then suffer rapid degradation or overoxidation in the following cycles. The low cycle life is a barrier to further development of applications.

1.3.2 PERFORMANCE UNDER LOADS

The strain generated by the actuator is often decreased when the actuator is subjected to an external force. Some practical uses for actuators require the actuator to lift or move an object with a certain weight. In this case, the actuator should generate strain that is not reduced by the force applied while moving the weight. The decreases in strain with increasing loads need to be overcome to give good actuation stability under loads.

1.3.3 LOW TENSILE STRENGTH

Last but not least, the actuator material is often not strong enough for the practical applications as it usually can only tolerate approximately 5 MPa or less stress. Increasing the maximum breaking stress is another challenge to improve the actuator performance.

In general, the main drawbacks of conducting polymer actuators are their weakness and instability both in cycle life and under loads.
1.4 CONTRIBUTIONS OF THIS PROJECT

The aims of this thesis were to construct conducting polymer actuators with optimized actuation performance in terms of the actuator strain, work-per-cycle and stability. The actuation performances of conducting polymer actuators have been significantly improved in this project through the actuator designs, materials and characterisations.

1.4.1 ENHANCING ACTUATOR STRAIN STABILITIES

More reproducible and stable strain response from polypyrrole actuators has been achieved by the combination of current pulsing control as electrochemical stimulation and ionic liquid as electrolyte. Current pulsing ensures that the oxidation and reduction processes are equal in their magnitude and prevents the slow net oxidation (or reduction) that typically occurs during symmetrical voltage cycling. Ionic liquid electrolytes permit higher current densities to be applied to the polymer because the polymer can endure wider a potential window in ionic liquids. Also operation of polypyrrole actuators in ionic liquids produces much smaller changes in elastic modulus and results in a more stable isotonic strain with increasing applied loads.

1.4.2 INCREASING STRAIN WITH INCREASING LOADS IN IONIC LIQUIDS

The effects of modulus shift during actuation have been investigated for polypyrrole, polyaniline and polythiophene in various electrolytes. Increasing strain response from polythiophene actuators was observed under
increasing applied loads when operated in ionic liquids as electrolytes. In ionic liquid, the Young’s modulus slightly increases from the expansion to contraction state. According to the relationship between the polymer displacement and Young’s modulus \([15, 111]\), the polymer displacement under loads is increased with the increasing loads. This is the first time for conducting polymer actuators exhibit an increasing strain with increasing applied loads. Based on this unique property, polythiophene can be considered as a promising material for developing artificial muscles.

1.4.3 INCREASING ACTUATOR’S MAXIMUM STRESS

Increased stress was achieved from composite actuators by incorporation of carbon nanotubes into polyaniline. The incorporation of CNT into PAn fibre has significantly improved the actuation strain stability, maximum stress and Young’s modulus of the composite materials. 2.5% carbon nanotubes loading in polyaniline can increase the breaking stress from 14 MPa to 30 MPa for neat polyaniline actuators and composite actuators, respectively.

1.5 ORGANIZATION OF THIS THESIS

After the general introduction given in this chapter, general experimental methods used in this project are described in chapter 2. This includes techniques used for polymer actuator preparation, polymer characterisation and actuation testing.
Polypyrrole actuators are investigated in chapter 3. The effect of electrochemical stimulation (current pulsing vs voltage cycling), different electrolytes (ionic liquid and propylene carbonate), dopants and the effect of temperature on performance are investigated.

The actuation performance of polythiophene actuators is described in chapter 4 with an unexpected finding of increasing strain with applied loads reported.

In chapter 5, polyaniline actuators in different geometrical configurations were prepared using the phase inversion technique. The effect of electrolytes, microstructure, and geometrical configuration on actuation performance is discussed.

Conducting polymer/carbon nanotube composite actuators are investigated in Chapter 6. Layered composite actuators consisting of polypyrrole, polyaniline and carbon nanotubes were constructed and characterized in the first part of this chapter. In the second part, polyaniline/carbon nanotube composite fibre actuators were prepared using a wet-spinning process. The presence of carbon nanotubes allowed high stresses applied to the composite actuators. It has confirmed that the actuation performance of the composite actuators is enhanced by the carbon nanotubes as reinforcement fillers in conducting polymers.

Finally a general conclusion is given in chapter 7.
1.6 REFERENCES


Chapter 1 General Introduction

Chapter 1 General Introduction


CHAPTER 2

EXPERIMENTAL TECHNIQUES
2.1 INTRODUCTION

The experimental techniques used in this thesis are briefly described in this chapter, including the techniques for polymer actuator preparation, characterisation and actuation tests. The general procedures are described below. Details of specific procedures will be given in the experimental part of each corresponding chapter.

2.2 TECHNIQUES USED FOR CONDUCTING POLYMER ACTUATOR PREPARATION

The techniques used for conducting polymer actuator preparation in this thesis included electrochemical polymerisation and polymer solution processing.

2.2.1 ELECTROCHEMICAL POLYMERISATION

In this thesis, polypyrrole and polythiophene actuators were prepared electrochemically in a polymerisation cell.

2.2.1.1 Polymerisation Cell Design

There were two types of electrochemical cells employed, one for electrochemical polymerisation and one for actuation testing. Although used for different purposes, the cells have similar constructions that usually consist of a working electrode, an auxiliary electrode and a reference electrode.
For electrochemical polymerisation, a two-electrode cell was used, as shown in Figure 2-1.

![Diagram of electrochemical polymerisation cell](image)

**Figure 2.1:** The electrochemical polymerisation cell used for actuator preparation.

The working electrode material was of critical consideration because it has a marked effect on the polymer’s microstructure, which in turn influences the mechanical properties of the polymer [1]. For example, strong, dense and flexible coatings can be obtained on platinum electrodes, whereas brittle, rough and stiff films are usually deposited on aluminum electrodes [2]. The working electrode material also should be stable under the polymerisation condition employed to prevent the oxidation of the electrode itself. The working electrode requires a geometry that is suitable for producing polymer in the desirable size and shape. In this thesis, the working electrode was a 250 μm platinum wire with a 50 μm platinum wire wound around it as a helix. The polymer was deposited on the platinum wire working electrode. The details of the polymerisation process are described in Chapter 3.
Chapter 2 Experimental Techniques

The auxiliary electrode material should be inert and capable of maintaining rapid cathodic reactions to keep the desired polymerisation rate at the working electrode surface [1]. It should have a large surface area to allow the passage of current, ideally 10-100 times larger than the working electrode. The most common auxiliary electrodes are stainless steel, platinum or carbon. In this thesis, the auxiliary electrode in the polymerisation cell was a piece of stainless steel mesh.

2.2.1.2 Electrochemical Polymerisation

According to the control of electrical signals, electrochemical polymerisation approaches can be divided into different types, namely galvanostatic, potentiostatic and potentiodynamic polymerisation. Galvanostatic polymerisation is a widely used technique and was employed to prepare polypyrrole and polythiophene actuators in this thesis.

During galvanostatic polymerisation, a constant current is applied between the working electrode and auxiliary electrode. Under the applied current, monomers are oxidized at the anode and eventually form a polymer coating. The thickness of the deposited polymer can be controlled by varying the current density and deposition time (i.e. charge). The amount of total charge passed, $Q$, can be easily calculated according to:

$$Q = it$$ (2.1)

Where $i$ is the current and $t$ is the deposition time. By controlling the total charge passed during polymerisation, it is possible to control the amount of
polymer formed. The magnitude of the current density applied during polymerisation is also known to affect the surface morphology, conductivity and mechanical properties of the polymer [3].

The polymerisation temperature is another factor that affects polymer properties. The conductivity of polymers decreases with increasing temperature, however at temperatures that are too low, no coherent polymer films can be obtained [4]. In this thesis, polypyrrole actuators were electropolymerized at -28~−25°C, and polythiophene actuators were electropolymerized at 0~5°C.

2.2.2 POLYMER SOLUTION PROCESSING

In this thesis, polyaniline actuators and polyaniline/carbon nanotubes composite actuators were prepared by processing polyaniline or polyaniline/carbon nanotubes solutions into different geometrical actuators using the phase inversion technique. As shown in Figure 2.2, polyaniline emeraldine base can be dissolved in DMPU (10 wt%) to form a viscous and homogeneous solution. The solution was cast onto different substrates, such as glass slides or platinum wires, and then immersed into a coagulation bath to allow the solvents be extracted out and form the solidified polymer. Then the polymer was separated from the substrate to leave the free-standing polyaniline films or tubes.
The wet spinning process was also used to produce polyaniline and polyaniline/carbon nanotubes composite fibres. The fibre spinning process was conducted in our laboratory by Mr. Vahid Mottaghitalab, and is shown in Figure 2.3. After dispersion of carbon nanotubes into polyaniline solution the spinning process was carried under Nitrogen (N₂) pressure. The spinning fibres were immersed in the coagulation bath to form the solidified polyaniline/carbon nanotubes composite fibres.
2.3 TECHNIQUES USED FOR POLYMER CHARACTERISATION

2.3.1 Cyclic Voltammetry (CV)

Cyclic voltammetry is the most convenient and reliable electrochemical technique to elucidate the nature of electrochemical process. It involves the measurement of current at the working electrode as a function of the applied potential. The resulting current-potential curve is termed a cyclic voltammogram. Cyclic voltammetry provides a rapid determination of chemical/electrochemical transitions occurring, the potentials at which these
occur, and the rate of these transitions. It is the most effective and versatile electrochemical technique available for the study of redox reactions.

In cyclic voltammetry, the potential is scanned at a given scan rate from an initial value to a final value and then back to the initial value. The current is monitored during the application of the triangular potential waveform (Figure 2.4).

![Figure 2.4: The triangular potential waveform and resultant current in a cyclic voltammetric experiment.](image)

Figure 2.5 shows a typical cyclic voltammogram for a reversible redox process. The voltammogram is characterized by a peak potential $E_{pa}$ (peak anodic potential) or $E_{pc}$ (peak cathodic potential), at which the current reaches the maximum value $i_{pa}$ (peak anodic current) or $i_{pc}$ (peak cathodic current).
Figure 2.5: Cyclic voltammogram of poly(3-methylthiophene) in EMI.TFSI at a scan rate of 50 mV/s.

The anodic and cathodic potential peaks do not appear at the same potential. The difference between these peaks depends on the actual electrode process and the charge transfer rate. For a reversible system, the potential difference is estimated as [5]:

$$\Delta E = E_{pa} - E_{pc} = 0.059 / n \ (V) \quad \text{at 25}^\circ \text{C}$$ (2.2)

where $n$ is the number of electrons transferred in the redox process. A quasi-reversible system shows a greater separation in peak potentials than that in a reversible system, i.e. $\Delta E > 0.059/n \ (V)$. In this case, the cyclic voltammograms are also broader, indicating a slow charge transfer rate. For an irreversible system, a complete separation of anodic and cathodic peaks would
occur in the cyclic voltammogram, reflecting a very slow charge transfer in such an electrode process.

2.3.2 Electrical Conductivity

Electrical conductivity is a fundamental property of conducting polymers; all the applications are based on their remarkable ability to conduct electric current. The accurate measurement of conductivity is an important step to understand and value conducting polymers.

The conductivity of a conducting polymer is generally measured using the ASTM (American Society for Testing and Material) four-point probe technique [6]. It involves using four electrodes that are arranged in a pattern as shown in Figure 2-6.

![Image of ASTM four point probe](image)

**Figure 2.6:** Top view of the ASTM four point probe used for conductivity measurement.
The polymer film to be tested is placed in contact on top of the four electrodes and then tightly sandwiched with an insulating top layer. A constant current \( i \) is applied between the outer electrodes and the voltage drop across the inner two electrodes is measured. According to Ohm’s Law, the resistance of the material is proportional to the potential drop. The resistivity can be calculated according to the cross-section area of the polymer film and the potential drop:

\[
\rho_s = \frac{whv}{il} \quad (2.3)
\]

where \( \rho_s \) is the surface resistivity, \( w \) is the sample width, \( h \) is the sample thickness, \( v \) is the potential drop across the two inner electrodes, \( i \) is current applied, \( l \) is the distance between the two inner electrodes.

The conductivity \( \sigma \) of the sample is given as:

\[
\sigma = \frac{1}{\rho_s} \quad \text{or} \quad \sigma = \frac{il}{whv} \quad (2.4)
\]

This method is widely used for the measurement of the electrical conductivity of conducting polymers. It should be mentioned that this method is based on a simple pattern of virtually parallel current stream-lines. The measurement might be affected by the uniformity of the actual current distributions and the unevenness of sample thickness.
2.3.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is widely used for the study of the morphology and microstructure of conducting polymers. It involves scanning of an electron beam across a sample surface and secondary electrons are ejected from the surface. Upon interacting with a solid, secondary electron images are generated by synchronizing the optical output of the detector system with the raster of the electron probe across the solid surface. SEM images are used to examine the surface morphology and microstructure or to investigate the inner microstructure from fracture cross-sections.

2.4 TECHNIQUES USED FOR ACTUATION TESTS

In this thesis, the early work of actuation tests was carried out on a beam balance before the purchase of a Dual Mode Lever System. Both systems employ an electrochemical cell and work in a similar way.

2.4.1 Electrochemical Cell Design

For actuation testing, the electrochemical cell was a two-electrode or three-electrode system depending on the use of a reference electrode. The working electrode was the polymer actuator and the auxiliary electrode was a piece of stainless steel mesh. In most cases the two-electrode cell was used. This was because practical actuator applications are likely to be used in the two-electrode arrangement. The two-electrode system offers a simple power supply instead of a potentiostat needed for the three-electrode system. In some cases the three-electrode system is used because the use of a reference
electrode enables the applied potentials to be measured or controlled relative to a constant value. In such cases an Ag/AgCl reference electrode was used in aqueous electrolyte, whilst in organic solvents, a Ag/Ag\textsuperscript{+} reference electrode was employed [7]. A two-electrode electrochemical cell used for actuation tests is shown in Figure 2.7.

**Figure 2.7:** The electrochemical cell used for actuation test.

### 2.4.2 Beam Balance

Actuation tests using a beam balance is shown schematically in Figure 2.8. The sample is maintained under tension during testing. The addition or removal of counter-weight from the sample side of the beam is used to alter the amount of force applied to the sample. An electrochemical cell is used where the sample is fully immersed in electrolyte. The extension/contraction
of sample was measured by a Linear Variable Distance Transducer (LVDT) and recorded by a computer.

**Figure 2.8:** Schematic diagram showing beam balance apparatus for measuring actuation strain under isotonic condition.

### 2.4.3 Dual Mode Lever System

As shown in Figure 2.9, a Dual Mode Lever System (Aurora Scientific Inc) was used for most actuation tests. The sample extension/contraction was measured by the movement of the arm on which the sample was attached. The extension/contraction was then recorded by a computer. The force can be
controlled by adjusting the force control from the dual mode lever system. Two system modes, 300B and 305B were used with a maximum force output of 500 mN or 5000 mN, respectively.

Figure 2.9: Dual mode lever system used for actuation test (a) and sample in an electrochemical cell (b).
2.5 REFERENCES


CHAPTER 3

PREPARATION AND CHARACTERIZATION OF ACTUATORS BASED ON POLYPYRROLE
3.1 INTRODUCTION

The practical application of conducting polymer actuators requires a stable strain response and a high degree of reproducibility from sample to sample. However, low cycle life, drift (creep), low efficiencies and lack of repeatability are common in actuator materials based on conducting polymers. Research work has demonstrated that the operating cycle life of electrochemical devices based on conducting polymers, including electromechanical actuators, was greatly enhanced by operating the devices in ionic liquid electrolytes \[1, 2\]. It has also been shown that significant difference in the mechanism of actuation for polypyrrole occurs when operated in ionic liquids (IL) as compared with propylene carbonate (PC) electrolyte \[2\]. For example, it has been shown that the isotonic strain decreases significantly in propylene carbonate electrolyte, while it changes very little in ionic liquid electrolyte \[2\]. Further studies showed that the isotonic performance of polypyrrole actuators is limited by the large changes in elastic modulus that can occur during electrochemical cycling in propylene carbonate electrolyte. A decrease in modulus of up to 5 times has been observed \[3\] and this reduction causes elastic stretching of the actuator material when subject to a tensile load that partially counteracts the simultaneous contraction due to the actuation process.

In this study, the use of conventional voltage cycling to control the actuation of polypyrrole is shown to result in a slow net oxidation of the polymer after several tens of cycles and leads to a sluggish deterioration in the actuation strain. The use of current pulsing reduces this problem and gives a more stable strain response. The operation of polypyrrole actuators in ionic liquid
electrolytes is further examined in combination with current control and confirms the enhanced stability and reproducibility of the actuation performance. The effect of dopant anions, potential scan rates and electrolyte temperature on actuation performance are also investigated in this study.

3.2 EXPERIMENTAL

3.2.1 Reagents and Materials

Propylene carbonate (PC, obtained from Aldrich), tetrabutylammonium hexafluorophosphate (TBA.PF₆, obtained from Sigma), tetrabutylammonium bistrifluoromethanesulfonimide (TBA.TFSI, obtained from Fluka), lithium bistrifluoromethanesulfonimide (LiTFSI, obtained from Fluka) and methyl benzoate (obtained from Aldrich) were all AR grade and used as received. Pyrrole monomer from Merck was distilled and stored under -18°C before use. Platinum wires in 250 µm and 50 µm diameter were from Goodfellow. The ionic liquid (IL) electrolyte ethylmethylimidazolium bistrifluoromethanesulfonimide (EMI.TFSI) was synthesised in-house using the method of Bonhote et al. in two steps [4]. Firstly, 1-ethyl-3-methylimidazolium bromide (EMI.Br) was synthesized by vigorous stirring of 1.35 mol of bromoethane (Aldrich) and 0.45 mol of 1-methylimidazole (Aldrich) for 24 hours, the resulting solid (EMI.Br) was washed with ether and dried. In the second step, equivalent mole of EMI.Br and Li.TFSI (Aldrich) were dissolved in water and stirred vigorously for a few hours. The resulting ionic liquid (EMI.TFSI) layer was separated, dried, and decolourised from charcoal.
3.2.2 Instrumentation

The current required for polymerisation and during actuation were applied using an EG & G Princeton Applied Research Model 363 potentiostat/galvanostat. A cyclic potential with a 50 mV/s scan rate was applied using a Voltammograph CV-27 (Bioanalytical Systems Inc). The actuation tests were conducted on a beam balance or a Dual Mode Lever System 300B. All the experimental data was processed with a MacLab/4e AD Instrument and computer.

3.2.3 Polypyrrole Actuator Preparation

Polypyrrole was synthesised electrochemically using a polymerisation cell as described in Chapter 2. Polypyrrole actuators were grown galvanostatically for 20 hours using a current density of 0.15 mA/cm². The polymerisation solution was propylene carbonate containing 0.06 M pyrrole and 0.05 M TBA.PF₆. The polymerisation temperature was controlled around -25°C to -28°C. A two-electrode configuration was used; the working electrode was a 250 µm platinum wire around which a 50 µm platinum wire was wound as a helix. The auxiliary electrode was a stainless steel mesh. After growth, the 250 µm platinum wire was pulled out leaving a hollow polypyrrole tube containing the thinner platinum wire embedded as a helix in the tube wall. For actuation tests, two pieces (length: ~3 cm) of 250 µm platinum wire were then inserted into each end of the polypyrrole helix tube to enable electrical connection. The connections were sealed by hot-melt polystyrene. Polypyrrole tubes were stored wet in propylene carbonate containing 0.25 M TBA.PF₆ before testing. Details of the “helix tube” manufacture and performance have
been reported previously [5] and the steps involved are summarised in Scheme 3.1.

Scheme 3.1: Schematic diagram showing method of construction of polypyrrole tube actuator with platinum wire embedded as helix [5].

TFSI-doped polypyrrole actuators were prepared using the same approach. In this case the polymerisation solution was methyl benzoate containing 0.25 M pyrrole and 0.2 M TBA.TFSI. The polymerisation temperature was controlled around 0~5°C. A current was applied for 6 hours using a current density of 0.2 mA/cm².
3.2.4 Actuation and Mechanical Tests

The actuation performance of polypyrrole helix tubes was tested on a beam balance or a Dual Mode Lever System 300B (Aurora Scientific Inc) as described in Chapter 2. The extension/contraction of the sample was measured by LVDT (Linear Variable Distance Transducer) and recorded by computer.

A two-electrode configuration was used when the effects of cyclic potential and pulse current applied as electrochemical stimulation were compared. 0.25 M TBA.PF₆ in PC or the ionic liquid EMI.TFSI were employed as electrolyte solutions. Mechanical properties (elastic modulus) of the polypyrrole helix tubes were measured in both electrolytes at different applied potentials using the force/length controller of Dual Mode Lever System 300B. The actuator was stretched continuously to a maximum force of 30 mN and then returned to the original length. The initial unloading portion of the stress/strain curve was used to estimate the elastic modulus.

3.3 RESULTS AND DISCUSSION

3.3.1 Polypyrrole Helix Tube Actuators

Figure 3.1 shows photographs of the polypyrrole tube actuators with a platinum wire helix embedded. The conductivity of the polypyrrole helix tube was 486 S/cm, which is much higher than polypyrrole tube without a helix (123 S/cm). The polypyrrole tubes prepared under low current density (0.15 mA/cm²) and low temperature (-25°C to -28°C) had a smoother appearance than those grown at high current density (1 mA/cm²) and room temperature.
Figure 3.1: Photographs of PPy/PF$_6$ tube actuators with platinum wire embedded as helix.

3.3.2 Improvements of Polypyrrole Actuator Stability

3.3.2.1 The Effect of Cyclic Potential Control and Pulse Current Control on Actuator Cycle Life

The polypyrrole helix tube actuator was tested in 0.25 M TBA.PF$_6$ in PC while the potential was scanned between ±2.5 V at a scan rate of 50 mV/s (i.e. cyclic potential). The potential waveform and the current flow are shown in Figure 3.2.
Figure 3.2: Chronoamperograms for voltage cycles between ± 2.5 V. Integration of the anodic and cathodic waves shows a difference in the amount of oxidation and reduction occurring.

In Figure 3.2 the current flow for multiple voltage cycles for the helix tube actuators is shown. Integration of the current for the oxidation and reduction waves indicates that the charge passed through the oxidation and reduction processes are different. During one oxidation cycle a charge of +127 mC is consumed, whilst the reduction process consumes only −117 mC per cycle. This observation indicates that the polymer is becoming progressively oxidised during repeated cycling, leading to a lower capacity to generate movement after several tens of cycles. With each cycle the polymer became slightly more oxidised so that in the subsequent cycle there was slightly less capacity for further oxidation leading to less expansion (strain) in the polymer (Figure 3.3). The actuation strain decreased by ~30% during the first 20-30 cycles.
Figure 3.3: Isotonic strain measured at a fixed applied stress (0.165 MPa) and cycled for 100 voltage cycles (+/-2.5V) in 0.25 M TBA.PF₆/PC electrolyte.

It was also observed that almost full recovery of the actuation strain occurred if the sample was left standing in the electrolyte solution (no potential applied) overnight. A similar observation was made by Lu et al with their studies on polypyrrole actuation in ionic liquids [1]. It was speculated that when left standing in the electrolyte solution the polymer returned to an equilibrium state because the voltage cycling used during the actuator testing did not produce exactly equivalent oxidation and reduction reactions in the polymer. The resting allowed the excess oxidation in the polymer to decay through parasitic reactions with the environment so that when voltage cycling was resumed, the original amount of strain was again observed.
In an attempt to overcome the problem of asymmetric redox cycling, the effect of current pulsing compared with voltage cycling was investigated. Figure 3.4 shows the pulse current waveform and the potential response. Current was applied to the sample and switched from positive to negative value for every 30 seconds. Integration of the current for the oxidation and reduction processes is of course exactly the same.

![Chronopotentiograms for pulse current cycles between ± 1 mA.](image)

Integration of the anodic and cathodic waves shows the same amount of oxidation and reduction occurring.

**Figure 3.4:** Chronopotentiograms for pulse current cycles between ± 1 mA. Integration of the anodic and cathodic waves shows the same amount of oxidation and reduction occurring.

The effect of current density on the actuation performance was then investigated (Figure 3.5). A linear trend between the strain produced and the current density applied was observed. A sudden decrease in strain occurred at a current density of ~25 mA/cm² probably due to over-oxidation of the polymer. The peak potential reached during the current pulse increased with
increasing current density, with selected values shown in the figure. The fall off in actuation strain corresponds to a peak potential of –6 V for reduction and +5 V for oxidation (measured in a two-electrode system) which may cause polymer overoxidation.

Figure 3.5: Isotonic strain measured when a current pulse was applied for 30s in 0.25 M TBA.PF<sub>6</sub>/PC electrolyte. Peak potentials measured during the positive and negative current pulses are shown for certain current pulses.

The linear dependency on strain with applied current shown in Figure 3.5 is similar to that reported previously. For example, Otero and co-workers [6] have shown that the movement of bilayer devices using polypyrrole coatings on either side of a flexible substrate is directly proportional to the applied current per mass of polymer. The current applied to the polymer controls the amount of electrochemical reaction that, in turn, dictates the degree of doping of the polymer. Since the volume changes in conducting polymers are due to
ion/solvent movements and conformational changes associated with doping, it is obvious that the degree of movement (bending or axial) should be proportional to the current applied.

The stability of the helix tube actuators was examined by cycling at fixed current densities for 100 cycles. In Figure 3.6, the strain for the first 100 cycles during current pulsing is shown to be very stable when a low current density was used (5 mA/cm$^2$) but only remained stable for around 30 cycles when a higher current density was used (12 mA/cm$^2$). The current pulsing maintains equivalent oxidation and reduction of the polypyrrole only when there are no parasitic redox reactions occurring. The results show that at the higher current density, such reactions may occur and result in lower cycle stability of the polypyrrole actuator.

![Figure 3.6](image)

*Figure 3.6:* Strain produced during the first 100 cycles of current pulsing at two different current densities for 30 s in 0.25 M TBA.PF$_6$/PC electrolyte.
By comparing the results in Figure 3.3 and Figure 3.6, it can be concluded that the actuator cycle life stability is improved by using pulse current control for electrochemical stimulation.

3.3.2.2 Effect of Organic Solvent and Ionic Liquid as Electrolytes on Actuator Cycle life

It has been shown from the above results that with pulsed current stimulation, polypyrrole actuators can maintain a stable strain at low current density when operated in propylene carbonate electrolyte. By utilising ionic liquid (EMI.TFSI) as electrolyte, further improvements in stability were observed in combination with pulsed current control (Figure 3.7). Strains of 1%, 2% and 3% at 6 mA/cm², 12 mA/cm², and 16 mA/cm² applied current densities, respectively were obtained. The strain remained constant even when high current densities (16 mA/cm²) were applied producing relatively large strains (3%).
Figure 3.7: Strain produced during the first 100 cycles of current pulsing at different current densities for 30 s in EMI.TFSI electrolyte.

The benefit of ionic liquids in terms of longer cycle life has previously been ascribed to the higher electrochemical stability of the ionic liquid compared with other electrolytes [1]. The electroactivity of polypyrrole is also shown to be stable in ionic liquid but is reduced in propylene carbonate when the polymer is scanned over the same potential ranges (−1 V to +1.55V vs Ag/Ag⁺) [2]. To investigate the potential limit at which polymer will be overoxidised and lose electroactivity, cyclic voltammograms of polypyrrole in propylene carbonate and ionic liquid EMI.TFSI were obtained (Figure 3.8 and Figure 3.9). Polypyrrole was overoxidised at +1.55 V in propylene carbonate, however in EMI.TFSI, polypyrrole started to lose electroactivity at +1.75 V. The cyclic voltammogram of polypyrrole reported by Ding et al [2] showed no degradation of electroactivity in EMI.TFSI in the same potential window (−1 to 1.55 V) as in Figure 3.8. Ionic liquid allows a wider potential window for
polypyrrole than propylene carbonate. As a result, in ionic liquid, higher current can be applied to polypyrrole actuators and leads to a higher stable strain without polymer degradation.

Figure 3.8: Cyclic voltammogram of PPy/PF$_6$ in 0.25 M TBA.PF$_6$/PC at 100 mV/s scan rate, potential window: -1 V to 1.55 V (vs Ag/Ag$^+$).
It is apparent from the present study that a high current density applied to the polymer in the propylene carbonate electrolyte produces sufficiently high potentials to begin to degrade the electrolyte. It is believed that the degradation products of this reaction then attack the polymer so that the conductivity is reduced and subsequent electroactivity is greatly reduced. In ionic liquids these degradation reactions do not occur until much higher potentials are achieved (at higher current densities), so it is possible to maintain stable polymer electroactivity at higher current densities.

**Figure 3.9:** Cyclic voltammogram of PPy/PF$_6$ in EMI.TFSI at 100 mV/s scan rate, potential window: -1 V to 1.75 V (vs Ag/Ag$^+$).
3.3.2.3 Effect of Organic Solvent and Ionic Liquid as Electrolytes on Actuator Stability under Load

The effect of applied stress on the isotonic strain produced by polypyrrole actuators was examined when the actuators were operated in propylene carbonate or the ionic liquid EMI.TFSI. As shown in Figure 3.10, in propylene carbonate electrolyte, actuation strain decreased quickly with increased stress, whereas a reasonably stable strain can be maintained in the ionic liquid EMI.TFSI. The polypyrrole actuator shows a 75% decrease in strain in propylene carbonate before breaking at 3.7 MPa. In comparison, when the actuator is operated in ionic liquid, only a 20% decrease in strain is observed before breaking at 4.5 MPa.

![Graph showing strain under different stress levels in propylene carbonate (PC) and ionic liquid (IL)](image_url)

**Figure 3.10:** Actuator strain recorded under isotonic conditions at different stress levels in 0.25 M TBA.PF₆/PC and ionic liquid EMI.TFSI electrolytes. A current pulse for 30 s was applied at 12 mA/cm².
The results shown in Figure 3.10 confirm the findings reported by Ding et al [2] showing a smaller decrease in actuation strain with increasing isotonic stress when the polypyrrole helix tubes were tested in ionic liquid compared with propylene carbonate.

The relationship between the actuation strain and the applied stress was first analysed by Baughman [7] and in more detail by Spinks and Truong [8] and Tahhan et al [9]. The total strain is the sum of the strain from electrochemical stimulation and the strain from external force. From this analysis, the following equation can be obtained:

\[ \Delta L_f = \Delta L_o + \frac{fL_o}{A} \left( \frac{1}{Y_d} - \frac{1}{Y_o} \right) \]  

(3.1)

where \( \Delta L_f \) is the displacement with a constant load \( f \); \( \Delta L_o \) is the displacement without load; \( L_o \) is the sample length at the contracted state without load; \( A \) is the cross sectional area; \( Y_d \) is the Young’s modulus at the expanded state and \( Y_o \) is the Young’s modulus at the contracted state.

From Equation 3.1 it can be seen that the Young’s modulii change in the contracted vs the expanded states determines the slope of the actuation strain vs stress line. If \( 1/Y_d = 1/Y_o \), (i.e. \( Y_d = Y_o \)), the actuation strain will remain independent with increasing load. If \( 1/Y_d > 1/Y_o \), (i.e. \( Y_d < Y_o \)), the actuation strain will increase with increasing load. On the other hand, If \( 1/Y_d < 1/Y_o \), (i.e. \( Y_d > Y_o \)), the actuation strain will decrease with increasing load. The relationship between strain vs applied stress curve and Young’s modulii in the contracted and expanded states is shown schematically in Figure 3.11.
Figure 3.11: The relationship between strain vs applied stress and Young’s modulii at the contracted and expanded states.

The Young’s modulus of the polypyrrole helix tube actuator was measured in ionic liquid EMI.TFSI at different applied potentials. The results are compared with the Young’s modulus measured in propylene carbonate (from reference [3]) in Figure 3.12.

In the case of propylene carbonate, the modulus decreases substantially at –2.5 V and increases sharply above +2.5 V (potential difference between two electrodes). The result of this modulus change is that the sample contracts (whilst under tension) when the voltage is switched from –2.5 V to +2.5 V (or from a positive current to a negative current). This contraction is proportional to the applied stress and partially counteracts the expansion due to the ion flow to the polymer caused by polymer oxidation. The measured actuation is the net length change resulting from the oxidation-induced expansion and the contraction caused by the modulus increase. At higher stress levels, the net
expansion becomes smaller. The experimental results in Figure 3.10 and Figure 3.12 have confirmed the relationship addressed in Equation 3.1.

![Graph showing modulus values for actuators](image)

**Figure 3.12:** Modulus values measured for PPy/PF₆ actuators in 0.25 M TBA.PF₆/PC and ionic liquid EMI.TFSI electrolytes.

In contrast, the elastic modulus of the polypyrrole in ionic liquid changes little with applied voltage within the range tested (Fig. 3.12). As a consequence, the length change in the polymer due to changing voltage (or current) is due almost entirely to the ion flow into and out of the polymer accompanying polymer reduction and oxidation, respectively. The isotonic strain, therefore, is virtually independent of the applied stress.
3.3.2.4 Reproducibility of Polypyrrole Actuators Operated in Ionic Liquid Using Pulsed Current

The reproducibility of performance in a number of polypyrrole helix tube actuators was examined. Five samples of polypyrrole helix tube actuators were tested in ionic liquid EMI.TFSI using pulsed current and at a constant stress. The strain range and average values observed are shown in Figure 3.13.

![Figure 3.13](image)

**Figure 3.13:** Average and standard deviations in actuation strain obtained for five identically prepared PPy/PF$_6$ helix tube actuators operated in ionic liquid EMI.TFSI electrolyte under current pulsing control.

As shown in Figure 3.13, the reproducibility of polypyrrole actuators is excellent with a variation of only 0.1% in the actuation strain observed at each current density used.
3.3.3 Work-Per-Cycle Performed by Polypyrrole Actuators

The work performed per expansion/contraction cycle, i.e. work-per-cycle is an important parameter in evaluating the performance of actuators. The work-per-cycle, $W$, can be defined under isotonic conditions as:

$$W = f\Delta l_f$$  \hspace{1cm} (3.2)

where $\Delta l_f$ is taken as the displacement produced by one expansion or contraction cycle under a load $f$.

The maximum work-per-cycle defines how effectively the actuator can perform mechanical work. The amount of the maximum work-per-cycle is often expressed as per volume or per mass of the actuator material. The calculation of work-per-cycle has been analysed by Baughman [7] and more details are given by Spinks et al [8, 10]. Based on Equation 3.1 and Equation 3.2, the work-per-cycle can be calculated according to:

$$W = f\Delta l_o + \frac{f^2 L_o}{A} \left( \frac{1}{Y_d} - \frac{1}{Y_o} \right)$$  \hspace{1cm} (3.3)

where $W$ is the work-per-cycle performed by the actuator. The analysis can also be extended to show that the maximum volumetric work ($W_V$) and gravimetric work ($W_G$) are given by:

$$W_V = \frac{1}{4} \varepsilon_o^2 \left( \frac{Y_o Y_d}{Y_o - Y_d} \right) \text{ (J/m}^3\text{)}$$  \hspace{1cm} (3.4)
\[ W_G = \frac{1}{4\rho} \varepsilon_o^2 \left( \frac{Y_d Y_o}{Y_o - Y_d} \right) \text{ (J/kg)} \]  

(3.5)

where \( \varepsilon \) is the actuation strain without external load, \( \rho \) is the actuator material density, and the maximum work occurs at an applied force of

\[ f = \frac{1}{2} \frac{\Delta L_o A}{L_o} \left( \frac{Y_d Y_o}{Y_o - Y_d} \right) \]  

(3.6)

In ionic liquid EMI.TFSI, the Young’s modulii at the contracted and expanded states are 80 MPa and 86 MPa, respectively. However, in propylene carbonate, Young’s modulii at the contracted and expanded states are 90 MPa and 120 MPa, respectively. Given that the strains without load \( \varepsilon_o \) in ionic liquid and propylene carbonate are 2.1% and 1.6%, respectively, the maximum work-per-cycle (\( W_V \)) can be calculated according to Equation 3.4 as 79 kJ/m\(^3\) in ionic liquid and 25 kJ/m\(^3\) in propylene carbonate. It can be seen that the work-per-cycle achieved in ionic liquid is substantially higher than that achieved in propylene carbonate under current control. The calculated results are in good agreement with the experimental results in Figure 3.14 according to Equation 3.2. As shown in Figure 3.14, the maximum measured value of work-per-cycle performed by polypyrrole actuators is 76 kJ/m\(^3\) in ionic liquid and 28 kJ/m\(^3\) in propylene carbonate.
Figure 3.14: Work-per-cycle performed by PPy/PF$_6$ helix tube actuators under different stress levels in 0.25 M TBA.PF$_6$/PC and ionic liquid EMI.TFSI electrolytes.

3.3.4 The Effect of Dopant and Potential Scan Rate on Actuation Performance

As described in Chapter 1, the actuation behaviour is closely related to dopant anion species, size and mobility. In Hara et al’s report [11], an extremely large strain (26%) was produced by polypyrrole actuators with bis(trifluoromethanesulfonfyl)imide (TFSI) as dopant. The large strain was due presumably to the large TFSI dopant anion which can easily go in and out of the TFSI-doped polypyrrole film. Also the use of a slow potential scan rate (0.2 mV/s) was another reason contributing to such a large strain.
To compare the effect of dopant on actuation performance, TFSI-doped polypyrrole helix tube actuators were prepared using the polymerisation conditions in reference [11] and described in the experimental section of this chapter. The actuation performance was compared with the PF₆-doped polypyrrole actuators.

Figure 3.15 shows the strain observed with the TFSI-doped polypyrrole helix tube actuator when tested in 1M LiTFSI aqueous solutions as electrolyte. The potential was scanned between –0.9 V to 1.0 V at 0.2 mV/s for 4 cycles. The first cycle gave 15% strain, the 2nd, 3rd and 4th cycles gave 10%, 5% and 4%, respectively. Compared with Hara et al’s report [11] the strain is lower than the reported value for the first cycle (20%). This is probably because the polymer thickness for the tube wall (0.01 mm) is smaller than the film used by the other workers (0.032 mm). The decrease of strain by cycling is similar to the previous report indicating the doping and dedoping of the large TFSI anion is not totally reversible after the very slow redox cycle. The gradual dedoping of the polymer causes the loss of electroactivity which can be clearly seen from the cyclic voltammogram in Figure 3.16.
Figure 3.15: The strain of PPy/TFSI helix tube actuator in 1 M LiTFSI aqueous solution electrolyte. The potential was scanned between –0.9 V to 1.0 V (vs Ag/AgCl) at a 0.2 mV/s scan rate.
Figure 3.16: Cyclic voltammogram of PPy/TFSI helix tube in 1M LiTFSI aqueous solution electrolyte. Potential was scanned between −0.9 V to 1.0 V (vs Ag/AgCl) at a 0.2 mV/s scan rate.

To investigate the dopant effect, PF₆⁻-doped polypyrrole was tested under similar test conditions. Figure 3.17 shows the actuation strain of PPy/PF₆⁺ helix tube actuator when potential was scanned at a 0.2 mV/s scan rate for 3 cycles. The strains for the 3 cycles were similar at 6% which was lower than TFSI doped polypyrrole. However, the actuation stability was better than TFSI doped polypyrrole. The cyclic voltammogram of PF₆⁻-doped polypyrrole during the actuation in Figure 3.18 also showed better electrochemical stability than TFSI doped polypyrrole in Figure 3.16.
Figure 3.17: The strain of PPy/PF$_6$ helix tube actuator in 0.25 M TBA.PF$_6$/PC electrolyte. The potential was scanned between –1.0 V to 1.0 V at a 0.2 mV/s scan rate.
Figure 3.18: Cyclic voltammogram of PPy/PF$_6$ helix tube in 0.25 M TBA.PF$_6$/PC electrolyte. Potential was scanned between $-1.0$ V to $1.0$ V ($\text{vs } \text{Ag/Ag}^+$) at a 0.2 mV/s scan rate.

It can be seen from Figure 3.15 and 3.17 that under similar actuation conditions, the dopant anions with large size lead to higher strain. However, the giant size makes incorporation or release during the redox cycling more difficult and leads to poor stability. In another paper by Hara et al [12], an even larger anion bis(nonafluorobutanesulfonyl)imide (NFSI) was used as the polypyrrole dopant and a strain of 39.6% was achieved for the first cycle but this rapidly deceased to 22.8% in the 2$^{nd}$ cycle. On the other hand for the smaller dopant anions such as PF$_6^-$, it is possible to achieve reversible anion incorporating and releasing, especially when equivalent charge is controlled for the polymer oxidation and reduction.
In this work, the large actuation strain observed is not only dependent on the size of dopant anion but also derived from the slow potential scan rate. The effect of scan rate on actuation strain can be clearly seen in Figure 3.19 which shows the strain observed for the PF$_6^-$-doped polypyrrole actuator. This shows that at slow scan rates, there is sufficient time for anion incorporation and solvent flux thus leading to more polymer expansion. The strain decreased with increasing the scan rates. At a 0.2 mV/s scan rate, the strain is 5 times higher than that at a 50 mV/s scan rate. This result agrees with the observations by Skaarup et al [13] on the effect of scan rates.

![Figure 3.19: The strain observed for a PPy/PF$_6$ helix tube actuator in 0.25 M TBA.PF$_6$/PC at different potential scan rates. The potential was scanned between −1.0 V to 1.0 V (vs Ag/Ag$^+$).](image-url)
3.3.5 The Effect of Actuator Geometries on Performance

The actuation performances of polypyrrole actuators in different geometries such as films, tubes and tube with helix have been compared by Ding et al [5]. It has been shown that the inclusion of the helix in the structure results in dramatic improvements in terms of strain, strain rate and energy efficiency. The actuation behaviour of the helix tube actuator, however, is also affected by the length and the helix pitch in the actuator.

3.3.5.1 The Effect of Actuator Length

The practical application of the polymer actuators requires a reasonable amount of expansion and contraction. Longer actuators are desirable because larger displacement can be achieved at a given strain. However, the $iR$ drop along the polymer affects the longer actuator much more than the short one. In this work, the effect of helix tube actuator length on the actuation performance is investigated.

To avoid polymer overoxidation, a safe current density ranging from 3 mA/cm$^2$ to 15 mA/cm$^2$ was chosen for the helix tube actuators of different length. It can be seen from Figure 3.20 that within the tested current density range, the samples from 1.5 cm long to 5.0 cm long gave similar strain and the strain increased linearly with increased current density. This indicates that under low current density, the actuator length does not significantly affect the actuation performance; the platinum helix wire can effectively reduce the $iR$ drop along the long tubes. However, in the case of high current density, the actuation strain produced by the longer actuator is affected by length.
Figure 3.20: Strain observed for PPy/PF$_6$ helix tube actuators of different length when low current density was applied in ionic liquid EMI.TFSI as electrolyte.

Figure 3.21 shows the actuation strains obtained for two helix tube actuators (1.5 cm or 5.0 cm long) when the current was applied until the maximum strain was achieved. When the current density was less than 15 mA/cm$^2$, the 1.5 cm sample and the 5.0 cm sample produced similar strain. However, the 5.0 cm sample gave the maximum strain of 3% at 17 mA/cm$^2$ current density then the strain started to decrease. The 1.5 cm sample could endure higher current until 30 mA/cm$^2$ where the maximum strain of 4% was obtained.
Figure 3.21: Strain observed for PPy/PF$_6$ helix tube actuators in 1.5 cm and 5.0 cm long when pulse current applied in ionic liquid EMI.TFSI.

3.3.5.2 The Effect of the Helix Pitch

The use of a platinum helix in the polypyrrole actuator has greatly improved the actuation performance. It is of interest to reveal the effect of the number of the helix turns on the actuator. Hara and co workers [14] have reported polypyrrole-metal coil composite actuators which are similar to our helix tube actuators. They investigated the dependence of the metal coil on actuation strain and found that the use of different pitch resulted in similar strain for the redox cycle but the fine pitch caused quicker strain response. This is because of a smaller voltage drop at the polymer between the metal wire and thinner polymer layer for the actuators with fine pitch. The polypyrrole helix tube actuators in this work usually possessed about 10 turns per centimetre. A
batch of samples with 20 turns of helix per centimetre was prepared and the actuation performance was compared with that of the sample with 10 turns per centimetre. Figure 3.22 shows the actuation strain produced by the actuators under identical test condition.

**Figure 3.22**: Comparison of strain produced by PPy/PF$_6$ helix tube actuators with 10 turns and 20 turns helix per centimetre in 0.25 M TBA.PF$_6$/PC as electrolyte. Potential was applied between –1 V to 1 V (vs Ag/Ag$^+$) at a 50 mV/s scan rate.

It can be seen from Figure 3.22 that under the same test conditions, the sample with 20 turns/cm helix gave a higher strain (2.5%) than the sample with 10 turns/cm (1.5%). This is different to Hara’s results [14] because the gap between the wires is much wider than in Hara’s report. For helix tubes at 10 turns/cm and 20 turns/cm, the widths of the gaps are 1 mm and 0.5 mm, respectively. However, the polypyrrole-metal coil actuators investigated by Hara et al only have 0.01 mm, 0.02 mm or 0.03 mm gaps between the wires.
For the helix tube with a wider gap, the increase of turns of platinum wire will certainly reduce the voltage drop along the polymer between the wires and lead to more efficient actuation. But for the actuator with a very narrow gap, the wires are not as effective as for the actuators with wider gaps.

The polypyrrole helix tube actuators with different turns of helix were also tested using short pulses (500 ms) of ±3 V (two electrode system). It can be seen from Figure 3.23 that a strain rate of 1.3%/s can be observed for the actuator with 20 turns/cm, giving a strain amplitude of 0.65% at 1 Hz. The strain rate and maximum strain for 10 turns/cm actuator are only 0.6%/s and 0.3%, respectively. The higher strain rate for the fine pitch sample is because of the reduced voltage drop and the decreased thickness of the polymer wall.

![Figure 3.23: Comparison of strain produced by PPy/PF₆ helix tube actuators with 10 turns and 20 turns helix per centimetre in 0.25 M TBA.PF₆/PC as electrolyte. A short pulse of ±3 V (1 Hz) was applied.](image-url)
3.3.6 Effect of Electrolyte Temperature on Actuation Strain

The performance of conducting polymer actuators is usually characterised at room temperature. Little work has been done to address the effect of temperature on actuation performance. Theoretically, temperature can affect the actuation behaviour because the conductivities of the polymers are known to vary with temperature [15]. Also electrolyte conductivity and ion diffusion rates are expected to increase at high temperature [16].

The actuation performances of polypyrrole helix tube actuators were tested at room temperature and 70ºC in propylene carbonate electrolyte. To compare the electroactivities of the polymer at different temperature a cyclic potential was applied between –1.0 V to +1.5 V (vs Ag/Ag⁺) at a scan rate of 50 mV/s (Figure 3.24). The actuation strain produced by the polypyrrole actuator was 5%, which is significantly higher than that at room temperature (2.3%).
Figure 3.24: The strain observed for PPy/PF₆ helix tube actuators under different electrolyte temperature in 0.25 M TBA.PF₆/PC. The potential was scanned between –1.0 V to 1.5 V (vs Ag/Ag⁺) at 50 mV/s scan rate.

The electroactivity of the polypyrrole actuators was compared using cyclic voltammetry during the actuation tests (Figure 3.25).
Figure 3.25: Cyclic voltammograms of PPy/PF$_6$ actuators during the actuation test in 0.25 M TBA.PF$_6$/PC under different electrolyte temperature. The potential was scanned between –1.0 V to 1.5 V at 50 mV/s scan rate.

Clearly at 70ºC, polypyrrole exhibits higher electroactivity than at 22ºC. This is due to the enhanced conductivity of the polymer and electrolyte and higher ion diffusion coefficient at higher temperature.

The general form of the temperature-dependent conductivity of Mott’s model is described as [15]:

$$\sigma = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{\frac{1}{d+1}} \right]$$

(3.7)

where $d$ is the dimensionality. The Equation 3.7 can also be expressed as:
\[
\sigma = \frac{\sigma_0}{\exp\left(T_0 \frac{T_0}{T}\right)^{1/\nu}} \quad (3.8)
\]

From equation 3.8 it is clearly shown that the polymer conductivity \(\sigma\) is increased when temperature \(T\) is increased. The increased conductivity at the higher temperature will no doubt lead to a higher electrochemical efficiency thus higher strain can be achieved.

The temperature is also known as a function of the ion diffusion coefficient \(D\) according to Einstein’s relation as [16]:

\[
D = \frac{uRT}{zF} \quad (3.9)
\]

where \(u\) is the mobility of the ion, \(F\) is Faraday’s constant, \(z\) is the charge number of the ion. Equation 3.9 shows that the ion diffusion coefficient can be improved at high temperature. As a result, when the potential was scanned at a certain scan rate, more ions could be incorporated into the polymer causing higher strain.

Similar to the discussions early in this chapter, the actuation strains both at room temperature and 70°C gradually decreased with the cycling. However, the strain decrease at 70°C was slower than that at room temperature. Obviously, the higher polymer conductivity at 70°C contributes to the polymer stability under electrochemical cycling.
3.4 CONCLUSION

Practical actuator devices must operate for many thousands of cycles reproducibly without frequent calibration or deterioration in performance. In this study it has been shown that more reproducible strain response can be achieved by the combination of current pulsing and ionic liquid electrolyte. Current pulsing ensures that the oxidation and reduction processes are equal in their magnitude and prevents the slow net oxidation (or reduction) that typically occurs during symmetrical voltage cycling. Although it would be possible to tailor an asymmetric voltage pulse to achieve the same result, it is practically easier to use current control.

The stability of polypyrrole actuators was also enhanced by the use of ionic liquid electrolytes. These electrolytes permit higher current densities to be used with the polymer (resulting in strains of ~3%) and maintain stability for at least 100 cycles. Finally, operation of polypyrrole actuators in ionic liquids produces much smaller changes in elastic modulus than in propylene carbonate electrolytes. The smaller modulus shift results in a more stable isotonic strain with increasing applied stress and a greater work-per-cycle in ionic liquids.

High actuation strain can be achieved by employing large dopant anions and sweeping the potential at a slow scan rate. However, the high strain can only be maintained for a few cycles thus stability is decreased. A preliminary study on the helix pitch has shown an influence of the pitch on actuation strain and strain rate, however, more work should be conducted to optimise the actuation performance.
The actuation strain can be increased when operated at higher electrolyte temperature as a result of higher polymer conductivity and higher ion diffusion coefficient at higher temperature.
3.5 REFERENCES


CHAPTER 4

PREPARATION AND CHARACTERIZATION OF ACTUATORS BASED ON POLYTHIOPHENE
4.1 INTRODUCTION

Polythiophenes (PTh) have attracted much attention in recent years [1-4]. They are more readily functionalised than other conducting polymers and thus enable the synthesis of highly regioregular polymers with high conductivity. Compared to polypyrrole, polythiophene and its derivatives are also much less susceptible to overoxidation and therefore have improved electrochemical stability. These advantageous properties make them promising materials for actuators.

For conducting polymer actuators, degradation of actuation strain by repeated operations and/or at increased applied loads is commonly observed and this compromises their application in a diverse range of areas. Most previous studies of conducting polymer actuators indicate a decreased actuation strain with increasing load applied to the actuators (see Chapters 1 and 3). Furthermore, the actuation performance is limited by $iR$ drop along the actuator length due to poor electrical connection and polymer resistance [5]. Some improvements have been made recently by incorporating a helical platinum wire into the polymer actuator to provide effective inter connection [6] and/or operating the devices in ionic liquid [7, 8].

One of the most intriguing aspects of actuation behaviour is the effect of applied load on the isotonic actuation strain. In theory the actuation strain of a material can decrease, be unchanged, or even increase with increased load [9]. The relationship between actuator strain and applied stress has been analyzed by a number of workers [9-12]. As discussed in Chapter 3, the difference in
Young’s modulus between the expanded and contracted states of a material is the key to understanding the effect of load on actuation strain stability.

In this work, poly(3-methylthiophene) (P3MT) based actuators have been fabricated electrochemically in a tubular geometrical configuration. A helical platinum wire was embedded in the polymer wall as an interconnect to provide better electrical connection and thus reduce $iR$ drop along the tube. The actuation performance was investigated both in propylene carbonate based electrolyte and ionic liquid (IL) ethyl-methyl-imidazolium bis(tetrafluorosulfonyl)amide (EMI.TFSI) with different applied loads. For the first time with conducting polymers, an increase in actuation strain with higher applied load is reported. This behaviour leads to higher work-per-cycle as the applied load increases– an intriguing and desirable characteristic for actuator materials.

4.2 EXPERIMENTAL

4.2.1 Reagents and Materials

The 3-methylthiophene (3MT, obtained from Aldrich), tetrabutylammonium hexafluorophosphate (TBA.PF$_6$, obtained from Sigma) and propylene carbonate (PC, form Aldrich) were all AR grade and used as received. Platinum (Pt) wires in 250 and 50 µm diameter were obtained from Goodfellow. The ionic liquid EMI.TFSI was synthesized in-house as described in Chapter 3.
4.2.2 Instrumentation

The instrumentation used in this chapter was similar to that described in chapter 3, except that the beam balance was not used, the actuation tests and mechanical tests were conducted using the Dual Mode Lever System 300B as described in Chapter 2 and 3.

4.2.3 Polythiophene Actuator Preparation

Poly(3-methylthiophene) helix tube actuators were prepared following the procedure described in Chapter 3. The poly(3-methylthiophene) actuators were grown galvanostatically for 15 hours using a 0.1 mA/cm² current density. The polymerisation solution was propylene carbonate containing 3-methylthiophene monomer (0.2 M) and TBA.PF₆ (0.03 M). The temperature was controlled in the range of 0 to 5°C. A two electrode configuration was used. The working electrode was a 250 µm platinum wire core tightly wound by a 50 µm platinum wire as a helix and the auxiliary electrode was a stainless steel mesh. After polymerisation, the 50 µm platinum wire was embedded in the polymer wall and the core was removed according to Scheme 3.1.

4.2.4 Actuation and Mechanical Tests

The performance of poly(3-methylthiophene) actuators was tested on a Dual Mode Lever System 300B. A triangular waveform from –1.0 V to 1.5 V at different potential scan rates from 2 to 50 mV/s was applied to the polymer using a Voltammograph CV-27. Propylene carbonate containing TBA.PF₆ (0.25 M) or ionic liquid (EMI.TFSI) were employed as electrolytes. The
expansion/contraction of samples was recorded during the test. Isotonic actuation tests were conducted at steadily increasing loads until the samples were broken.

The Young’s modulus of the poly(3-methylthiophene) actuator was measured with a Dual Mode Lever System 300B while the sample was in the oxidized or reduced state. Similar to the actuation test, the potential was scanned between –1.0 and 1.5 V at a scan rate of 50 mV/s to drive the sample between the oxidized and reduced states. At the oxidized or reduced states, the potential was switched off, and then the sample was gradually stretched to a desirable strain (3%), while a corresponding stress was recorded. The Young’s modulus was obtained from the linear section of the stress vs strain curve using linear regression.

4.3 RESULTS AND DISCUSSION

4.3.1 Poly(3-methylthiophene) Helix Tube Actuators

Figure 4.1 shows a poly(3-methylthiophene) (P3MT/PF₆) tube actuator with a platinum wire helix imbedded into the polymer wall.
The electrical conductivity of poly(3-methylthiophene) was measured using the four-point-probe method. Before measuring, the platinum helix wire was removed from the tube so that the conductivity of the polymer could be determined. The conductivity of the poly(3-methylthiophene) tube was 217 S/cm.

4.3.2 Actuation Strain of Poly(3-methylthiophene) Actuators under Different Potential Scan Rate in Propylene Carbonate and Ionic Liquid

The actuation performance of poly(3-methylthiophene) actuator was tested in propylene carbonate and ionic liquid EMI.TFSI as electrolytes. Figure 4.2 and Figure 4.3 show the actuation strain obtained for the P3MT/PF₆ actuator in the two different electrolytes under investigation. In propylene carbonate, the recoverable actuation strain increased significantly from 0.3% to 0.8%, 1.5% and 2.1% when the potential scan rate was decreased from 50 mV/s to 20
mV/s, 10 mV/s and 2 mV/s, respectively. Whereas in ionic liquid, only a slight increase of actuation strain from 0.4 to 0.5% was observed when the potential scan rate was decreased from 50 mV/s to 20 mV/s and 10 mV/s. When the potential scan rate was decreased to 2 mV/s, the maximum recoverable strain was only 0.6%. These results indicated that poly(3-methylthiophene) actuators produced lower strain in ionic liquid and the actuation strain was less affected by the potential scan rate in ionic liquid.

Figure 4.2: Actuation strain of P3MT/PF₆ helix tube actuator in 0.25 M TBA.PF₆/PC at different potential scan rates: (a): 2 mV/s, (b): 10 mV/s, (c): 20 mV/s, (d): 50 mV/s.
Figure 4.3: Actuation strain of P3MT/PF₆ helix tube actuator in ionic liquid EMI.TFSI at different potential scan rates: (a): 2 mV/s, (b): 10 mV/s, (c): 20 mV/s, (d): 50 mV/s.

The actuation strains under different scan rates in propylene carbonate based electrolyte and ionic liquid electrolyte are summarized in Figure 4.4.
As described in Chapter 1, anion and/or cation exchange is the fundamental mechanism of actuation in conducting polymers. As can be seen in Figure 4.2 and Figure 4.3, in propylene carbonate, the P3MT/PF$_6$ actuator expanded at positive potentials and contracted at negative potentials. This behaviour indicates that the polymer incorporates electrolyte anion (PF$_6^-$) during oxidation (positive potential) and releases PF$_6^-$ during reduction (negative potential). In contrast, when ionic liquid was used as the electrolyte, the actuator expanded at negative potentials and contracted at positive potentials. This is similar to results obtained with polypyrrole actuators [8]. In ionic liquid, the polymer incorporated ethyl-methyl-imidazolium (EMI$^+$) cations from the electrolyte during reduction (negative potential) causing polymer expansion and released cations during oxidation (positive potential) resulting

**Figure 4.4:** Actuation strain of P3MT/PF$_6$ helix tube actuator at different potential scan rates in 0.25M TBA.PF6/PC and ionic liquid EMI.TFSI electrolytes.
in polymer contraction. The redox process may also involve the dopant anions moving in and out of the polymer but the cations from the electrolyte dominate the actuation performance in ionic liquid. Thus, the polymer expansion caused by cation incorporation may be partly counteracted by the dopant anion released from the polymer. These mixed ion movements may be the reason why the actuation strain in ionic liquid is lower than that in propylene carbonate.

As described in Chapter 1, solvent flux accompanying ion exchange also contributes to the actuation strain. When the P3MT/PF₆ actuator was operated in propylene carbonate (0.25 M TBA.PF₆) electrolyte, the solvent molecules may move into the polymer with PF₆⁻ anions and contribute to the polymer expansion. Whilst in ionic liquid electrolyte, which is a pure electrolyte without any solvent, the actuation strain is merely derived from the ion exchange and there is no solvent contribution to the polymer expansion. This solvent contribution may lead to higher actuation strain in propylene carbonate than in ionic liquid. According to the EQCM study on poly(3-hexylthiophene) by Brown et al [13], under low scan rate 2 mV/s, the solvent transfer during the redox process swells the polymer by 48% in thickness, which is a remarkable contribution compared to the total observed 63% swelling. As shown in Figure 4.4, 2.1% strain can be achieved in propylene carbonate electrolyte at 2 mV/s scan rate where solvent transfer is likely to play an important role in the actuation performance.

The actuation strain resulting from ion exchange and solvent transfer does not only depend on the amount of ions and solvent molecules that move, but is
also related to the diffusion rate of these ions and molecules. There are a number of factors that control diffusion, such as ion mobility, solution concentration, temperature, viscosity, etc. [14]. Under low potential scan rates, the potentials required for actuation are held for longer times. As a result, there will be sufficient time for more ion exchange and solvent transfer to occur. Consequently, as shown in Figure 4.4, the actuation strains produced by the actuators are higher at low scan rates. Skaarup and coworkers have reported the effect of the scan rate on actuation strain; a decrease of strain from 1% to less than 0.2% was observed when the potential scan rate was increased from 1 mV/s to 100 mV/s [15].

Ion concentration in the electrolyte may also influence the amount of actuation occurring at different scan rates. In the case of the organic solvent electrolyte, the ions are dispersed in the solvent, so that they need to travel some distance to arrive to the polymer surface and participate in the ion exchange processes. Under low potential scan rates, there is sufficient time for more anions to be incorporated in or be released from the polymer. Whereas in ionic liquid electrolyte, the concentration of ions is much higher so that the diffusion distance are shorter. The potential scan rate will not affect the ion diffusion as much as in organic solvent electrolyte.

It can be seen that in Figure 4.4, the actuator produces a similar strain in the organic solvent electrolyte and ionic liquid electrolyte at a higher scan rate 50 mV/s. Brown et al also reported that a hysteresis was observed with a slow solvent transfer in response to the potential changes [13], thus it can be assumed that solvent transfer at high scan rate is not as significant as that at low scan rate. As a result, solvent transfer may not significantly contribute to
actuation at higher potential scan rates. The actuation strain is mainly dependent then on the ion exchange at high scan rate. Given that the cation EMI$^+$ (molecular weight 131, dominating actuation in ionic liquid electrolyte) and anion PF$_6^-$ (molecular weight 117, dominating actuation in propylene carbonate electrolyte) have similar size, the actuation strains are at a similar level in the two electrolytes. Similar strains were observed for PF$_6^-$-doped polypyrrole actuators when tested in these two electrolytes with the potential (±5 V, two-electrode system) pulsed at 1 Hz or cycled between ± 2.5 V (two-electrode system) using a potential scan rate of 50 mV/s [8].

The cyclic voltammograms of poly(3-methylthiophene) in propylene carbonate and ionic liquid during actuation tests are shown in Figure 4.5 and Figure 4.6.

![Cyclic Voltammograms of P3MT/PF$_6$ helix tube actuator in 0.25 M TBA.PF$_6$/PC at different scan rates: (a): 2 mV/s, (b): 10 mV/s, (c): 20 mV/s, (d): 50 mV/s.](attachment:image.png)

**Figure 4.5:** Cyclic Voltammograms of P3MT/PF$_6$ helix tube actuator in 0.25 M TBA.PF$_6$/PC at different scan rates: (a): 2 mV/s, (b): 10 mV/s, (c): 20 mV/s, (d): 50 mV/s.
Figure 4.6: Cyclic Voltammograms of P3MT/PF$_6$ helix tube actuator in ionic liquid EMI.TFSI at different scan rates: (a): 2 mV/s, (b): 10 mV/s, (c): 20 mV/s, (d): 50 mV/s.

As expected, the current levels observed during cyclic voltammetry increase with increasing scan rate. For both electrolytes, there is a significant current increase from 2 mV/s to 10 mV/s scan rate and another considerable increase occurs from 20 mV/s to 50 mV/s. Between 10 mV/s and 20 mV/s scan rate, the current increase is less. The current increase from low scan rate to high scan rate is approximately proportional to the difference of the scan rates.

In propylene carbonate electrolyte, the increase in scan rate shifts the position of the peak potential towards higher potentials. This observation is similar to the TFSI-doped polypyrrole actuator when cycled in aqueous electrolyte at different scan rates [16]. This shift indicates that under higher scan rates, the polymer redox reaction is limited by diffusion of ions to the reaction zone.
Again the lower ion concentration in the propylene carbonate electrolyte may slow down the redox reactions due to the larger diffusion distances. In ionic liquid electrolyte, the position of the peak potential is much more stable at different scan rates. As a result, the actuation strain in ionic liquid is less affected by the scan rates than in propylene carbonate.

4.3.3 Strain Response of Poly(3-methylthiophene) Actuators under Load

Figure 4.7 illustrates the relationship between the applied stress and the isotonic strain of the poly(3-methylthiophene) helix tube actuator in propylene carbonate containing 0.25 M TBA.PF$_6$ and ionic liquid EMI.TFSI electrolyte. Similar to the previous results for polypyrrole actuators [17], a rapid decrease in strain from 1.5% to 0.1% occurred in propylene carbonate with increasing applied load and the sample eventually failed at 2.5 MPa. On the other hand, in ionic liquid the actuation strain slightly increased from 0.4% to 0.6% until the sample failed at 3.9 MPa.
Figure 4.7: Actuation strain of P3MT/PF₆ helix tube actuator under isotonic condition at different stress levels in 0.25 M TBA.PF₆/PC and ionic liquid EMI.TFSI electrolytes. Potential was scanned between –1.0 V to 1.5 V (vs Ag/Ag+) at a 50 mV/s scan rate.

The test was repeated with another two samples in ionic liquid EMI.TFSI. The actuation strains of 3 tested samples under isotonic stress levels are plotted in Figure 4.8. These results have confirmed the increasing trend of the actuation strain with increasing applied loads. This is a promising result that can overcome the limitation in applications due to the normal strain decay with increasing load. It has been reported by Ding et al. [8] that the use of ionic liquid as electrolyte can significantly improve the actuation strain stability under load. This improvement was also observed and described in Chapter 3 for polypyrrole actuators. This work shows that the strain decays with load at a slower rate in ionic liquid compared with propylene carbonate. The present work, however, is the first report in which the actuation strain produced by a
conducting polymer actuator actually increases under increasing load before failure.

![Graph showing actuation strain vs stress](image)

**Figure 4.8:** Actuation strain of 3 samples of P3MT/PF₆ helix tube actuator under isotonic condition at different stress levels in ionic liquid EMI.TFSI electrolyte. Potential was scanned between –1.0 V to 1.5 V (vs Ag/Ag+) at a 50 mV/s scan rate.

The relationship between the actuation strain and applied stress has been analyzed in Chapter 3. The Young’s modulus of the actuator material is a key parameter when determining the isotonic actuation strain. To understand this intriguing actuation behaviour of the poly(3-methylthiophene) actuator under load, the Young’s modulus of poly(3-methylthiophene) helix tube actuators was measured in propylene carbonate based and ionic liquid electrolytes (Table 4.1).
Table 4.1: Young’s Modulus of P3MT/ PF₆ helix tube actuator measured in propylene carbonate and ionic liquid electrolytes.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$Y_d$ Expanded state (MPa)</th>
<th>$Y_o$ Contracted state (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>109.4</td>
<td>69.6</td>
</tr>
<tr>
<td>IL</td>
<td>70.5</td>
<td>72.5</td>
</tr>
</tbody>
</table>

In propylene carbonate, the Young’s modulus decreases significantly (~40%) from the expanded to contracted state. In ionic liquid, however, the Young’s modulus slightly increases (~3%) from the expanded to contracted state. As a result, in propylene carbonate based electrolyte, the actuation strain will decrease with increasing load. On the contrary in ionic liquid electrolyte, the actuation strain will increase with increasing load. The increasing strain is expected because expansion occurs during polymer reduction (due to cation incorporation) and this strain is augmented by an extension due to the decreasing modulus.

According to Equation 3.1 and the Young’s modulii in Table 4.1, the calculated actuation strains under increasing load were obtained and shown as dashed lines in Figure 4.9. It can be seen that the calculated values are in good agreement with the experimental results. The slight shift between the experimental and calculated results in propylene carbonate at higher loads is probably due to the polymer degradation occurring after several cycles in propylene carbonate electrolyte.
Figure 4.9: Comparison of experimental strain and calculated strain of P3MT/PF₆ helix tube actuator under isotonic condition.

4.3.4 Work-Per-Cycle Performed by Poly(3-methylthiophene) Actuators

As described in Chapter 3, the work performed per expansion/contraction cycle is another important parameter in evaluating the performance of actuators. According to Equation 3.2 and the results shown in Figure 4.7, the work-per-cycle performed by a poly(3-methylthiophene) helix tube actuator when operated in propylene carbonate based and ionic liquid electrolytes are plotted in Figure 4.10.
Figure 4.10: Work-per-cycle for a P3MT/PF$_6$ helix tube at different applied stress levels in 0.25 M TBA.PF6/PC and ionic liquid EMI.TFSI electrolytes.

In propylene carbonate, where the Young’s modulus at expanded state $Y_d$ is about 1.57 times of that at contracted state $Y_o$, i.e. $Y_d = 1.57Y_o$, the work per cycle and applied stress curve shows a parabolic behaviour. In contrast, when an actuator is operated in ionic liquid, where the Young’s modulus $Y_d = 0.97Y_o$, the work-per-cycle increases continuously with increasing applied stress. These results are in good agreement with the analysis by Spinks and Truong [18].

As described in Chapter 3, the actuator displacement can be calculated from the actuator Young’s modulii according to Equation 3.1. Using the calculated actuator displacement and isotonic load, the work-per-cycle can be predicted according to Equation 3.3. The calculated work-per-cycle in propylene
carbonate and ionic liquid are shown in Figure 4.11 as dashed lines and compared with the experimental results. It can be seen that in propylene carbonate based electrolyte, the calculated values are an overestimation when the applied stress is larger than 1 MPa. This is due to the polymer cycle degradation in propylene carbonate. Whereas in ionic liquid, the calculated values are in excellent agreement with the measured values. This implies the performance stability is rendered by ionic liquid as found for polypyrrole actuators.

Figure 4.11: Comparison of experimental and calculated work-per-cycle of P3MT/PF$_{6}$ helix tube actuator under isotonic condition at different applied stress levels in 0.25 M TBA.PF6/PC and ionic liquid EMI.TFSI electrolytes.

The maximum work-per-cycle is given as Equation 3.4 [18] in Chapter 3. According to Equation 3.4 and the Young’s modulii in Table 4.1, the maximum work-per-cycle in propylene carbonate can be calculated as 12.2
kJ/m³. Due to polymer cycle degradation, the experimental maximum work-per-cycle is only 8.7 kJ/m³.

According to the analysis by Spinks and Truong [18], in the case of $Y_d = Y_o$, the value of $f_{\text{max}}$ increased to infinity and therefore an infinity work-per-cycle can be obtained. In reality, the maximum load that can be applied is limited by yield or rupture. Baughman [9] has suggested that the practical maximum applied load is 50% of the breaking or yield force ($f_b$), so that the maximum work-per-cycle can be given as:

$$W_{\text{max}} = \Delta L_o f_b$$  \hspace{1cm} (4.1)

In ionic liquid electrolyte, the Young’s modulus measurement shows $Y_d = 0.97\ Y_o$ which is very close to the situation of $Y_d = Y_o$. Thus the maximum work-per-cycle in ionic liquid can be calculated according to Equation 4.1 as 17.9 kJ/m³. The experimental maximum work-per-cycle is 23.9 kJ/m³ which is higher than the calculated value. This is because the actual Young’s modulus $Y_d$ is smaller than $Y_o$ and causes more actuator displacement.

### 4.4 CONCLUSION

Practical applications of actuators will require operation under load. Most previous studies of conducting polymer actuators indicate a decreased actuation strain when increasing applied loads to the actuators. In this study, for the first time the actuator based on poly(3-methylthiophene) having a tubular configuration with embedded Pt wire helix exhibits an increasing
actuation strain with increasing applied stress when operated in ionic liquid EMI.TFSI. Based on this unique property, poly(3-methylthiophene) can be considered as a promising material for developing artificial muscles.

The maximum work per cycle achieved in ionic liquid electrolyte (24 kJ/m$^3$) is about 3 times of that achieved in propylene carbonate based electrolyte (8.7 kJ/m$^3$). This result has confirmed the benefit of ionic liquid as electrolyte for conducting polymer actuators as reported by other researchers [7, 8].
4.5 REFERENCES


CHAPTER 5

PREPARATION AND CHARACTERIZATION OF POLYANILINE ACTUATORS PREPARED USING PHASE INVERSION TECHNIQUE
5.1 INTRODUCTION

The actuation behaviour of polyaniline and its derivatives in aqueous solutions has been investigated in detail, most notably by Kaneto’s group [1], Lu and Mattes [2] and more recently by Smela et al [3, 4]. The samples used in these previous studies were polyaniline free standing films obtained by casting polyaniline emeraldine base (EB) form from N-methyl-2-pyrrolidinone (NMP) solution onto a glass substrate with the residual NMP removed by heating. Phase inversion techniques are often used to produce films or membranes with controlled microstructure [5]. The approach allows a degree of control over the size of pores and the ability to produce asymmetric membranes. Recently, a phase-inversion technique was used to prepare polyaniline fibres where a solution of polyaniline (EB form) in N, N-dimethyl propylene urea (DMPU) was coagulated in a water or non-solvent bath [6].

Using the phase inversion technique, the polymer film morphology produced is dependent on the nature of the solvent and non-solvent used [5]. The polymer film can possess porous structures due to an instantaneous demixing or a dense structure from a delayed demixing. Sansinena et al [7] reported an asymmetric porous polyaniline film prepared using a phase inversion technique. The membrane structure produced undergoes bending actuation in aqueous electrolyte when the polyaniline is oxidised/reduced. The mechanical strength of the film is closely related to film porosity.

As described in Chapter 1, the actuation performance of polypyrrole is greatly improved by incorporating a platinum wire into the tubular actuators. Encouraged by this outcome, it was of interest to investigate the effect of
microstructure on polyaniline actuators. In this work, polyaniline actuators were prepared by a phase inversion technique to form free standing polyaniline films and tubes with or without a platinum wire helix. The effect of electrolyte, coagulation bath, dopant and actuator geometry on the actuation behaviour was investigated.

5.2 EXPERIMENTAL

5.2.1 Reagents and Materials

N, N-dimethyl propylene urea (DMPU), N-methyl-2-pyrrolidinone (NMP), phenylhydrazine and methanesulfonic acid (MSA) were obtained from Aldrich and used as received. Polyaniline emeraldine base (EB) (MW: 300,000) was purchased from Santa Fe Science & Technology (USA). Nitric acid (HNO₃) and hydrochloric acid (HCl) was obtained from Asia Pacific Specialty Chemicals Limited. Platinum wire (250 or 50 µm diameter) was obtained from Goodfellow Cambridge Limited.

5.2.2 Instrumentation

The pulse current during actuation testing was applied using an EG & G Princeton Applied Research Mode 363 potentiostat/galvanostat. The actuation tests were conducted on an Aurora Scientific Dual Mode Lever System 300B. All data was processed and recorded using a AD Instruments MacLab/4e and computer.
5.2.3 Polyaniline Actuator Preparation

The reducing agent, phenylhydrazine, was first added to DMPU solvent to 3% (w/w) concentration to prevent polymer gelation. Polyaniline EB was then gradually added to phenylhydrazine/DMPU mixture to give a concentration of 10% (w/w). The solution was then constantly stirred for 24 hours with the temperature controlled at 0°C. Polyaniline EB was converted to polyaniline leucoemeraldine base (LEB) by the presence of the phenylhydrazine.

The preparation of polyaniline actuators was carried out using the phase inversion technique described previously by Loeb and Sourirajan [8]. As-prepared polyaniline LEB/DMPU solution was cast on a glass slide to form a thin layer of polymer solution. The glass slide with the polymer solution layer was immediately immersed in a water coagulation bath for 24 hours to ensure removal of the DMPU through a solvent/non-solvent exchange process. After removing from the water, the film was peeled off and cut into strips (20 mm long and 3 mm wide). Similarly, another batch of polyaniline film was coagulated in a 30% (w/w) NMP/water bath for 24 hours.

A polyaniline tube was prepared by dipping a 250 µm platinum wire into the polyaniline EB/DMPU solution, allowing the solution to coat onto the surface of the platinum wire. For a polyaniline tube with a platinum helix, a 250 µm platinum wire wound with another 50 µm platinum wire into a helix was used. The platinum wire (with or without the platinum helix) with polymer solution coating was then immersed in the water coagulation bath as described above. After removing from the water coagulation bath, the 250 µm platinum wire
was pulled out leaving a polyaniline hollow tube with or without the platinum helix.

Polyaniline films and tubes were doped in HCl (1 M) aqueous solution for 24 hours or in MSA (1 M) aqueous solution for 6 hours and then dried at room temperature for further tests. The doping process converted the polyaniline LEB to polyaniline emeraldine salt (ES) which is the most conductive state of polyaniline.

### 5.2.4 Actuation Tests

The actuation performance of polyaniline actuators was tested using a Dual Mode Lever System 300B. A two-electrode configuration was used while a pulsed current was applied as electrochemical stimulation. Positive and negative currents were applied for 30 s each alternatively from ±1 mA until the current at which polyaniline actuators produced a maximum actuation strain. HNO₃ (1 M) and NaNO₃ (1 M) aqueous solutions were employed as electrolytes. Isotonic actuation tests were conducted at steadily increasing loads until samples were broken. The applied current for the isotonic actuation tests was close to the current where the maximum actuation strain was obtained.

### 5.2.5 Young’s modulus measurements

Samples of the same dimensions as those employed for actuation tests were used to obtain the Young’s modulus at both the expanded and contracted states of the polymer. Similar to the isotonic actuation testing conditions, a
positive/negative current density was applied to the test sample for 30 s prior to the test to obtain the expanded/contracted (oxidised/reduced) state. The sample was gradually stretched to a desirable strain, while corresponding stress was recorded. The Young’s modulus was calculated from the linear portion of the stress/strain curve with linear regression.

5.3 RESULTS AND DISCUSSION

5.3.1 Effect of Electrolyte on Actuation Performance of Polyaniline films

Polyaniline films were prepared from the water based coagulation bath and doped in 1M HCl aqueous solutions. The average conductivity of the polyaniline films was measured as 0.34 S/cm. The conductivity is relatively low presumably due to the porous nature of the sample.

The actuation performance of polyaniline films was compared in acid, neutral salt and the mixture of acid and neutral salt electrolytes. Figure 5.1 shows the actuation strain under increasing current density when the samples were tested in HNO₃ (1 M), NaNO₃ (1 M) and a mixture of HNO₃ (0.5 M) and NaNO₃ (0.5 M) aqueous solutions.
Figure 5.1: PAn/HCl film strain under increasing current density in different electrolytes. A current pulse of 30 s was used.

In HNO₃, the polyaniline film gave the highest strain (0.9%) whereas in NaNO₃ the strain was the lowest (0.3%). When tested in the mixture of HNO₃ and NaNO₃, the pH of the electrolyte was lower compared to 7 for the 1M NaNO₃ electrolyte. The actuation strain was thus intermediate in value (0.65%). This comparison confirmed that an acid electrolyte could maintain polyaniline doping levels during the actuation test. In contrast, in neutral NaNO₃ electrolyte polyaniline gradually became deprotonated and non-conductive. Similar results were observed using the polyaniline doped with MSA. This result is different from the PPy/PAn composite actuators that showed very good stability with NaNO₃ used as electrolyte. With PPy/PAn, the polypyrrole dominated the actuation behaviour (see Chapter 6).
To compare the electroactivity of polyaniline films in acid and neutral salt electrolytes, cyclic voltammetry of polyaniline films doped with HCl (PAn/HCl) and MSA (PAn/MSA) were studied in the different electrolytes (Figure 5.2).
Figure 5.2: Cyclic voltammograms of PAn recorded at 50 mV/s sweep rate (a): PAn/HCl in 1 M HNO₃, (b): PAn/MSA in 1 M HNO₃, (c): PAn/HCl in 1 M NaNO₃.
It can be seen from Figure 5.2 that in 1M HNO₃, three redox pairs were observed with oxidation peaks at ~0.2 V, ~0.5 V and ~0.7 V. The first peak (0.2V) corresponds to the first oxidation of polyaniline, from polyleucoemeraldine salt to polyemeraldine salt. The third peak (~0.7 V) corresponds to the further oxidation of polyaniline from polyemeraldine salt to polypernigraniline salt. The middle pair is from the presence of ortho-coupled polymer or the degradation of polyaniline. These results correspond well with results by Pruneanu et al [9] when polyaniline was tested in HClO₄ (1 M) solution. In contrast, a very different CV was observed in 1M NaNO₃ reflecting low electroactivity (Figure 5.2(c)). Only one pair of redox peaks was observed with oxidation peak at ~0.5 V. Compared to the stable CVs of PAn/HCl and PAn/MSA in acid aqueous solution (Figures 5.2(a) and 5.2(b)), the current decreased quickly from the first cycle to the sixth cycle and again to the twelfth cycle, indicating poor electrochemical properties and stability of polyaniline in NaNO₃. The poor electroactivity of polyaniline in nitrate is due to the neutral pH that results in the conversion of the polyemeraldine salt to the non-conductive polyemeraldine base.

### 5.3.2 Polyaniline Film Actuators Prepared from Different Coagulation Baths

Polyaniline films were prepared from either a water coagulation bath or a 30% NMP/water coagulation bath. The films were doped in 1M MSA aqueous solutions. Compared with HCl as dopant, the MSA doped films showed improved conductivity. Values of 1.2 S/cm and 2.7 S/cm were obtained for films produced using water coagulation bath or the 30% NMP/water
coagulation bath, respectively. The effect of dopants on polyaniline conductivity has been reported by Tzou and Eaprasertsak et al [10, 11].

The microstructure of the films prepared by the phase inversion technique is best thought of as a porous asymmetric membrane [7]. The SEM cross section images shown in Figure 5.3 confirm the asymmetric structures of the polyaniline films. The top surface in Figure 5.3 corresponds to the side of the film in contact with the coagulation bath, and the bottom side corresponds to the side in contact with the substrate. Clearly, the size of the pores increases from the more dense top side to the more porous bottom side. The thickness of the dense top layer is larger for the pure water bath than for the NMP/water bath. Similar observations were reported by Kim et al [12]. Similarly, the porosity of the top layer is larger for the NMP/water bath relative to the water bath due to a slower coagulation, indeed some evidence of the deep macrovoid structure is already present and shown in the SEM surface images in Figure 5.4.
Chapter 5 Preparation & Characterization of PAN Actuators Prepared Using Phase Inversion Technique

(a) Water as coagulation bath                        (b) NMP/water as coagulation bath

Figure 5.3: SEM cross section images of PAN films coagulated from (a) a water bath, and (b) a 30% NMP/water bath.

(a) Water as coagulation bath                 (b) NMP/water as coagulation bath

Figure 5.4: SEM top surface images of PAN films coagulated from (a) a water bath, and (b) a 30% NMP/water bath.

Figure 5.5 shows the actuation strain data obtained for a PAN/MSA film coagulated in a water bath or in a 30% NMP/water bath. Both samples showed similar actuation behaviour probably due to the similar highly porous structures obtained. The maximum actuation strain is approximately 0.7% for the film from 30% NMP/water coagulation bath and 0.65% for the film from...
water coagulation bath. The slightly higher strain obtained from the NMP/water coagulated sample is probably due to the higher conductivity of this sample, although the small improvement may not be statistically significant.

![Graph showing actuation strain of PAn/MSA films](image)

**Figure 5.5:** Actuation strain of PAn/MSA films coagulated in water or 30% NMP/water bath under increasing current density in 1 M HNO₃ aqueous solution electrolyte. A cast and dried film is included for comparison. A current pulse of 30 s was used.

The actuation strain of the highly porous polyaniline films prepared using phase inversion technique was also compared to a relatively dense film. This sample was prepared from solution casting and drying on a hotplate. The actuation strain of this sample is included in Figure 5.5. The surface SEM image in Figure 5.6 shows the film has much less pores than the film prepared by phase inversion technique. It can be seen from Figure 5.5 that the actuation strain produced by the dense film is higher than the porous films. This is due
to its higher conductivity (3.6 S/cm) and more polyaniline per unit volume, thus lead to a lower $iR$ drop and more anions being incorporated/expelled.

![SEM top surface image of PAn film dried on a hot plate.](image)

**Figure 5.6:** SEM top surface image of PAn film dried on a hot plate.

The different microstructures of these films also affected the actuation strain rates under electrochemical stimulation. During the actuation tests, a pulse current was applied for 30 seconds. Under the same current density (8 mA/cm$^2$), the strain responses of a dense film and a porous film as a function of time were measured and these are plotted in Figure 5.7. In the beginning of the stimulation, the porous films prepared from phase inversion technique exhibited higher strain than the dense film at the same time. After the current was applied for 15 seconds, the dense film started to display a much higher strain than the porous films. As discussed in Chapter 1, the actuation mechanism involves a few steps. Under the applied charge, the polymeric structure will be opened by the formation of channels to allow the passage of ions, and then the ion exchange occurs to balance the charge. Accompanying
the ion exchange, solvent flux also contributes to the polymer volume change. For the dense film, it will take more time to open the polymer chains whereas the porous film already has a loose structure. Also for the dense film, the ion exchange is limited by the slow ion diffusing into the inner part of the film. These facts result in a slower strain rate for the dense film than the porous films in the beginning of the stimulation. Later on once the polymer chains are opened, the higher conductivity of the dense film leads to a lower iR drop. In addition, more anions will be incorporated/expelled for an equal volume of film. As a result, a higher strain was achieved for the dense film.

![Graph](image)

**Figure 5.7:** Actuation strain of PAn/MSA films as a function of time in 1 M HNO₃ aqueous solution electrolyte. A current density of 8 mA/cm² was applied.

As shown in Figure 5.8, the PAn/MSA films had low strength with the maximum applied stress limited to approximately 0.3 MPa before the samples failed. The value for PAn/HCl films and tubes was slightly better at 0.4 MPa
but it was still very low compared with polypyrrole based actuators (1 – 1.5 MPa) [13]. The dense polyaniline film described above gave a maximum stress of 1.7 MPa which is about 5 times higher than the porous films. The lower breaking strengths of the polyaniline films tested here is no doubt due to their highly porous microstructure.

![Figure 5.8: Effect of applied stress on the actuation strain of PAn/MSA films coagulated in water or 30% NMP/water bath in 1 M HNO₃ aqueous solution electrolyte.](image)

Table 5.1 lists the Young’s modulus, \( Y \), of the PAn/MSA films. Compared to other conducting polymers such as polypyrrole in a propylene carbonate electrolyte (Young’s modulus is around 80 MPa), the values obtained were low reflecting the porous nature of the polyaniline films.
Table 5.1: Young’s modulus, $Y$, at expanded (oxidised) and contracted (reduced) states in HNO$_3$ (1 M) aqueous solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$Y_{\text{expanded}}$ (MPa)</th>
<th>$Y_{\text{contracted}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAn film*</td>
<td>3.06</td>
<td>3.45</td>
</tr>
<tr>
<td>PAn film**</td>
<td>1.75</td>
<td>1.93</td>
</tr>
</tbody>
</table>

* Coagulated in a water bath doped with MSA (1 M) for 6 hours.
** Coagulated in a 30% NMP/water bath doped with MSA (1 M) for 6 hours.

The higher value obtained for the Young’s modulus in the contracted state suggests the actuation strain should increase with applied load [13]. As shown in Figure 5.8, an initial increase of the strain with increasing applied load was observed up to 0.05 MPa. According to the analysis of the relationship between the actuation strain and the Young’s modulus in Chapter 3 (see Equation 3.1), the actuation strain can be calculated within a 0.05 MPa stress range. The calculated strains obtained for the polyaniline films produced using the water coagulation or using the 30% NMP/water coagulation bath are shown as dished lines in Figure 5.9.
It can be seen from Figure 5.9 that the increasing trend of the actuation strains agrees reasonably well with the predicted tendency even though the experimental results are consistently lower than the predicted values. The difference between the predicted and observed actuation strains may be due to the appearance of micro cracks resulting from the brittle nature of the sample. As a result, although the actuators have the intrinsic ability to produce an increasing strain with the increasing applied stress, the porosity and brittleness of the film cause the final decline in strain.

**Figure 5.9:** Comparison of experimental strain and calculated strain of PAn films form different coagulation baths.
5.3.3 Conductivities of Polyaniline Actuators in Different Geometrical Configurations

The conductivities of polyaniline film and polyaniline tube with or without the platinum helix are shown in Table 5.2. The cross-section area of the polymer wall was used for measuring conductivity of tubular actuators.

Table 5.2: Conductivities of polyaniline film, tube and tube with helix

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAn film*</td>
<td>0.34</td>
</tr>
<tr>
<td>PAn tube*</td>
<td>1.34</td>
</tr>
<tr>
<td>PAn tube with helix*</td>
<td>244</td>
</tr>
</tbody>
</table>

* Coagulated in water bath and doped with HCl (1 M) for 24 hours.

It can be seen from Table 5.2 that the conductivity increased by a factor of 4 by changing the geometric shape of the actuator from film to tube. When casting films, the polymer solution was spread out on the surface of a glass slide, after coagulation the solidified film likely had no preferred molecular orientation. On the other hand, in the process of making a tube the polymer solution was coated onto a platinum wire, the platinum wire was then drawn out from the solution very rapidly. As a result, the polymer layer around the platinum wire may have possibly been aligned along the length of the wire. The orientation may also have been preserved by the rapid coagulation process. Molecular alignment would contribute to the observed increased conductivity. This enhancement in conductivity was clearly observed in spun polyaniline fibres with axial alignment induced by stretching, producing significantly higher conductivity compared to cast films [14, 15]. Incorporation of a platinum helix into the polyaniline tube increased the
conductivity of the actuator by 180 times compared with that of the tube without the helix.

5.3.4 Effect of Geometrical Configuration on Actuation Strain

Popolyaniline actuators were doped in HCl (1M) solution and actuation performance in different geometrical configurations was investigated in 1 M HNO₃ aqueous solution using pulsed current (Figure 5.10). The strain increased to a maximum value before declining. The polyaniline film gave the maximum actuation strain of 0.9% whereas the polyaniline tube with the platinum helix produced 2.7% strain, which was the highest among the three tested samples. Similar results were found in polypyrrole (PPy) actuators [16]. The improvement of the actuation behaviour of the tube over the film is likely due to the higher conductivity of the tube. Furthermore, the platinum wire inside the polyaniline tube significantly reduced the $iR$ drop along the actuator and produced a more even voltage distribution along the length of the actuator.
Figure 5.10: Actuation strain of PAn/HCl film, tube and tube with Pt helix in 1 M HNO₃ aqueous solution under increasing current density. A current pulse of 30 s was used.

While the conductivity of the polyaniline tube with platinum helix (244 S/cm) was substantially higher than that of the polyaniline tube (1.34 S/cm), the actuation strain could only increase to 2.7% from the 2.0% strain of the polyaniline tube (Table 1). Thus, the value of 2.7% can be considered as the maximum isotonic actuation strain for the polyaniline doped with HCl operated in HNO₃ aqueous solution under the given test conditions. This value was much higher than the strain (1%) of the polyaniline film sample tested in H₂SO₄ (0.5 M) [17]. Kaneko and Kaneto [1] reported a strain of 2.5% for polyaniline samples cast from NMP solution at the potential scan rate of 5 mV/s in HCl aqueous solutions. In the present study, the actuation test was operated under controlled current conditions that equated to an average rate of change in potential of 100 mV/s. A disadvantage of the controlled current
method is that the applied potential cannot be regulated. It has been reported that maximum strain from polyaniline actuators is achieved by switching between the leucoemeraldine and emeraldine states and avoiding the pernigraniline state [18]. The decline in strain observed at higher current density may be due to a higher potential being applied such that the polyaniline was fully oxidised to pernigraniline. It is expected that the maximum strain of 2.7% for the polyaniline tube with the platinum helix can be increased by controlling the potential and decreasing the potential scan rate. In this way, the oxidation state can be controlled and the transport of the dopant would be in phase with electrical stimulus.

5.4 CONCLUSION

The phase inversion technique enables fabrication of polyaniline in different geometrical configurations. The conductivity can be increased by a factor of 4 by changing the geometric shape of the actuator from film to tube. Incorporation of a platinum helix into the polyaniline tube increased the conductivity by a factor of 180 to 244 S/cm. The increased conductivity leaded to a higher actuation strain of 2.7% for tube with platinum helix actuator compared to 0.9% for the film actuator. HNO₃ aqueous electrolyte, in which polyaniline maintains its doping level, provided a stable actuation environment.

The porous nature and subsequent brittleness of the polyaniline samples prepared by the phase inversion method would limit practical application. It was expected that high molecular weight (MW = 300,000) of polyaniline EB would have rendered reasonable mechanical properties, but the porous nature
seems to have dominated in determining the strength of the polyaniline materials used in this study.

The practical application of actuators requires reasonable actuator strength and stress generation. The use of a spinning process to make polyaniline fibres where in the advantage of high molecular weight can be fully exploited is one method that may be used to obtain a tough material by molecular alignments [19]. With the incorporation of carbon nanotubes as reinforcement in the polyaniline matrix, composite spun fibres would be expected to be an ideal actuator material with improved electrical and mechanical properties [20].
Chapter 5 Preparation & Characterization of PAN Actuators Prepared Using Phase Inversion Technique

5.5 REFERENCES

Chapter 5 Preparation & Characterization of PAN Actuators Prepared Using Phase Inversion Technique

CHAPTER 6

PREPARATION AND CHARACTERIZATION OF COMPOSITE ACTUATORS
6.1 INTRODUCTION

In various studies of the forces and displacements generated from conducting polymer actuators, it has been noted that the force generation is limited by the breaking strength of the actuator materials. Hara [1] reported 22 MPa stress can be sustained by polypyrrole films during the actuation work cycle. The highest stress of 34 MPa was reported by Madden [2] for polypyrrole film during actuation testing. Many studies show that the maximum stress values are less than 10 MPa [3-5]. The low force generation and low breaking strength have restricted practical application of these materials as actuators.

Processability of polyaniline makes it an attractive material for electrochemical actuators. A phase inversion technique has been used to prepare polyaniline actuators [6, 7]. However, as shown in Chapter 5, the mechanical properties of polyaniline films prepared using this approach are very poor. To overcome this problem, a wet spinning process was introduced to fabricate polyaniline fibres which are much tougher than polyaniline films.

Previous work has shown that the addition of carbon nanotubes to polymers can produce significant improvements in strength and conductivity [8]. Carbon nanotubes, with their remarkable properties, function as reinforcement fillers in polyaniline/carbon nanotube (PAn/CNT) composites. It has been shown that polyaniline/carbon nanotube composites can be used as an actuator material where in the polyaniline component contributes a high actuation strain and the carbon nanotubes act as a reinforcing component due to the high modulus.
In this study, as a first step to construct polymer/carbon nanotube composite actuators, a layered composite actuator was prepared by coating polyaniline or polyaniline/carbon nanotubes onto a polypyrrole tube. In the second part of this work, polyaniline/carbon nanotube composite fibres prepared by a wet spinning process were evaluated as actuators.

6.2 EXPERIMENTAL

6.2.1 Reagents and Materials

Propylene carbonate (PC, Aldrich), tetrabutylammonium hexafluorophosphate (TBA-PF6, Sigma), N, N-dimethyl propylene urea (DMPU, Aldrich), N-methyl-2-pyrrolidinone (NMP, Aldrich), phenylhydrazine, methanesulfonic acid (MSA, Aldrich) and sodium nitrate (NaNO3, Sigma) were all AR grade and used as received. Nitric acid (HNO3) and hydrochloric acid (HCl) was obtained from Asia Pacific Specialty Chemicals Limited. Pyrrole monomer from Merck was distilled and stored under -18°C before use. Platinum wires in 250 µm and 50 µm diameter were from Goodfellow. Polyaniline emeraldine base (EB) (MW: 300,000) was purchased from Santa Fe Science & Technology (USA). Single walled CNT (Carbon Nanotechnologies Inc.) were used as received.

6.2.2 Instrumentation

The constant current required for polymerization and the pulse current used during actuation tests were applied using a Model 363 potentiostat/golvanostat
(EG & Princeton Applied Research). Dual-Mode Lever System (Aurora Scientific Inc.) was used when measuring Young’s modulus. All the experimental data was processed and recorded by a PowerLab 4/20 (AD Instruments) connected to a computer.

6.2.3 Layered Composite Actuator Preparation

Polypyrrole helix tubes were prepared as described in Chapter 3.

Polypyrrole/polyaniline composite tubes were fabricated by coating 4% (w/w) polyaniline EB in NMP solution onto the polypyrrole helix tube and then drying on a hot plate. This composite tube was soaked in 1 M HCl solution for 20 minutes before testing. Typically, for 2.5 mg of polypyrrole 1 mg of polyaniline (i.e. 28% w/w) was applied. Certain coated samples were prepared for optical microscopy by mounting in epoxy resin followed by grinding and polishing.

The polypyrrole/polyaniline/carbon nanotube composite tube was prepared by coating a polyaniline/carbon nanotube solution onto the polypyrrole tube. A solution of 0.2% (w/w) of single-walled carbon nanotubes and 4% (w/w) of polyaniline EB in NMP was sonicated for 30 minutes. This solution was then coated on the polypyrrole tube (with and without a platinum helix) and dried on a hot plate. The composite tube was soaked in 1M HCl solution for 20 minutes before testing. Typically, for 2.5 mg of polypyrrole 1 mg of polyaniline/carbon nanotubes (i.e. 1.3% of carbon nanotubes and 27% of polyaniline) was gained.
6.2.4 Polyaniline and Polyaniline/Carbon Nanotube composite fibre Actuator Preparation

All fibres were prepared by Mr. Vahid Mottaghitalab as part of his PhD studies at University of Wollongong.

Polyaniline and polyaniline/carbon nanotube composite fibres were prepared by a wet spinning process. 10% (w/w) polyaniline EB powder was gradually added to DMPU with phenylhydrazine (30% of EB) while the solution was constantly stirred by a mechanical overhead stirrer. A water bath was used to keep the solution temperature around 0°C. For polyaniline/carbon nanotube composite fibre, before adding in polyaniline EB, an appropriate amount of carbon nanotubes (1.25% and 2.5% of polyaniline EB) was sonicated in DMPU for 2 hours at 60°C to drive the carbon nanotubes into the solution. The prepared spinning solution was filtrated and then transferred to a Nitrogen (N₂) pressure vessel. Nitrogen pressure was used to drive the spinning solution through a single hole spinneret with 250µm diameter to the coagulation bath containing 30% NMP in water. In the coagulation bath the spinning solution solidified and the emerging fibre was wrapped on a bobbin. The fibre was stretched 2 times through a hot drawing process using a soldering iron wrapped with Teflon tape and heated to 100°C. The complete removal of residual solvent was carried out firstly by extraction in the water bath for 24 hours followed by drying in a vacuum dryer at 50°C for 12 hours. The fibres were then doped in 1M MSA for 6 hours and then dried in an oven for further test.
6.2.5 Actuation Tests

The actuation performance of the layered composite tubes was tested on a beam balance as described in Chapter 2. The composite fibres were tested on a Dual Mode Lever System 300B. A two-electrode configuration was used when pulse current was applied as electrochemical stimulation. The positive and negative current was applied for 30 s each alternatively from $\pm 1$ mA to the current at which polyaniline actuators produced a maximum actuation strain. The 1 M NaNO$_3$ aqueous solution and 1 M HNO$_3$ aqueous solution were used as electrolyte for the layered composite actuators and composite fibres, respectively.

6.2.6 Young’s Modulus Measurements

Young’s moduli of the layered composite actuators were measured by Dual-Mode Lever System when different potentials ($\pm 0.5$ V $\sim \pm 3.0$ V) were applied. Force was applied to samples in the range of 0 to 20 mN. The strain produced by samples under different stresses was recorded by a computer. The stress vs strain curve was plotted and the Young’s modulus was obtained from the slope of stress/strain line by linear regression.
6.3 RESULTS AND DISCUSSION PART I – LAYERED COMPOSITE ACTUATORS

6.3.1 Electrical and Electrochemical Characterisation

The polyaniline coating of the layered composite tubes was found to be non-uniform and up to 50 µm in thickness. The electrical conductivity as determined by the 4-probe method was measured for all samples and the results are given in Table 6.1. In each case, the helix wire was removed so that the conductivity of the polymer could be determined. Very little difference in conductivity of the samples was observed, probably reflecting the dominance of the more conductive underlying polypyrrole substrate.

Table 6.1: Electrical conductivity of various samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>PPy</th>
<th>PPy/PAn</th>
<th>PPy/PAn/CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (S/cm)</td>
<td>148</td>
<td>125</td>
<td>132</td>
</tr>
</tbody>
</table>

To compare the electrochemical activities of the layered composite tube and pure polypyrrole tube, cyclic voltammetry was performed on these two samples in 1 M NaNO₃ electrolyte. The cyclic voltammograms obtained for the PPy/PAn sample were run for 3 cycles and the second cycle is shown in Figure 6.1. Interestingly, when a polyaniline outer layer was applied to the polypyrrole helix tube, the cyclic voltammogram showed only the results of the outer layer. As shown in Chapter 5, the cyclic voltammogram of polyaniline in NaNO₃ (Figure 5.2(c)) shows that polyaniline is gradually dedoped in neutral electrolyte and the electroactivity is reduced. The
implication of this observation is that in the beginning of the electrochemical cycling, polyaniline dominates the electrochemical reaction. But after cycling for a period of time, polyaniline slowly loses electroactivity then polypyrrole may dominate the electrochemical reaction.

![Cyclic voltammograms](image)

**Figure 6.1:** Cyclic voltammograms in 1 M NaNO₃ for PPy helix tube and PPy/PAn helix tube at a scan rate of 50 mV/s.

### 6.3.2 Actuation Strain under Applied Current

In Chapter 3 it has been demonstrated that the use of cyclic voltage to control the actuation of polypyrrole actuators can lead to a slow net oxidation (or reduction) causing deterioration in the actuation strain. Current pulsing has been adopted to eliminate this problem and more stable actuation strain has been achieved. In this work, current pulsing was applied as electrochemical stimulation. Figure 6.2 shows the relationship between the actuation strain and
the current density applied to the different composite samples in 1 M NaNO₃ aqueous solution electrolytes.

![Graph showing actuation strain at different applied current densities for different composite tubes in 1 M NaNO₃.](image)

**Figure 6.2:** Actuation strain at different applied current densities for different composite tubes in 1 M NaNO₃.

It can be seen from Figure 6.2 that the polypyrrole helix tube shows a higher strain at equivalent current densities than all of the layered composites. These results suggest that the coatings of polyaniline and polyaniline/carbon nanotubes are less active than the polypyrrole substrate and restrict the actuation movement of the polypyrrole. The lack of redox response from the polypyrrole when polyaniline was applied as a coating (Figure 6.1) also explains the smaller movement from the layered composites. This is similar to the results reported by Tahhan et al [9] where a polyaniline/carbon nanotube composite film produced less strain than a neat polyaniline film in NaNO₃ aqueous solution.
6.3.3 Actuation Strain under Applied Stress

As described in Chapter 3, polypyrrole actuators produce much more stable strain with increasing applied stress in ionic liquid electrolyte than in propylene carbonate. The electrolyte plays an important role in actuation performance. NaNO$_3$ aqueous solution as electrolyte for the polypyrrole actuator was examined and compared with the results obtained from ionic liquid and propylene carbonate electrolytes. Figure 6.3 shows the isotonic strain of polypyrrole helix tube actuators in different electrolytes under increasing stress. The current density was chosen so that the strain at zero stress (the free stroke) was the same in all 3 electrolytes (at ~2%).

Figure 6.3: Isotonic actuation strain at different applied stress levels for PPy helix tubes tested in IL and PC (at 13 mA/cm$^2$) and aqueous (NaNO$_3$) (at 19 mA/cm$^2$) electrolytes.
In propylene carbonate the negative slope is sharp with the actuation strain decreasing by 75% when the stress was increased to 4 MPa. The effect of isotonic stress on actuator strain is much less pronounced for the ionic liquid and NaNO₃ aqueous solution electrolytes. Thus, the strain of ~2% is maintained to 6 MPa and 4.5 MPa in aqueous NaNO₃ and ionic liquid, respectively. The maximum isotonic stress that can be applied is limited by the breaking strength of the actuator. As shown in Figure 5.3 the electrolyte clearly influences the tensile strength: increasing in the order PC<IL<NaNO₃(aq). The effect of electrolyte on mechanical properties of polypyrrole has been reported previously [10] with the different breaking stress and extension at break when different electrolytes were employed.

In 1 M NaNO₃ aqueous solution electrolytes, the effect of applied stress on the isotonic strain produced by the composite actuators was investigated. Figure 6.4 illustrates the relationship between the applied stress and the actuation strain of the different layered composites.
Figure 6.4: Isotonic actuation strain at different stress levels measured in 1 M NaNO₃ for different layered composite samples.

The actuation strain of polyaniline in this electrolyte was previously found to be in the range 0.7 – 1.2% and that of neat CNT mat samples was 0.05% in NaNO₃ [9]. In this work, the polyaniline coating on the polypyrrole tube reduces the actuation strain of polypyrrole from 2% to an average value of 1.4% (30% reduction) due to the polyaniline coating. Cross-sectional optical microscopy in Figure 6.5 showed the coating to be non-uniform in thickness and up to 20-50 µm thick. Gravimetric analysis showed the polyaniline to make up 27% of the layered composite. The actuation strain for the PPy helix/PAn/CNT sample decreases further to 1% even though the CNT component is only 1.3% of the composite. Without the platinum helix, the strain for the PPy no helix/PAn/CNT composite was 0.5% (at zero applied stress) decreasing to 0.35% (at 12 MPa applied stress). Obviously, incorporation of components of low actuation strain such as polyaniline and
carbon nanotubes causes restriction of the movement of the composite as a whole.

![Optical micrograph of polished cross-section of polypyrrole helix tube coated with polyaniline.](image)

**Figure 6.5:** Optical micrograph of polished cross-section of polypyrrole helix tube coated with polyaniline.

The importance of the platinum helix in reducing the $iR$ drop along the fibre length is also noted from the comparison of the strain produced by PPy helix/PAn/CNT and PPy no helix/PAn/CNT. The strain produced by the composite without a platinum helix is only half the amount of that produced by the composite with a platinum helix. Despite the high conductivity of the carbon nanotubes, the PAn/CNT composite layer was not as effective in providing good electrical conduction along the fibre length as the platinum helix. The conductivity measurements reported above confirm that the incorporation of a small amount of carbon nanotubes does not change the overall conductivity of the composite structure. This is because the non-
uniform coating of polyaniline/carbon nanotubes and the dispersion of carbon nanotubes in polyaniline need to be improved.

The maximum stress achieved in this study was approximately 12 MPa for the PPy no helix/PAn/CNT composite sample and the lowest value was 4.5 MPa for the PPy helix/PAn/CNT. Apparently, although the platinum helix increases the actuation strain by reducing $iR$ drop along the fibre length, it does not reinforce the strength of the materials (i.e. toughness) that is controlled by inherent imperfections formed in the material bulk during the polymerization. It has also been previously reported that the incorporation of the platinum helix into the polypyrrole tube decreases the tensile strength [11]. It is possible that the platinum-polymer interface is a source of stress concentration leading to lower tensile strength. Higher strengths may be achieved by increasing the platinum-polymer adhesion.

### 6.3.4 Actuation Behaviour and Young’s Modulus

The relationship between the isotonic actuation strain and the Young’s modulus has been described in detail in Chapter 3. To understand the isotonic actuation behaviour of the actuators (Figure 6.4), the Young’s modulus of the different layered composite samples were measured in 1M NaNO$_3$ at various voltages from $-3.0$ to $3.0$ V. Figure 6.6 shows the stress/strain curves of the polypyrrole helix tube at various voltages from $-3.0$ to $3.0$ V in 1M NaNO$_3$ aqueous solutions. The slopes of the stress-strain curves at different voltages are almost unchanged. Similar results were also found for PPy helix/PAn and PPy helix/PAn/CNT samples.
Figure 6.6: The stress-strain curves of the polypyrrole helix tube at various voltages from –3.0 to 3.0 V in 1 M NaNO₃ aqueous solution.

Average values of the Young’s modulus at positive voltages ($Y_d$) and those at negative voltages ($Y_o$) are shown in Table 6.2. The Young’s modulus obtained
from previous studies of polypyrrole helix tubes measured in ionic liquid and propylene carbonate based electrolyte [3, 12] are shown in Table 6.3 and compared with those obtained in NaNO₃ aqueous solution electrolyte.

Table 6.2: Young’s modulus of different layered composite samples measured in 1 M NaNO₃

<table>
<thead>
<tr>
<th>Sample</th>
<th>PPy helix tube</th>
<th>PPy helix/PAn</th>
<th>PPy helix/PAn/CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y_d</td>
<td>34.1</td>
<td>39.3</td>
<td>51.7</td>
</tr>
<tr>
<td>Y_o</td>
<td>34.1</td>
<td>39.6</td>
<td>54.9</td>
</tr>
</tbody>
</table>

Table 6.3: Young’s modulus of PPy helix tube measured in different electrolyte

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>PC</th>
<th>IL</th>
<th>NaNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y_d</td>
<td>120</td>
<td>90</td>
<td>34.1</td>
</tr>
<tr>
<td>Y_o</td>
<td>90</td>
<td>80</td>
<td>34.1</td>
</tr>
</tbody>
</table>

All the samples tested in 1M NaNO₃ show almost no change in modulus across the entire potential range. For the polypyrrole helix tube in ionic liquid, a decrease of 11% in modulus was observed, while in propylene carbonate a larger decrease of 25% was noted between the expanded and contracted states. Thus as predicted by Equation 3.1, the unchanged modulus in NaNO₃ means that the actuation strain (PPy helix and PPy helix/PAn/CNT samples) is independent of the applied stress (Figure 6.4). Only a slight decrease in the strain with increasing applied stress was observed for the polypyrrole actuator in IL (Figure 5.3). The small change in actuation strain corresponds to a relatively constant modulus value over the potential range used. In contrast, a large decrease in actuation strain with applied stress (Figure 5.3) for the
polypyrrole actuator in propylene carbonate is due to the fact that the Young’s modulus decreased by a factor of 4 (i.e. $E_d = 4 E_o$).

As shown in Figure 6.4 for the PPy helix/PAn composite sample, the actuation strain increases from 0.9% to 1.6% when the applied stress increases to 7 MPa and then becomes constant at 8.5 MPa. Obviously, this behaviour cannot be explained by the Young’s modulus that is unchanged with the applied voltage (Table 6.2). The restriction on the expansion/contraction of the composite due to the polyaniline component seems to be less effective at high applied load. As the applied stress increases, the polyaniline component seems to “detach” from the polypyrrole substrate. In fact, as a first approximation if polypyrrole and polyaniline components in the composite are assumed to operate independently, 28% (w/w) of PAn (with 0.8% actuation strain [9] and 72% (w/w) of PPy (with 2% actuation strain) will give theoretical average strain of 1.66% for the composite. Therefore, when the layers are well bonded, the composite behaves according to the rule-of-mixtures approach. If the layers become detached at high loads, then the strain is dominated by the polypyrrole layer. In addition assuming that the layered composite PPy helix/PAn works from the outer layer, at low applied load, polyaniline layer dominates the actuation performance and produces low strain. This has been confirmed by the cyclic voltammogram studies in Figure 6.1. At high applied load, however, because of the non-uniform coating (Figure 6.5), the polyaniline layer will gradually “detach” from the polypyrrole tube. Moreover, because polyaniline become gradually dedoped in neutral electrolyte, it will lose electroactivity with cycling. As a result, the polypyrrole layer progressively dominates the actuation behaviour and gives an increasing strain.
6.3.5 Work-per-Cycle Performed by the Layered Composite Actuators

The mechanical work done per actuation cycle is an important performance parameter for practical actuators. Figure 6.7 shows the work per cycle for each of the layered composite actuator tested in aqueous NaNO₃ electrolyte. The volumetric work per cycle under isotonic conditions is simply given by the product of the applied stress and the actuation strain in Equation 4.2.

![Graph showing work-per-cycle performed by different layered composite samples at different stress levels in 1 M NaNO₃ aqueous solution electrolytes.]

**Figure 6.7:** Work-per-cycle performed by different layered composite samples at different stress levels in 1 M NaNO₃ aqueous solution electrolytes.

It has been described in Chapter 3 that when tested in ionic liquid and propylene carbonate based electrolytes, the work-per-cycle performed by the polypyrrole helix tube actuator was 79 kJ/m³ and 25 kJ/m³, respectively. In this work, when NaNO₃ was used as electrolyte, the same actuator performed
125 kJ/m$^3$ work. For each layered composite actuator, an approximately linear increase in the work occurs with increasing applied stress. The maximum practical work per cycle in these tests is limited by the breaking stress of the actuator material. In the present study, the highest work per cycle was achieved using the PAn/PPy composite sample (at 135 kJ/m$^3$) due to its higher breaking stress than the other samples tested.

### 6.4 RESULTS AND DISCUSSION PART II – COMPOSITE FIBRES

The polyaniline and polyaniline/carbon nanotube composite fibres were about 100–150 µm in diameter with a smooth surface. Compared to the polyaniline films and tubes prepared using the phase inversion technique (Chapter 5), the fibres had good mechanical property and flexibility.

#### 6.4.1 Conductivity Measurement of Polyaniline/Carbon Nanotube Composite Fibres

The electrical conductivities as determined by the 4-probe method were measured for neat polyaniline fibre (F0: 0% CNT) and polyaniline/carbon nanotube composite fibres with different carbon nanotube loading (F1.25: 1.25% CNT; F2.5: 2.5% CNT). The results are given in Table 6.4. Very little difference in conductivity between F0 and F1.25 was observed, however for F2.5, conductivity is significantly increased. This is probably because carbon nanotubes in the F1.25 fibre had not achieved the percolation threshold.
### Table 6.4: Electrical conductivity of various samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>F0 (0% CNT)</th>
<th>F1.25 (1.25% CNT)</th>
<th>F2.5 (2.5% CNT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (S/cm)</td>
<td>50</td>
<td>52</td>
<td>90</td>
</tr>
</tbody>
</table>

#### 6.4.2 Actuation Strain of Polyaniline and Polyaniline/Carbon Nanotube Composite Fibres

In Chapter 5, the actuation behaviour of polyaniline was examined in neutral salt and acid electrolytes. It was shown that acidic electrolyte could maintain the polyaniline doping level and electroactivity, hence improve the actuation performance. So in this work, HNO$_3$ aqueous solution was used as electrolyte. The actuation performance of polyaniline and polyaniline/carbon nanotube composite fibres was investigated in 1 M HNO$_3$ when a pulsed current was applied as electrochemical stimulation. Figure 6.8 shows the actuation strain of the fibres with increasing current density.
Figure 6.8: Actuation strain of different fibres under increasing current density in 1 M HNO₃ electrolytes.

It can be seen from Figure 6.8 that fibres F0 and F1.25 gave a similar maximum strain with 0.97% at 66 mA/cm² current density, and 0.94% at 128 mA/cm² current density, respectively. Under the same current density, the strain produced by F1.25 is much lower than that produced by F0. Fibre F2.5 only gave a maximum strain of 0.4%. Analogous to the previous report [9] and the work in Chapter 5, these results further confirm that the addition of carbon nanotubes with low actuation strain response causes restriction of the movement of the composite as a whole. The higher current densities associated with the carbon nanotubes reinforced fibres may be due to capacitive charging at the nanotube surface.
6.4.3 Strain Response of Polyaniline and Polyaniline/Carbon Nanotube Composite Fibres under Load

The effect of applied stress on the isotonic strain produced by polyaniline and polyaniline/carbon nanotube fibres was examined in 1M HNO₃ aqueous solution electrolytes. The current density was chosen so that the strain was nearly the maximum value in each case. Figure 6.9 shows the isotonic strain of the different fibres under increasing stress. Each sample was tested at increasing loads until rupture occurred.

![Figure 6.9: Isotonic actuation strain of different fibres at different applied stress levels in 1 M HNO₃ electrolytes.](image)

It is shown from Figure 6.9 that the addition of nanotubes greatly increases the breaking strength of the composite fibres under actuation conditions. The fibre F2.5 with 2.5% carbon nanotube loading could sustain stresses of up to 30 MPa without failure during electrochemical cycling. In contrast, the neat
polyaniline can only sustain stresses to 6 MPa. The fibre F1.25 with 1.25% carbon nanotubes breaks at 14 MPa stresses. The increased tensile strength of the composite fibres demonstrates that the carbon nanotubes act as a reinforcing agent to improve the mechanical properties of fibres.

It is also of interest to note that the influence of applied stress on the actuation strain is significantly reduced when the polyaniline fibre is reinforced with carbon nanotubes. In the case of neat polyaniline fibre F0, the actuation decreases rapidly with the increasing applied stress. This behaviour is similar to other conducting polymer actuators such as polypyrrole and polythiophene when tested in organic electrolytes like propylene carbonate. However for fibres incorporating carbon nanotubes, the actuation strains are much more stable with increasing applied stress. The effect of applied stress on isotonic strain has been well established \[13\] and is discussed in detail in Chapter 3 as being due to the change in Young’s modulus that accompanies oxidation and reduction of the actuating polymer. Clearly, the presence of carbon nanotubes diminishes the effect of stress on the actuation strain during the redox cycling.

### 6.4.4 Reinforcing Effect of Carbon Nanotubes

The reinforcement contributed by the small additions of carbon nanotubes to the polyaniline fibres is demonstrated by the dry state tensile test which was conducted by group member Mr. Vahid Mottaghitalab. Figure 6.10 shows the stress-strain curves of polyaniline fibre F0 and polyaniline/carbon nanotube composite fibre F1.25 and F2.5.
Figure 6.10: Tensile test of different fibres at dry state.

It is clearly shown in Figure 6.10 that small amounts of carbon nanotubes produce a remarkable increase in modulus and tensile strength. For neat polyaniline fibre, the elastic modulus is only 0.5 GPa, whereas the elastic modulus increases by a factor of 3 with 1.25% carbon nanotube loadings. For 2.5% carbon nanotube loading fibres, the elastic modulus is about 9 times of the neat polyaniline fibres. On the other hand, the 2.5% carbon nanotube loadings lead to a slight reduction in elongation at break from 13 MPa to 9 MPa. A similar modulus increase of polyethylene/carbon nanotube composite was also reported by Frankland et al [14].

Young’s modulus measurements for the composite fibres were conducted in 1 M HNO₃ electrolyte under different potentials from ± 0.5 V to ± 3.0 V. The Young’s modulus of the fibre is significantly increased by the carbon
nanotube loadings at all applied potential levels. As an example, Figure 6.11 shows the stress-strain curves of the fibres at –2.0 V applied potential.

![Stress-strain curves of composite fibres at –2.0 V](image)

**Figure 6.11:** The stress-strain curves of the composite fibres at –2.0 V in 1 M HNO₃ electrolyte.

Average values of the Young’s modulus at positive potential (Yₐ, polymer expanded state) and those at negative potential (Y₀, polymer contracted state) are shown in Table 6.5. It can be seen that the Young’s moduli of the fibres are increased with increasing carbon nanotube loadings in the composites. The increased maximum stress of the composite fibres shown in Figure 6.9 is no doubt derived from the increased modulus.
Table 6.5: Young’s modulus of the composite fibres measured in 1 M HNO₃ electrolyte

<table>
<thead>
<tr>
<th>Fibres</th>
<th>$Y_d$ Expanded state (MPa)</th>
<th>$Y_d$ Contracted state (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0</td>
<td>156</td>
<td>166</td>
</tr>
<tr>
<td>F1.25</td>
<td>341</td>
<td>445</td>
</tr>
<tr>
<td>F2.5</td>
<td>447</td>
<td>612</td>
</tr>
</tbody>
</table>

It is also noted that for all fibres, the value of Young’s modulus at the contracted state is higher than that at the expanded state. Similar results with higher Young’s modulus at the contracted state were observed for polyaniline films as reported in Chapter 5. Obviously, these results cannot explain the actuation behaviour in Figure 6.9 where the strain is decreased with increasing stress. This is probably due to sample variation and uneven dispersion of carbon nanotubes in the composite fibres.

6.4.5 Work-per-Cycle Performed by Polyaniline and Polyaniline/Carbon Nanotube Composite Fibres

According to Equation 3.2, the work-per-cycle performed by the fibre actuators can be calculated (Figure 6.12).
The maximum work-per-cycle performed by the neat polyaniline fibre F0 was only 17 kJ/m$^3$. This is very low compared with other reported values of up to 83 kJ/m$^3$ for polypyrrole actuators [13] and 135 kJ/m$^3$ reported in the first part of this chapter for PPy/PAn composite actuators. With the addition of 1.25% carbon nanotubes, however, the maximum work-per-cycle increases to 136 kJ/m$^3$, which is nearly 4 times of that performed by the neat polyaniline fibre. This value is also more than 100 times higher than that can be achieved by skeletal muscle [15]. The dramatic increase in work-per-cycle is due to the higher strain and stress level produced by the composite fibre. For 2.5% carbon nanotube composite fibre F2.5, the maximum work-per-cycle decreases to 55 kJ/m$^3$. The low strain (0.2~0.4%) of F2.5 fibre has restricted the work-per-cycle achievement.
6.5 CONCLUSION

It has previously been shown that the use of a platinum helix improves the actuation performance of polypyrrole actuators by reducing the $iR$ drop along the actuator length. In this study, carbon nanotubes have been applied to polypyrrole as a coating within a polyaniline binder in an effort to improve the electrical conductivity and also reduce $iR$ drop. However, the layered composites showed lower actuation strains than the polypyrrole helix tubes (uncoated) because the polyaniline coating prevented the oxidation/reduction of the underlying polypyrrole and restricted the actuation strain.

Despite the lower actuation strain, the actuation under load was improved by the addition of carbon nanotubes. The layered composites of PPy/Pan/CNT allowed stresses in excess of 10 MPa to be applied, while all other samples mechanically failed at much lower stresses. The improved actuation under load may be due to the reinforcing effect of the carbon nanotubes and the absence of the platinum helix.

It was found that the use of aqueous NaNO$_3$ electrolyte allowed a higher strain to be achieved from the polypyrrole helix tube actuator at high isotonic stresses than in ionic liquid and propylene carbonate electrolytes. Also the isotonic strain obtained from aqueous NaNO$_3$ electrolyte is more independent with the applied stress than those acquired from ionic liquid and propylene carbonate based electrolyte. In this point, aqueous NaNO$_3$ electrolyte works with a similar benefit to, and even slightly better than ionic liquid electrolyte for conducting polymer actuators.
Even though the actuator stress has been improved by the reinforcing effect of the carbon nanotubes, the non-uniform coating of the polyaniline/carbon nanotube layer and the poor dispersion of carbon nanotubes in polyaniline are still the obstacles of good actuation behaviour. To enhance the benefit of carbon nanotubes and optimize the actuation performance of the composite actuator, better dispersion of the carbon nanotubes is required.

Wet spinning process provides an alternative way to fabricate polyaniline/carbon nanotube composite actuators. It has been shown from this work that the addition of a small amount of carbon nanotubes into polyaniline fibres leads to improved actuation performance. Much higher strain and breaking strength have been achieved during the actuation cycling for the composite fibre actuators. The actuation strains could be maintained up to 30 MPa stress, which is 5 times higher than the neat polyaniline fibre and 100 times higher than skeletal muscle. These improvements lead to a significant increase in work-per-cycle of the composite fibre compared with the neat polyaniline fibre.

This preliminary study has provided a useful model for the fabrication of polyaniline/carbon nanotube composite actuators where the polyaniline component will provide high actuation strain and the carbon nanotubes as reinforcement, will improve the electrical and mechanical properties of the composite actuators.
6.6 REFERENCES


CHAPTER 7

GENERAL CONCLUSION
The construction and optimisation of conducting polymer electrochemical actuators were the main objectives of this project. These objectives have been achieved through the actuator design and selection of the actuation conditions. Different actuator materials have been investigated including polypyrrole, polythiophene, polyaniline and polymer/carbon nanotube composites. The actuation performances in terms of the actuator strain, work-per-cycle and stability have been significantly improved during this project. The actuation performances of the investigated actuators at certain test conditions are summarised in Table 7.1.


Table 7.1 Summary of actuation performance of conducting polymer actuators

<table>
<thead>
<tr>
<th>Actuator material</th>
<th>Actuator configuration</th>
<th>Conductivity (S/cm)</th>
<th>Electrolyte</th>
<th>Actuation stimulation</th>
<th>Young’s modulus (MPa)</th>
<th>Maximum strain (%)</th>
<th>Maximum stress (MPa)</th>
<th>Work-per-cycle (kJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Expanded state</td>
<td>Contracted state</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPy/PF₆</td>
<td>Helix tube</td>
<td>486</td>
<td>PC</td>
<td>Pulsed current</td>
<td>120</td>
<td>90</td>
<td>4.2</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>IL</td>
<td>Pulsed current</td>
<td>90</td>
<td>80</td>
<td>4</td>
<td>4.5</td>
</tr>
<tr>
<td>P3MT/PF₆</td>
<td>Helix tube</td>
<td>749</td>
<td>PC</td>
<td>Cyclic potential</td>
<td>109.4</td>
<td>69.6</td>
<td>2.1</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>IL</td>
<td>Cyclic potential</td>
<td>70.5</td>
<td>72.5</td>
<td>0.6</td>
<td>4</td>
</tr>
<tr>
<td>PAn</td>
<td>Film</td>
<td>0.3</td>
<td>HNO₃</td>
<td>Pulsed current</td>
<td>3.06</td>
<td>3.45</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Tube</td>
<td>1.3</td>
<td>HNO₃</td>
<td>Pulsed current</td>
<td>-----</td>
<td>-----</td>
<td>2.7</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>Helix tube</td>
<td>244</td>
<td>HNO₃</td>
<td>Pulsed current</td>
<td>-----</td>
<td>-----</td>
<td>2</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>Fibre</td>
<td>50</td>
<td>HNO₃</td>
<td>Pulsed current</td>
<td>156</td>
<td>166</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Composite</td>
<td>PPy/PAn/CNTs</td>
<td>Tube</td>
<td>132</td>
<td>NaNO₃</td>
<td>-----</td>
<td>-----</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>PAn/1.25%CNTs</td>
<td>Fibre</td>
<td>52</td>
<td>HNO₃</td>
<td>341</td>
<td>445</td>
<td>0.9</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>PAn/2.5%CNT</td>
<td>Fibre</td>
<td>90</td>
<td>HNO₃</td>
<td>447</td>
<td>612</td>
<td>0.4</td>
<td>30</td>
</tr>
</tbody>
</table>
In this work, pulsed current control was employed as electrochemical stimulation and compared with the conventional cyclic potential control. It was found that more reproducible and stable strain response had been achieved for polypyrrole actuators using pulsed current control. Current pulsing ensures that the oxidation and reduction processes are equal in their magnitude and prevents the slow net oxidation (or reduction) that typically occurs during symmetrical voltage cycling. Although not tested, it assumed that these benefits would also apply to other actuator materials.

Also in this work, the benefits of ionic liquid as electrolyte have been confirmed for polypyrrole and polythiophene actuators. Firstly, the ionic liquid allows a wider potential window for the polymers and leads to a higher stable strain without polymer degradation thus improving the actuator cycle life. Secondly, a smaller change in Young’s modulus between the polymer redox states results in a more stable isotonic strain and a higher work-per-cycle when the actuators are operated under load.

Although the use of ionic liquid as electrolyte has enhanced the performance of polypyrrole and polythiophene actuators, the polyaniline actuators prepared in this work hardly produced any strain in ionic liquid. This is because the polyaniline actuators require an acidic environment to maintain the doping level and the electroactivity. Ionic liquids that have a high acidity may enable good actuation in polyaniline. The development of such ionic liquids was beyond the scope of the current investigation.

The actuation performance of conducting polymer actuators is mainly determined by the inherent properties of the polymer materials. The ideal
Chapter 7 General Conclusion

actuator materials should have good electroactivity and mechanical property. In this work, the polythiophene and polypyrrole possess high conductivities and good mechanical properties, they can be considered as the leading materials for electrochemical actuators. The electrical and mechanical properties of the polyaniline actuators in this work were limited by the preparation process, however, the processability of the polyaniline makes it an ideal hosting polymer to produce polymer/carbon nanotube composite materials.

In this work, the carbon nanotubes was introduced into conducting polymers as reinforcement fillers aiming to improve the tensile strength, Young’s modulus, and electrical conductivity of the composite materials. The actuation performance of the composite actuators was enhanced; in particular, the presence of carbon nanotubes allowed high stresses to be applied to the composite actuators during the actuation.

The Young’s modulus value of the conducting polymer actuators in the expanded and contracted states is a key parameter to determine the actuation behaviour when operated under load. The Young’s modulus change in the contracted vs the expanded states determines the slope of the actuation strain vs stress line for isotonic conditions. In the case of the polymer with the same Young’s modulus value in the expanded and contracted states, the actuation strain will remain independent of the applied load. If the Young’s modulus value at the expanded state is higher than that at the contracted state, the actuation strain will decrease with increasing load. This behaviour was observed for the polypyrrole actuators when operated in propylene carbonate based electrolyte where the Young’s modulus increases substantially at the
expanded state and decreases sharply at the contracted state. However, when the polypyrrole actuators were operated in ionic liquid as electrolyte, the Young’s modulus change is much smaller thus a less decreased strain was obtained with increasing load. Also in ionic liquid, a higher value of Young’s modulus at the contracted state than that at the expanded state was observed for the polythiophene actuators and leaded to an increasing strain under load. This is the first time for conducting polymer actuators exhibit an increasing strain with increasing load.

In conclusion, to improve the material properties and optimise the actuation conditions are the key approaches for the development of electrochemical actuators based on conducting polymers. With these efforts, significant progresses can be achieved towards the goals of developing the higher, faster and stronger actuators.