E-kursuse "Artificial Muscles" materjalid

Aine maht 6 EAP

Rudolf Kiefer (Tartu Ülikool), 2013

“Artificial muscles”

For many years scientist focused in their research based on the idea to create bionic muscle for human interface structure. The adaption’s of human muscles based on artificial muscles are not succeeding yet but many new developments of artificial muscles based on Electro active polymers (EAP) are in focus for new technologies and applications.

Images taken from: http://www.isi.t.u-tokyo.ac.jp/~niiyama/projects/proj_athlete_en.html

Electroactive polymers, or artificial muscles, are lightweight strips of highly flexible plastic that bend or stretch and function similarly to biological muscles when subjected to electric voltage. This lecture will give an overview of new trends and current development, and discuss future possibilities for EAP technologies.

Contents

Overview “Artificial muscle” course

So called “Artificial muscles” are a group of materials that describe the functionality of muscle work in comparison to natural muscles. The main part of their common functionality is that through an electrical stimuli a mechanical response is triggered which leads to reversible changing in shape or size of the material. The goal for polymeric materials is to reach the efficiency and nearly perfect muscle work of a natural muscle.

Science and technology nowadays requires more and more smart materials with advanced functionality. These smart materials should be lightweight, inexpensive, fracture tolerant, pliable and easily processed and manufactured. To address the requirements of new smart materials the field of EAPs will be introduced in this course and the principle functionality of actuation at different stimuli (electrical, thermal, chemical, magnetic, light-induced) will be addressed on different materials and their functionality. Polymers that showing change in size and shape by applying external stimuli is well studied over several years and named intelligent materials or active polymers[1]. One of the biggest approaches in application of active polymers is found in biomimetics which implements concepts from nature to artificial devices such as birds, fish, insects and plants[2]. The main ideas behind these concepts are to create lifelike robots and to investigate how active polymers can replace limbs and organs in future applications. The “artificial muscle,, course will give new ideas, state of the art research and future vision how these active polymers work and can be adapted in new designs on smart applications. In most books, literature and research the field of active polymers and materials are compared with the efficiency in strain, stress and durability with a natural muscle. To understand how natural muscles work, what are their advantages and where do we get our inspiration to create active polymers, the first chapter will introduce the functionality of natural muscles.

1. Natural Muscle

Muscles are the natural contractile systems that interact over thick and thin filaments of proteins sliding into each other. In early research it was proposed by Huxley[3] in the year of 1957, that protein folding were the reason, developing the cross-bridge model of muscle contraction. To draw a simpler picture for this model, imagine you are sitting in a boat on a still lake. „To move across the lake, you must row, so you have to put the oars in the water and pull backwards. After you finish one drawback you lift the oars out of the water, move them forward and dip them back into the lake for the next stroke“[4]. The natural muscles are composed of two major filaments – a thick filament named myosin and a thin filament defined as actin. The muscle contraction appears when both filaments slide over one another in a series or repetitive events. The energy unit for the stroke (oars of the boat) comes from the energy molecule ATP (adenosine triphosphate). At least 40 kg of ATP is formed in the human body daily, to maintain the energy for functioning.

1.1 Types of muscles

Defined for their functionality there are three different types of muscles shown in Figure 1.

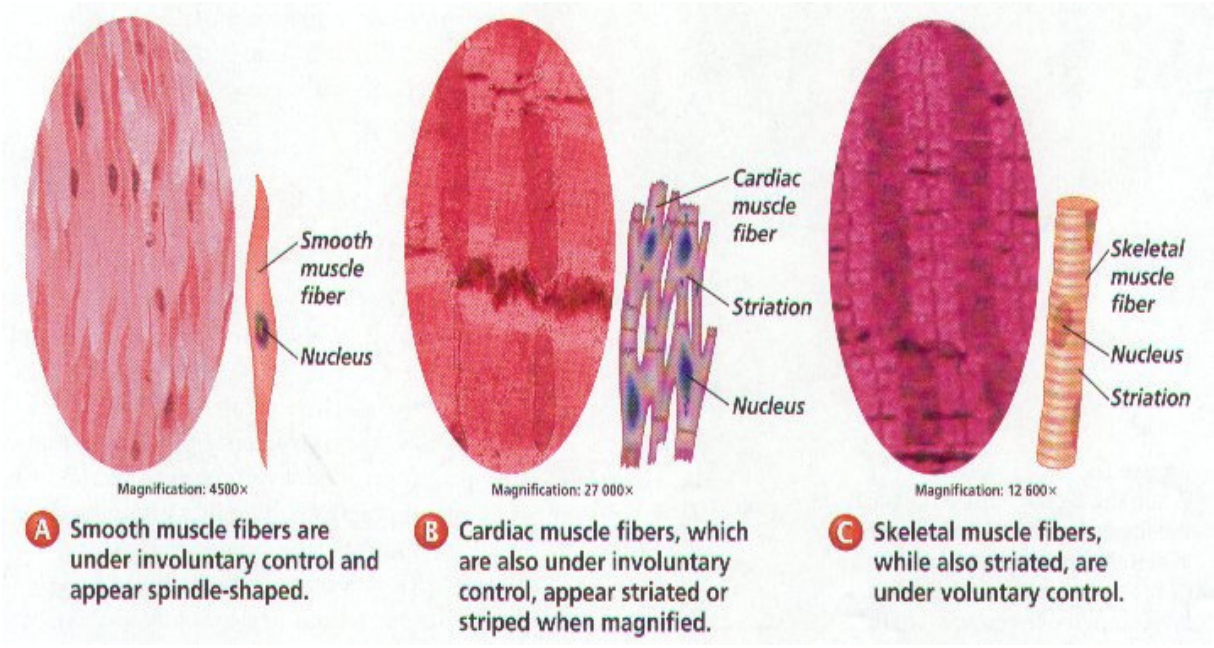


Figure 1: Muscle types based on their structure and functionality. A: smooth, B: cardiac and C: skeletal[5]

The smooth muscles (Figure 1A) are involuntary muscles that make up the walls of blood vessels, stomach, intestines and other groups. The main different to the skeletal muscle is that the control of smooth muscles are involuntary (e.g. under the control of the autonomous nervous system). The primary purpose of smooth muscles is to digest food, pump blood, vomit, control bladder and give birth. The cardiac muscles' main functionality is to pump blood. Similarly to the smooth muscle the cardiac muscle is autorythmic and is controlled by the autonomic nervous system. The cardiac muscles are a special kind of striated (striped) muscles found only in the heart whose fibers are branched and interconnected in complex networks. Each cell has a single nucleus and there is a specialized intercellular junction called an intercalated disc between the two cells, which occurs only in cardiac tissue. Cardiac muscles are controlled involuntarily and, in fact, can continue to function without being stimulated by nerve impulses, which make it possible to reactivate them with outer impulses (reanimation) after heart attacks. The skeletal muscle is the main focus of our comparison to „artificial muscles". It is attached to bones and makes up 40% of the body's weight. It's responsible for locomotion, facial expression, posture, respiratory movements and other types of body movements. The main difference to smooth and cardiac muscle cells can be found in the voluntary action and control by somatic motor neurons. To understand the muscle units, functionality, structure and the signal control, the skeletal muscle will be described in more details.

1.2 Structure and functionality of the skeletal muscle

The units of the muscle are hierarchically arranged. The functional unit of contraction is the myofibril that contains hundreds of protein filaments. The parallel orientated myofibrils form the muscle fiber and the fibers in turn form the muscle. Figure 2 shows the structure of a skeletal muscle from the big to the small units. The muscle is connected to the bone via the tendon and if contraction takes place the movement of the arm or other limps can be obtained.

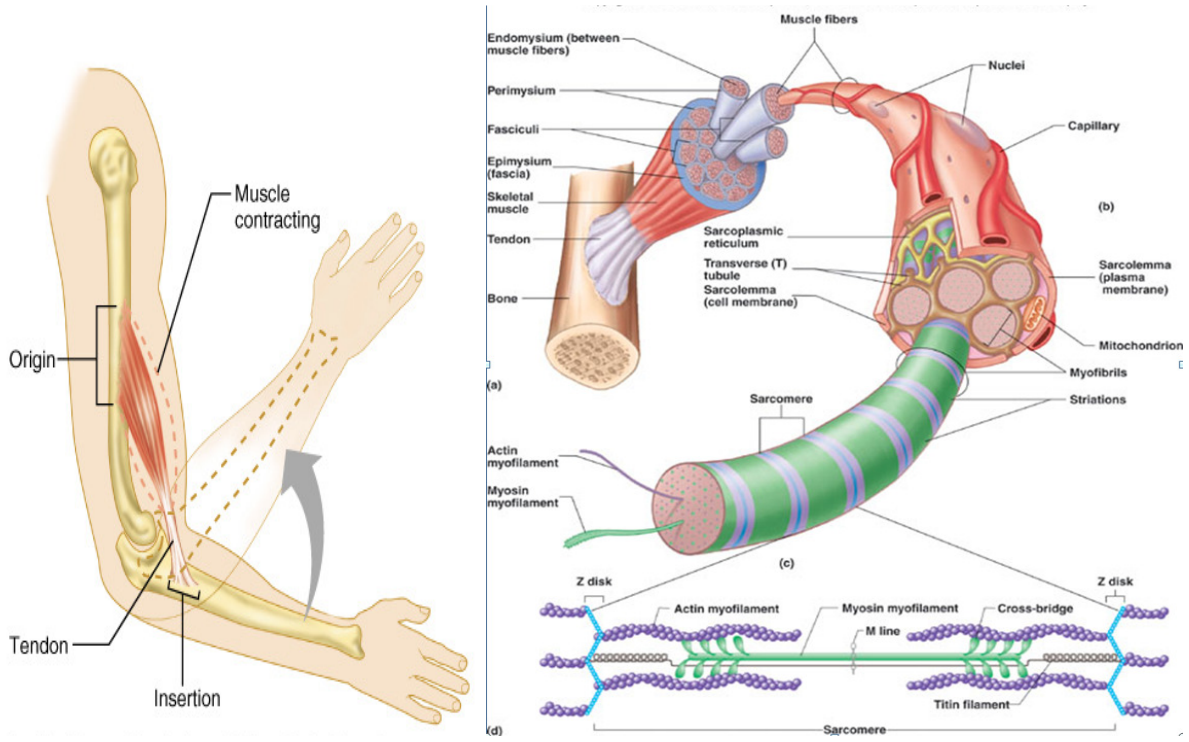


Figure 2: Schema of skeletal muscle contraction and fragmentation of muscle to the muscle fiber, myofibrils, sarcomere and filaments[5].

To analyze which units are responsible on a molecular level, the single structures over muscle fibers to myofibrils, sarcomere and filaments goes to the subunit sarcomere which is the contractile unit of a muscle fiber. The Z-disk is a filamentous network of proteins functioning as an attachment for actin filaments. The M-line is a protein where myosin is attached. To understand how the sliding mechanism works, a nerve signal must be given to contract the muscle. The *trans*formation of the signal takes place over the motor unit also described as nerve functional unit. The number of muscle fibers connecting to the motor units can vary from 4-6 to 1200-1500. The size of the motor units depends of the muscle applied, as an example small motor units can be found at fine movements (eyes or fingers) and large motor units are mostly at large weight-bearing muscles (thighs or hips). The signal processing takes place over the neuromuscular junction forming a synaptic cleft which is a gap filled with interstitial fluids to *trans*form the nerve signal to the muscle fibers via the neuro*trans*mitter (acetylcholine). The sliding mechanism is presented at Figure 3.

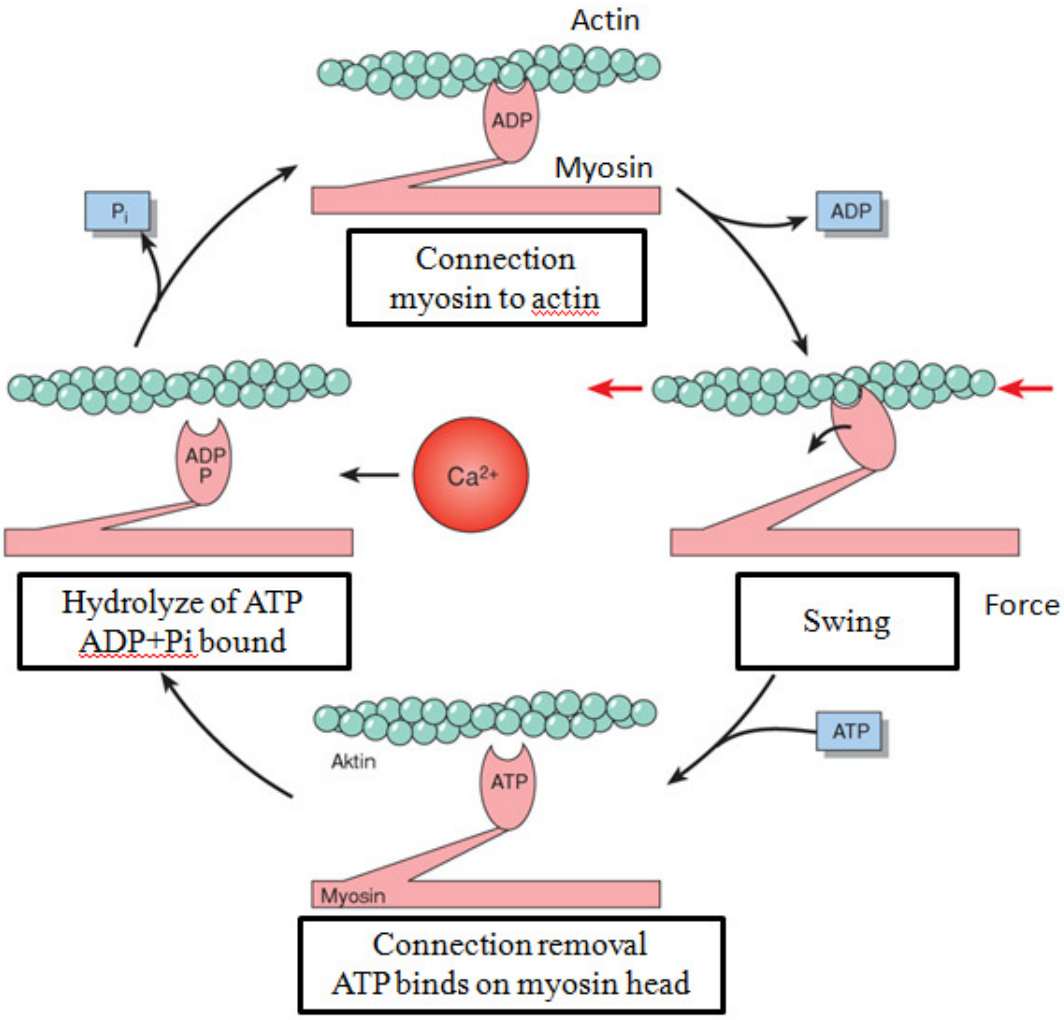


Figure 3: Sliding mechanism over actin, myosin and ATP[6]

The muscle contraction starting with activating of the myosin head with ATP that split into ADP + Pi (Pi: Phosphate unit) with gaining energy in the range of 7.3 kcal/mol per splitting of ATP to ADP + Pi to move the myosin head to the binding site of the actin filament. Over a weak to strong connection the removal of Pi gives the necessary energy resulting in the bending of the myosin head (row of the boat, swing). When the ADP is removed from the myosin head a second swing appears. The place where ATP was sitting is now free and with a new ATP molecule the strong connection between myosin head and actin loosens. Ions like Ca^{2+} plays a vital role for the signal *trans*port in the contraction of the muscles. If the concentration of Ca^{2+} increases, the process of binding myosin to actin will start again. This continued action causes a sliding of the myosin along the actin and as results the muscle is shortened (contracted).

1.3 New research topics in natural muscles

To connect polymeric actuators to the natural muscle contraction some simplification needs to be made. If we assume that a natural muscle behaves like a polymer gel and the polymeric filaments contract in phase-*trans*ition of the polymer gel, then we have a link to the synthetic polymer actuators. However the cooperative manner of the filaments leads to simultaneous shortening. "Thus, the connecting filaments shorten in the absent of any activation; it behaves as a discrete elastic band"[7], that makes biological system much smarter than any present-day artificial replacements. A recent research paper[8] applied cardiac muscles on synthetic hydrogels to apply them in actuator developments. The idea behind this concept comes from the functionality of cardiac muscles to contract if one stroke given to the muscle cells that the whole layer of cells is reacting. The researcher designed bimorph cantilevers based on a solid base and a flexible cantilever where the cardiac cells seeded (Figure 4).

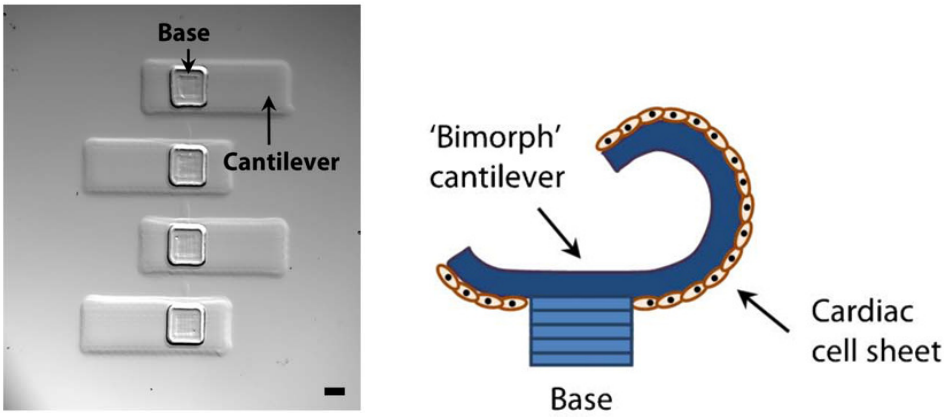


Figure 4: Design of cardiac cell actuator with flexible cantilever and solid base fabricated from hydrogels PEGDA[8]

To achieve a walking robot here named as bio-bot 1-3, the solid base needs to be arranged asymmetrically that in activation, the displacement of the flexible cantilever leads to a movement of the device as demonstrated in Figure 5.

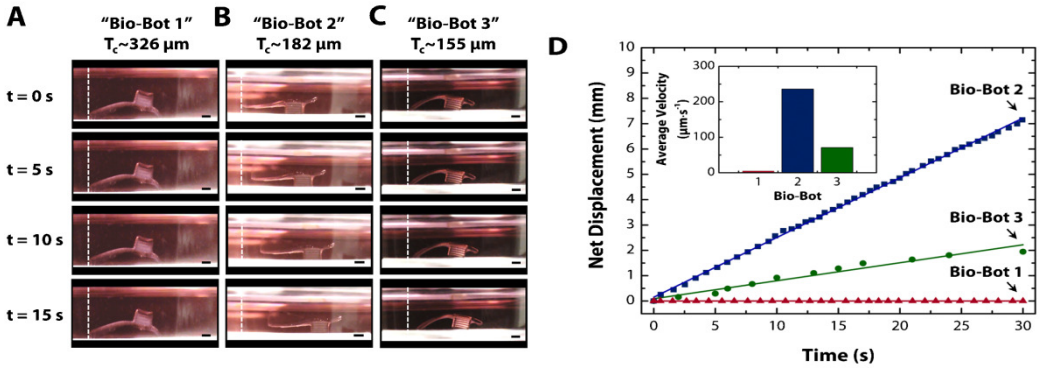


Figure 5: Bio-Bot 1-3 in different arrangement lead to walking robots for Bio-Bot 2 and 3 seen at A-D. Bio-Bot 2 shows the best velocity in this study[8]

The maximum velocity of the bio-bot was found to be 236 µm s^{-1}, the average displacement per power stroke was 354 µm at an average beating frequency of 1.5 Hz. The researcher believes that the bio-bots can find application in bio-sensing, drug delivery, energy production, environmental remediation and the development of artificial immune systems. The combination of biological elements with synthetic polymers will give new insight how muscle cells react to each other and open new applications applying robots in living organisms.

The working principle of active polymers and smart materials is given in the next chapter to evaluate how those materials perform in comparison to natural muscles. The application and actuality for each sample of EAPs and non-EAPs will be presented.

2. Infrastructure of "Artificial muscle"

The group of "artificial muscles" is divided into the EAPs and the non-EAPs, which all have different properties in efficiency, density, force, actuation strain and reaction speed. For all actuators there is a common effect, where by applying energy on it (light, magnetic impulse, electricity, pressure or other) the mechanical actions will respond within a certain time. Since the name artificial muscle is used, the comparisons to the real muscle of all materials are presented in Figure 6.

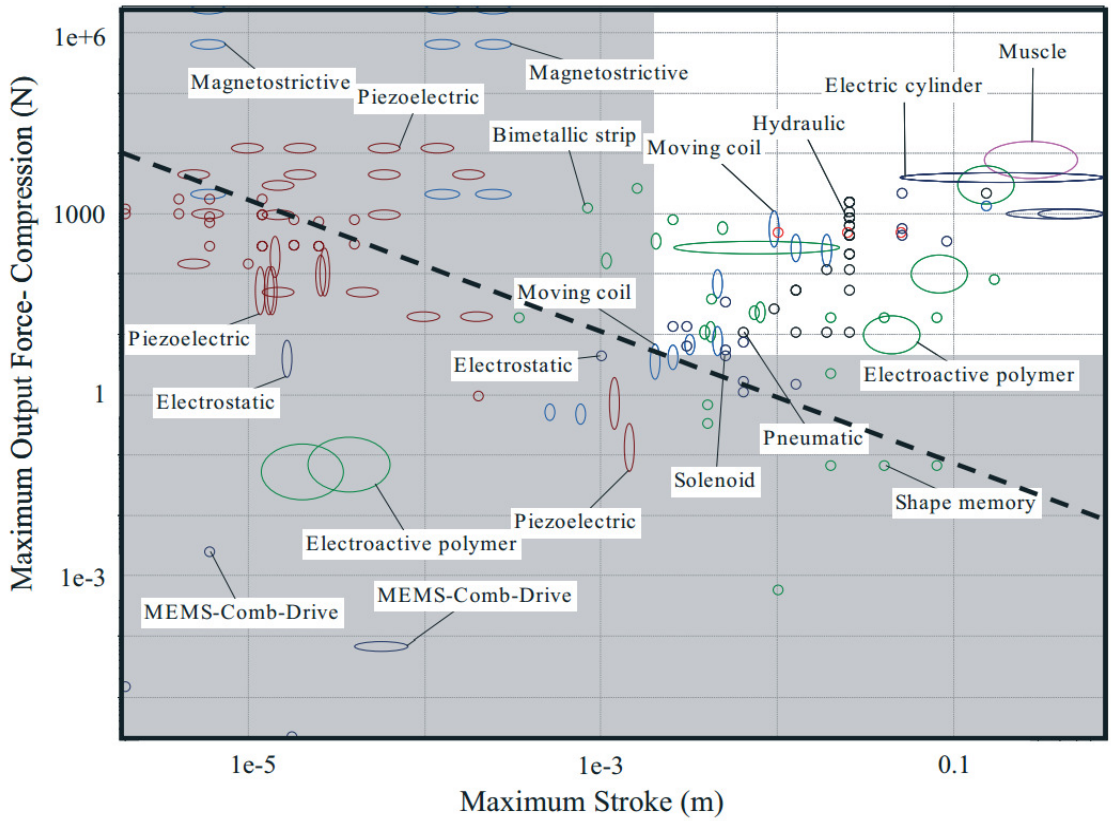


Figure 6: Map of all types of actuators in relation force to stroke output[7]

The natural muscle properties are found in the right corner of the map shown in Figure 6. However it is difficult to determine the properties of natural muscles, because most measurements are made on large shell-closing muscles of scallops[9]. The peak stress of 150-300 kPa is developed at a strain of 25% with a maximum power of 150-225 W/kg. The average power is in the range of 50 W/kg with an energy density of 20-70 J/kg which decreases with an increasing speed. It should also be noticed that the muscles produce a linear force and all motion in joints are rotary. The properties of the natural muscles can be found (Figure 6) for electrical cylinder and hydraulic motors with force output above 1000 N and stroke in the range of 0.1 m. Most applied robots or biomimetic applications nowadays are still designed for electro motors. The largest focus for robots can be found in military use, space, toys and artificial limbs. „Realistically looking and behaving robots are believed possible, using artificial intelligence, effective artificial muscles, and biomimetic technologies"[10]. To achieve robots based on active polymers (EAPs and non-EAPs) more research and development has to be made. The following section will introduce the non-EAP group.

2.1 Non-EAPs

Under this group, chemical activated polymers such as PAN (polyacrylenitrile), inorganic materials like electroactive ceramics (EACs) and alloys who change their form under stress or temperature (shape memory alloys, SMA) will be briefly introduced. An early invented actuator that named McKibben muscle or pneumatic artificial muscle (PAM) will be given in the next section which is different from the traditional actuators. The actuator mechanism is very simple by pressing air in a flexible bladder that changes size and form.

2.1.1 McKibben muscle (PAMs)

The first design PAM was designed in 1929[11] but did not show good performance due to the bad design and properties. Further development made by Joseph L. McKibben in the year 1950 and was originally intended to actuate artificial limbs for amputees. The first models and principles are shown in Figure 7.

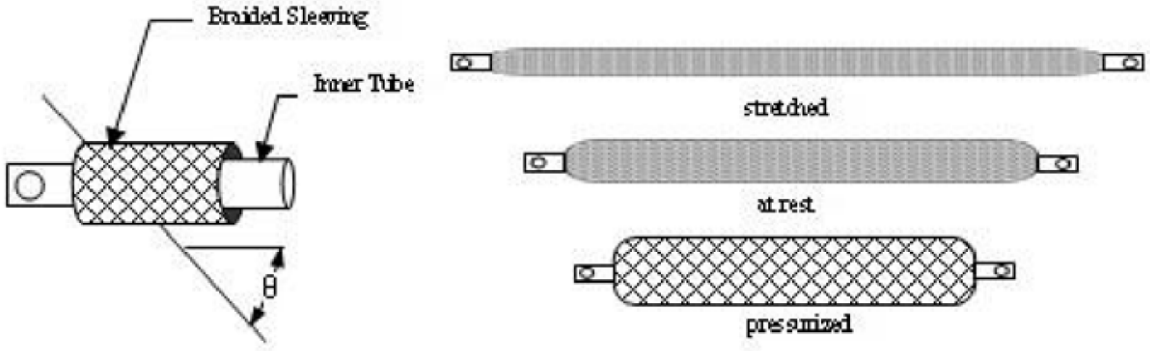


Figure 7: McKibben muscle design[11]

McKibben muscles (PAM) can operate under-pressure and over-pressure. Usually over-pressure is applied because of higher energy transfer. There exists a linear relationship between applied gas pressure and generated force, but the actuation depends from the change in the volume of the bladder which also is determined by the length and design of the PAM actuator. "The unique, physical configuration of these actuators gives them variable stiffness and spring like characteristics: nonlinear passive elasticity, physical flexibility, and light weight"[12]. Some different designs of PAMs are presented in Figure 8.

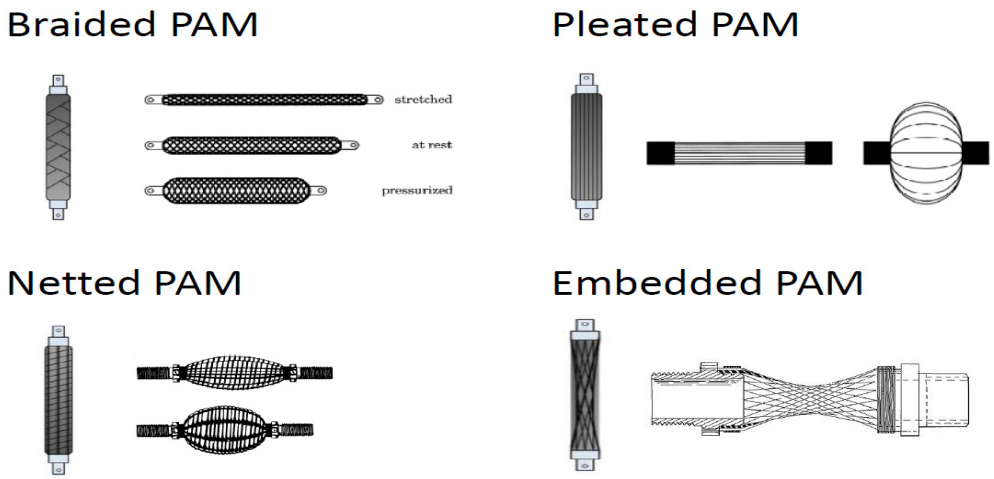


Figure 8: Designs of PAM (braided, pleated, netted and embedded)[13]

The pleated PAM is also called PPAM (Figure 8) and the membrane has a special arrangement by folding along its central axis to form accordion bellows that unfurls during inflation of the membrane[11]. The PPAM design is very strong and can operate with large strokes and show nearly no friction. As an example a 60g actuator can pull 3500 N of load. To make the adaptation of skeletal muscles the PAM can be arranged in antagonist pairs and giving an actuator control of its stiffness and compliance[14]. Several applications of robotic devices such as arms, limbs and legs by applying PAM are developed[15]. PAM is also presented in soft actuators without endo- or exoskeletons. The special design architecture of pneumatic channels (PN, Pneu-net) are embedded in a layer of extensible elastomer and bonded to inextensible layers. As a result the soft actuator can be arranged as a quadrupedal "walker"[16] applicable for soft robots with camouflage displays[17].

2.1.2 Shape-Memory alloys (SMA) and polymers (SMP)

Shape-Memory alloys (SMA) are materials that can remember their shape. SMA was first discovered in 1932 with AuCd alloys[7]. Further research in the following years established the most known and nowadays still applied NiTi (NiTinol) alloys which are non-toxic, made of inexpensive materials, showing high strength and found to be super elastic. The shape memory effects of SMA are the effect to deform above their critical temperature presenting large reversible elastic deformation. Two different crystal structures called austenite and martensite are formed over a phase transition induced by different temperature gradients (Figure 9).

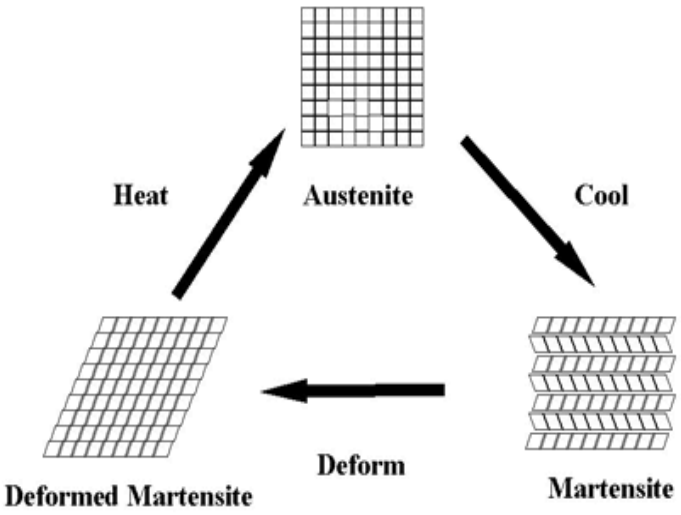


Figure 9: Phase transition of SMA by heating, cooling and induced stress[18]

The austenite structure is a cubic crystal structure and is formed at high temperature. If the SMA alloy is cooled down the monoclinic crystal martensite is formed. With induced stress the alloy can be deformed and by heating, the original austenite can be achieved. For a simpler picture the SMA wire can be pre-stressed by bending or pressing in some form, then by heating it goes back into its original form with extent strain of 3-5%[19]. Many applications for SMA are found, starting from an invention in 1970 to use a motor which transforms heat into mechanical movement[20], building wings for robotic insects[21] and include SMA in medical applications.

Some shape memory polymers (SMP) such as co-acrylic acid-n-stearyl acrylate hydrogels and polyurethane[22] show a shape memory effect by switching between two phases with different dimensions.

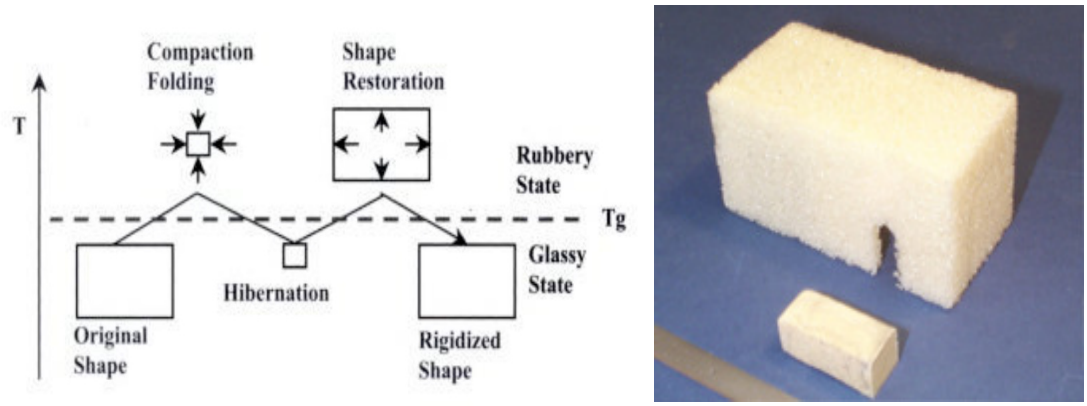


Figure 10: SMP different phases lead to volume expansion and contraction[7]

Shape-memory polymer (SMP) applications are found in different fields such as deploying objects in space to manufacturing dynamic tools[23]. One type of SMP is the cold hibernated elastic memory (CHEM) structure that can be compressed into a small volume at a temperature higher than the glass transition temperature (Tg) and stored at temperatures

below this Tg. When this material is heated again above Tg, the original volume of the structure is restored. Volume ratios of up to forty times have been obtained[11]. The advantages of these materials are their lightweight properties and their small size in comparison to their normal size if they are compressed and stored below T_g. CHEM materials can be found in shelters, hangars, camping tents, rafts and outdoor furniture due CHEM's good impact and radiation resistance and strong thermal and electrical insulation. The disadvantages of CHEM materials are the availability to apply pressure to them, which makes them not applicable in all outdoors equipment. In case of biodegradable and biocompatible SMP the main focus is set for invasive surgery materials that, in case of thin SMP fibers, can be used in stitching wounds, which can then be heated to about transition temperatures, thus expanding and closing the wound[24].

2.1.3 Light activated polymers

Polymers that change volume and shape when exposed to light were discovered in the early 1970s by Aviram in applying a polymer named poly(N,N-dimethylglutamanilide) to obtain expansion in the range of 30% under UV light[7]. Over the years of research until 2000 the class of polymers that could be activated by light were collected and named "jump molecules". Such polymer gels can contract up to 20% when exposed to 455 nm light source and return to original size if light is switched off[25]. In another experiment the source of laser light was applied on polymer water gel based N-isopropylacrylamide (PNIPAM) (Figure 11) where the beam excites localized polymer molecules, causing functional groups on nearby molecules temporarily attract each other. This attraction leads to shrinkage of the polymer gel induced by laser phase transition[26]. Potential applications envisaged include printing, photocopying and actinometrical applications.

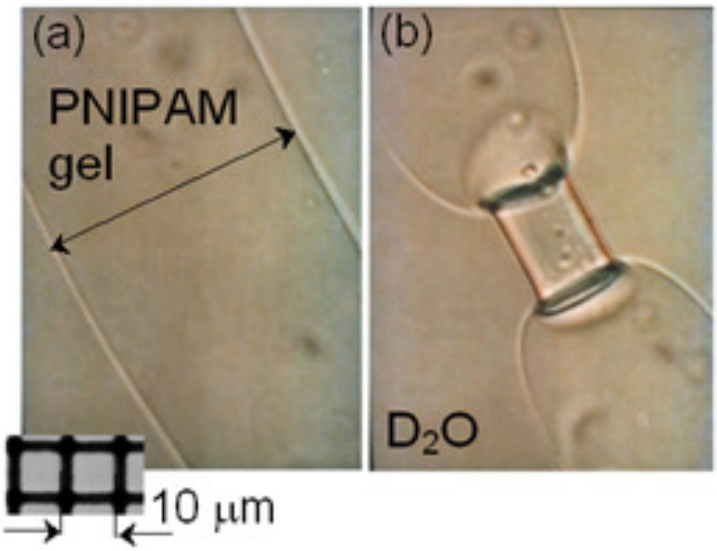


Figure 11: Micro-video image of PNIPAM gel rod in of a: before and b: after laser light illumination[7]

Stimuli responsive polymer gels (Figure 11) by laser light activated will lead to new developmens of gel-based systems applicable in artificial muscles, switches and memory devices[27].

2.1.4 Magentically activated polymers

The groups of magnetically activated gels are called ferrogels, which are polymer networks, which in the presence of a magnetic field start to swell or contract[28]. To enhance the effect of the magnetic field on ferrogels, solid (particle size ~ 10 nm) and fluid like materials are included[29]. The solid magnetical particles are attached to the polymer backbone via strong adhesive forces. The ferrogel shows no expansion or contraction under a uniform magnetic field, but if a magnetic field gradient applied the particles produces a net forward force, inflecting a macroscopic deformation of the gel, then the polymer gel can bend, contract or rotate in dependence of the geometric arrangement of the magnetical particles in the gel. The applied magnetic field on the gel can be more easily controlled using an electromagnet, where the current intensity gives the controllability[30]. In a ferrogel the magnetic particles show no net magnetic field in the material. It was observed that the magnetization of the ferrogel is directly proportional to the concentration of the magnetic particles and their saturation magnetization. An example of a ferrogel subjected to the effect of two different magnetic fields is given in Figure 12.

A B

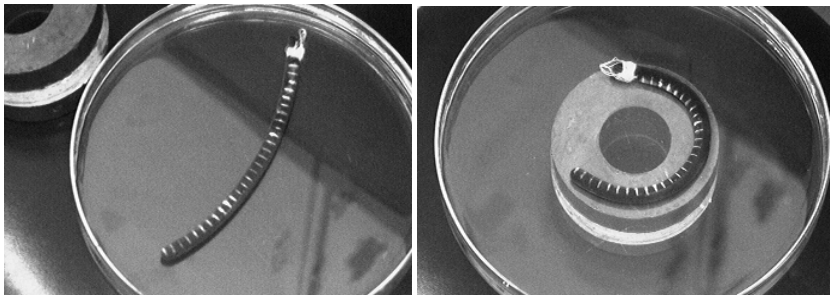


Figure 12: Shape change of ferrogel induced by nonuniform magnetic fields. A: ferrogel is 15 cm from the magnet and B: magnet is placed under ferrogel[7]

In small fields, it was determined that the magnetization is linearly dependent on the field intensity, whereas in high fields, saturation magnetization was achieved[30]. If the ferrogel is suspended along the axis of the magnet, the elongation induced by non-uniform magnetic field depends on steady current flow. It was discovered that the modulus of the ferrogel is independent of the field strength or the field gradient. “Through induction, magnetically heated, triggerable gels have been developed, where the heat generated from various loss mechanisms in the gel produces a thermal phase transition”[11]. The loss mechanisms include ohmic heating from eddy current losses, hysteresis losses, and mechanical (frictional) losses. Volume change was observed in these materials when a quasi-static (frequency of 240 kHz to 3 MHz) magnetic field was applied. When the field is removed, the gel returned to its initial shape, due to cooling of the material. Power electronic drives are being developed which will

aid in the development of closed-loop servomechanisms for actuators. These materials show the potential in contact-less actuation and deformation wherever the magnetic field can reach, e.g. triggering gels under the skin[31]. MR rubber materials are being used in the development of adaptively tuned vibration absorbers, stiffness-tunable mounts and suspensions, and automotive bushings. These materials usually show continuously controllable and reversible rheological properties while under an applied magnetic field[32]. Magnetic polymers, with magnetic particles dispersed in a rubber matrix, have been used in magnetic tapes and magnetic gums for more than three decades[33].

2.1.5 Thermally activated gels

Another way to induce volume change of a polymer gel includes a thermal phase transition that was first discovered in 1984 by Hirokawa and Tanaka[34] by using poly(N-isopropylacrylamide) (PNIPAAm) gels. The phase transition of the material was observed in temperature range of 20-40^{0}C with contractile force of 100kPa in a response time of 20-90s. Most of the studies on thermal phase transitions of gels were done on N-substituted polyacrylamide derivatives. Another example for a thermoresponsive gel widely used based on poly(vinyl methyl ether) (PVME) which shows phase transition at 38^{0}C. One of the main advantages of PMVE is the water solubility and the precipitation of the polymer as a result of increasing the temperature, which are the effect of transformation between the hydrophilic to hydrophobic structure. PVME polymer gels can be cross-linked by gamma-ray irradiation. The volume phase transition that is induced by temperature changes makes the polymer gels suitable for soft actuators or thermoresponsive separators[35]. The thermal responsiveness of the gel actuators with the use of hot and cold water is presented at Figure 13.

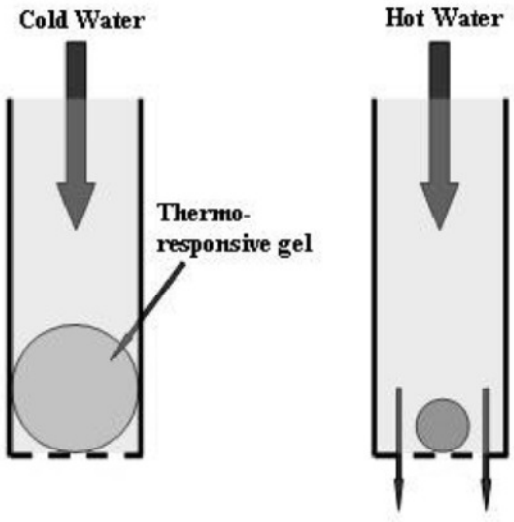


Figure 13: Thermoresponsive gels applied as valves, which allows only hot water through the pipe[11]

Thermoresponsive gels are investigated to apply those materials in different applications, such as NIPAAm gels for controlled drug release or as substrate for immobilized enzymes. As seen

in Figure 13 the application of thermoresponsive gels as valves – the gel blocks the flow of cold water, but permits the flow of hot water, because the gel shrinks and opens the valve[35]. The cold and hot water valve is applied on microscale for lab-on-a-chip applications.

3. Electroactive polymers (EAPs)

EAPs can be divided into two major categories based on their activation mechanism including ionic and electronic (Table 1).

Table 1: EAP group[7]

Dielectric EAP	Ionic EAP
Ferroelectric Polymers	Carbon Nanotubes (CNT)
Dielectric Elastomers (DE)	Carbide-derived Carbon (CDC)
Electrostrictive Graft Elastomers	Ionic Polymer Metallic Composite (IPMC)
Liquid Crystal Elastomers (LCE)	Conductive Polymers (CP)
	ElectroRheological Fluids (ERF)
	Ionic Polymer Gels (IPG)

Coulomb forces drive electronic EAPs, which include electrostrictive, electrostatic, piezoelectric and ferroelectric effects. This type of EAP materials can be made to hold the induced displacement while activated under a DC voltage, allowing them to be considered for robotic applications. These EAP materials have a greater mechanical energy density and they can be operated in air with no major constraints. However, the electronic EAP require high activation fields (>100 V/μm) that may be close to the electrical breakdown level. In contrast to the electronic EAP, ionic EAPs are materials that involve mobility or diffusion of ions and they consist of two electrodes and an electrolyte. The activation of the ionic EAP can be made by as low as 1-2 Volts and mostly a bending displacement is induced. Examples of ionic EAP include gels, polymer-metal composites, conductive polymers, carbide-derived carbon and carbon nanotubes. Their disadvantages are the need to maintain wetness and they pose difficulties to sustain constant displacement under activation of a DC voltage (except for conductive polymers). The induced displacement of both the electronic and ionic EAP can be designed geometrically to bend, stretch or contract. Any of the existing EAP materials can be made to bend with a significant bending response. However, bending actuators have relatively limited applications due to the low force and torque that can be induced. EAP materials are still custom made mostly by researchers and they are not available commercially. The advantages and disadvantages of EAP materials are listed in Table 2.

Table 2: Advantages and Disadvantages of EAP types[7]

EAP type	Advantages	Disadvantages
Electronic EAP	▪ Can operate in room conditions for a long time ▪ Rapid response (mSec levels) ▪ Can hold strain under DC activation ▪ Induces relatively large actuation forces	▪ Requires high voltages (~150V/μm) ▪ Requires compromise between strain and stress ▪ Glass transition temperature is inadequate for low temperature actuation tasks
Ionic EAP	▪ Large bending displacements ▪ Provides mostly bending actuation (longitudinal mechanisms can be constructed) ▪ Requires low voltage	▪ Except for CPs, ionic EAPs do not hold strain under DC voltage ▪ Slow response (fraction of a second) ▪ Bending EAPs induce a relatively low actuation force ▪ Except for CPs, it is difficult to produce a consistent material (particularly IPMC) ▪ In aqueous systems the material sustains hydrolysis at >1.23-V

To apply those new materials in commercial applications several attempts or innovations have been done. The most common interest are new engine technologies because the commercially available combustion engines are generally most efficient when operated continuously and are therefore not ideal for applications in which motion is frequently interrupted, such as valves or walking robots. Electric motors are low in torque to mass compared to muscles making them very bulky for medical, robotic and fluidic applications. Piezoceramics achieve very high power densities but strain is small (0.1 %), making massive mechanical amplification necessary if significant displacements are needed. There is currently no technology that is widely used to replace or simulate muscles, providing a strong motivation for research and development[36].

The composition, mechanisms, properties and material's challenges are described in this manuscript for each technology and material. The key properties of interest are elastic modulus, strain, stress, work density, power density and electromechanical coupling. Work density is the amount of mechanical work per unit volume in one actuator stroke. The convention in work density used in the piezoelectric and dielectric elastomer is to report the work done in elastically deforming the actuator materials itself in one dimension. The full range of compliances has been explored, from dielectric elastomers (E< 1 MPa) to carbon nanotubes (E_{tube}~640 GPa). The electronic EAP material will be introduced in the next chapter including an in-depth review of nowadays commercial materials based on piezoelectric and dielectric elastomers.

3.1 Electronic EAPs

The advantages and disadvantages of the different types of electronic EAPs are presented in Table 3.

Table 3: Electronic EAPs types, their actuation principle, advantages, disadvantages and materials[7]

Actuator type	Principle	Advantages	Disadvantages	Reported Types
Ferroelectric Polymers	Polymers that exhibit noncentrosymmetric sustained shape change in response to electric field. Some of these polymers have spontaneous electric polarization making them ferroelectric. Recent introduction of electron radiation in P(VDF-TrFE) copolymer with defects in their crystalline structure dramatically increased the induced strain.	• Induce relatively large strain (~5%). • Offer high mechanical energy density resulting from the relatively high elastic modulus • Permit ac switching with little generated heat • Rapid response (msec levels)	• Require high voltage (~150 MV/m). Recent development allows an order of magnitude less voltage. • Difficult to mass produce • Making thin multilayers is still a challenge and sensitive to defects. • High temperature applications are limited by the Curie temperature	• Electron-radiated P(VDF-TrFE) • P(VDF-TrFE) Terpolymers • P(VDF-TrFE-CTFE) - CTFE disrupts the order in place of the irradiation.
Dielectric EAP or ESSP	Coulomb forces between the electrodes squeeze the material, causing it to expand in the plane of the electrodes. When the stiffness is low a thin film can be shown to stretch 200-380%.	• Large displacements reaching levels of 200–380% strain area • Rapid response (msec levels) • Inexpensive to produce	• Require high voltage (~150 MV/m) • Obtaining large displacements compromises the actuation force • Require prestrain	• Silicone • Polyurethane • Polyacrylate
Electrostric-tive Graft Elastomers	Electric field causes molecular alignment of the pendant group made of graft crystalline elastomers that are attached to the backbone.	• Strain levels of 5% • Relatively large force • Cheaper to produce • Rapid response (msec levels)	• Require high voltage (~150 MV/m)	Copolymer – poly(vinylidene-fluoride-trifluoroethylene)
Liquid Crystal Elastomers [Lehman et al., 2001]	• Exhibit spontaneous ferroelectricity • Contracts when heated offering no-electroactive excitation	• When heated it induces large stress and strain (~ 200kPa and 45%, respec-tively) • Requires much lower field than ferroelectrics & Dielectric EAP (1.5 MV/m, 4 % strain). • Fast response (<133 Hz).	• Low electro-strictive response • Slow response • Hysteresis	• Polyacrylate • Polysiloxane

"The simplest field driven actuation mechanism is the result of the electrostatic interactions between electrodes. This mechanism dominates in low modulus materials such as dielectric elastomers (section 2.1) in which extremely large strains (> 40 %) can be obtained. A second mechanism is observed in electrostrictive polymers, where electric dipoles within the polymer are pushed or pulled by the applied field, resulting in displacement. The highest strains are achieved in ferroelectric polymers in which imperfections are introduced to disrupt long range order such that field applied to a paraelectric phase leads to conformational changes in the backbone, induced polarization, and large strains (up to 7 %). Graft copolymers in which polar side chains form crystalline domains also produce substantial strains, as do liquid crystal elastomers in which polar groups are oriented by the applied field. A perceived drawback with this class of actuators is their use of high voltages (> 1 kV typical) due to the very high fields that are needed (~ 100 MV/m). This challenge is being addressed by reducing film dimensions and increasing dielectric constant. These materials feature good electromagnetic coupling coefficients, and high work densities (100 x that of muscle)"[36].

3.1.1 Ferroelectric polymers

This chapter will discuss the electronic EAP class of materials, such as typical piezoelectric polymers or electrets, which have linear electrochemical responses, and electrostrictive polymers, which have non-linear electrochemical responses.

3.1.1.1 Historical background

Researchers knew that as early as 1919 Japanese Navy Captain Kawao Wantachi had been able to create an artificial membrane by mixing beeswax with Brazilian palm gum (usually carnauba wax and resin)[7]. The resulting material was then polarized in an electric field, and maintained its charge for a long time afterward, resulting in the world's very first electrets. There have been several hints in historical documents that the first Japanese telephones operated with this material. Some years later at 1925 the Professor Eguchi rediscovered the marks made by Wantachi on electrets work and he published the first developed EAP material[37]. "ELECTRET" is the name given to the dielectric which is electrized permanently by a special treatment according to the author[37]. Some waxes and resinous materials have moderate conductivity in their liquid state, while they are very good insulators in the solid state. The electrical conductivity of these materials varies gradually with the degree of solidification, and when the materials get moderately hard the conductivity becomes practically zero. From several subsequent studies it has become evident that the electrical change of the dielectric is not of a superficial nature, but that it is a permanent internal change within the material[37]. Further research and development have been done by Kawai in the year of 1969[38] where he could observe piezoelectric activity in poly(vinylidene fluoride) (PVdF) and he discovered that those materials can be applied as sensors, actuators and loudspeakers. Permanent polarization exists even after the removal of the field, and the Curie temperature in ferroelectric materials, similar to ferromagnetic materials, disrupts the permanent polarization through thermal energy[39].

3.1.1.2 Piezoelectric Effect

The piezoelectric effect is a linear electromechanical effect where the mechanical strain (S) and stress (T) are coupled to the electric field (E) and displacement (or charge density D) [7].

$$S = d\,E \qquad (1)$$

$$D = d\,T \qquad (2)$$

The nature of the piezoelectric effect is closely related to the occurrence of electric dipole moments in solids. The latter may either be induced for ions on crystal lattice sites with asymmetric charge surroundings (as in BaTiO3 and PZTs) or may directly be carried by molecular groups (as in cane sugar). The dipole density or polarization (dimensionality [Cm/m^3]) may easily be calculated for crystals by summing up the dipole moments per volume of the crystallographic unit cell. As every dipole is a vector, the dipole density P is a vector field. Dipoles near each other tend to be aligned in regions called Weiss domains. The domains are usually randomly oriented, but can be aligned using the process of poling (not the same as magnetic poling), a process by which a strong electric field is applied across the

material, usually at elevated temperatures. Piezoelectric materials show the opposite effect, called converse piezoelectric effect, where the application of an electrical field creates mechanical deformation in the material[40].

3.1.1.3 PVdF based ferroelectric polymers

Poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) is a commonly used ferroelectric polymer. Local dipoles are created on the polymer backbone due to the high electronegativity of fluorine atoms. Polarized domains are generated by these local dipoles aligning in an electric field. The alignment is retained even after the removal of electric field, and the reversible, conformational changes produced by this realignment are used for actuation[39]. The polymers have a Young's modulus of nearly 1–10 GPa, which allows high mechanical energy density to be obtained. Up to 2% electrostatic strains were obtained with the application of a large electric field (~200 MV/m) which is nearly equal to the dielectric breakdown field of the material[2]. Up to a 10% strain was observed in ferroelectric polymers during the *trans*ition from the ferroelectric phase to the paraelectric phase, but the presence of hysteresis is a drawback. Hysteresis in ferroelectric materials is due to the energy barrier present when switching from one polarization direction to the other or when *trans*forming from one phase to another (Figure 14)[41]. A large field, in a direction opposite to the initial field, is required to reverse the polarization, dissipating substantial energy.

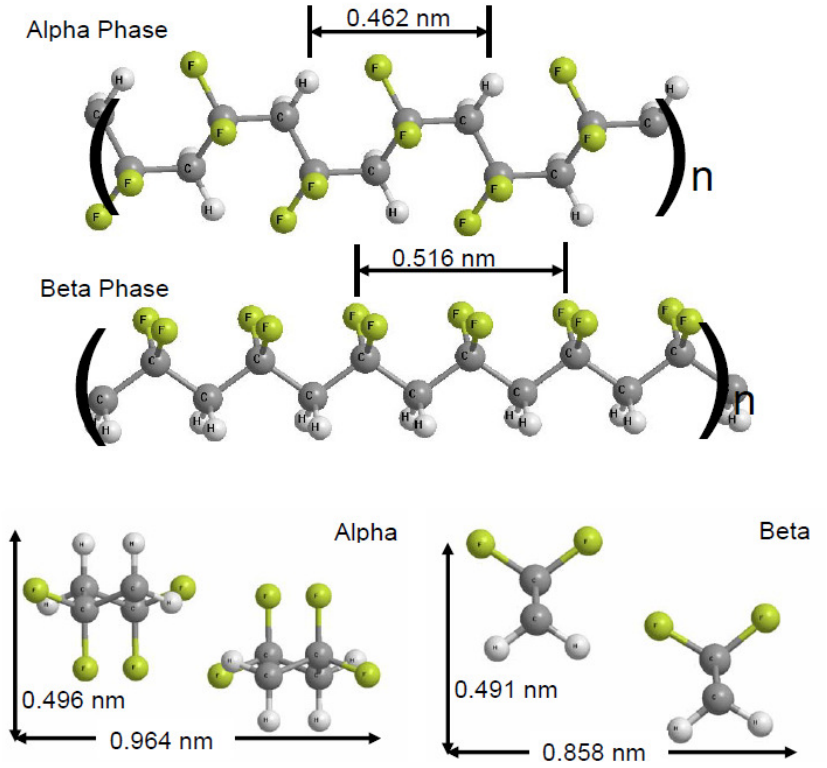


Figure 14: Alpha and beta phases in PVDF, looking along the chains (top) and perpendicular to the chains (bottom). A similar alpha to beta phase changes is induced in PVdF-TrFE ferroelectrics upon the application of an electric field, which results in dimensional changes[42].

P(VDF-TrFE) contracts in a direction of the field and expands in the direction perpendicular to the field. The strain can be enlarged by pre-straining, and moderate strains (up to 7%), with high stresses (reaching 45 MPa) have been achieved. High stiffness (70.4 GPa) was achieved but was dependent on the density of imperfections and a large work per cycle (approaching 1 MJ.m-3)[39]. The advantages of ferroelectric polymers can be found in their production process, their light weight and conformability in complex shapes and surfaces. The main disadvantages can be found in their low strain level and low strain energy, which limits these materials in application. Due to the sensitivity of these materials to chemical, thermal and mechanical factors, only limited applications in sensors and micro actuators can be addressed. The usage of P(VDF-TrFE) material is hindered due to the occurence of the fluorocarbon in the environment, which became an issue in the last years and the e-beam irradiation process to activate the material makes it expensive for practical applications. The maximum strain of the polymers can be achieved only at an optimal loading condition that is dependent on the material used. To improve the properties of the P(VDF-TrFE), polymer modification by adding fillers with high dielectric constant will increase the dielectric constant. The reduced film thickness (< 100 nm) and the applied operation temperature depend on the degree of imperfections in the polymeric material. The typical operation range is between 20^0C and 80^0C. Reversible actuation can be obtained when the materials are heated and cooled above and below their Curie points, which is just below room temperature[39]. The main restriction for ferroelectric polymers lies in their high applied voltage that can be found for most electronic EAP materials. A recent research[43] paper shows P(VDF-TrFE) piezoelectric polymers with graphene electrodes with applications in acoustic actuator and highly efficient nanogenerators. The fabrication procedure for this device is presented at Figure 15.

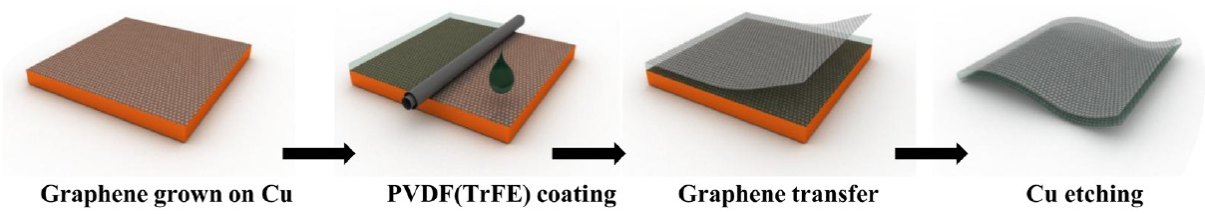


Figure 15: Fabrication scheme for graphene/P(VDF-TrEE) flexible device[43]

"The resulting graphene/P(VDF-TrFE)/graphene multilayer-based actuator and nanogenerator exhibits good mechanical durability and sensitivity, optical *trans*mittance, and simple device design, which is compatible with conventional batch fabrication steps as it is essential for realizing practical devices and systems"[43]. The incorporation of the PVDF/graphene in the device and their mechanism principle in piezoelectric response to sound are given in Figure 16.

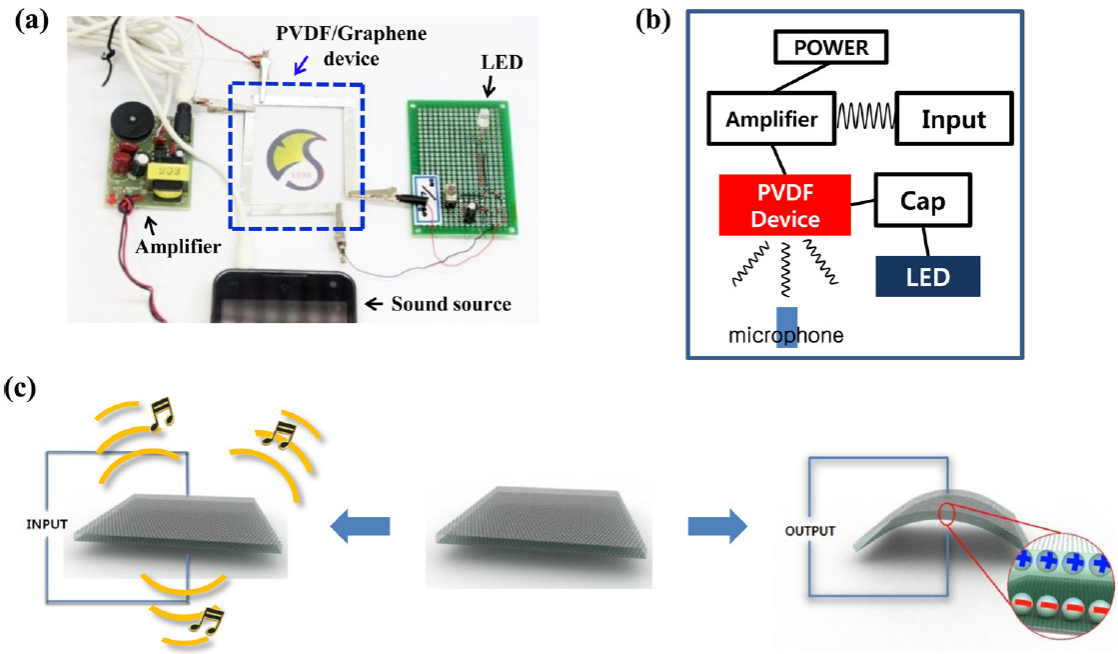


Figure 16: "Photograph showing the electrical connections of sound source, amplifier, graphene/P(VDF-TrFE)/graphene based acoustic device and electrical circuit with red LED during the measurement. (b) Schematic representation of electrical circuit including the entire component in the measurement of acoustic device. (c) Schematic depiction showing graphene/P(VDF-TrFE)/graphene-based device can work as an actuator as well as a nanogenerator"[43].

This research of P(VDF-TrFE) piezoelectric polymers shows the wide range of applications of this EAP. Many other applications of P(VDF-TrFE) are already on the market, which include acoustic components (microphones, sonar, etc), electrical equipments (switches, miniature fans), medical instrumentation (blood pressure detector, catheter), robotics (artificial skin, sensors), security devices and others.

Another type of electronic EAP of great interest for the industry will be introduced in the next chapter as a dielectric elastomer actuator (DEA).

3.1.2 Dielectric elastomer actuators (DEA)

Dielectric elastomers actuators are built of an incompressible and highly deformable dielectric medium. The dielectric medium is in most cases an elastomer that can be prestrained to achieve uniform deformation in one direction. Materials such as Dow Corning HS3 Silicone, Nusil CF 19-2186 Silicone, and 3M VHB 4910 acrylic are the most applied elastomers. On both sides of the elastomers electrodes are attached by coating conductive material such as grease or conductive paints serving as capacitors. If an electric field is applied between the parallel electrodes the Coulombic forces between the charges generates a stress which is named Maxwell Stress and causes the electrodes to move closer to each other. The Maxwell Stress is defined as:

$p=e*e_0*(V/t)^2$ (3)

where p is effective compressive stress

e is relative dielectric constant

e_0 is permittivity of free space (a constant)

E = V/t is strength of electric field between diodes

The material between the electrodes is pressed and due their elastic nature an expansion is induced in lateral direction[44]. The principle mechanism of DEA is shown at Figure 17.

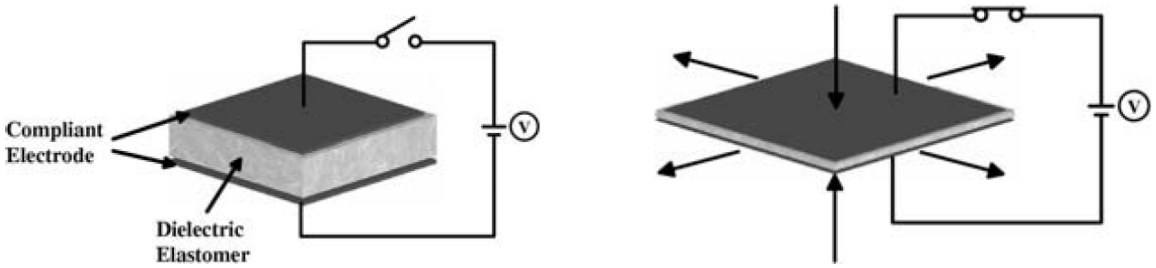


Figure 17: Operating principle of a DEA

Despite the simple operation mode of the device, there are several factors that can damage the operation mode of the DEA. From the expression that the induced strain in the material is proportional to the square of the electric field and dielectric constant, a higher electric field would then produce a larger strain. But the limitation of the material (elastomer) in their dielectric properties can induce a dielectric breakdown at high voltages. An electric breakdown field is defined as the maximum electric field that can be applied to dielectric elastomers without damaging them[45]. The dielectric breakdown strength of the applied material depends on the structure, temperature, and on the presence of impurities. It was also observed that the breakdown field increases with the prestrain of the elastomer. Dielectric elastomers require high electric fields for actuation (~100 V/μm), and it is a challenge to increase the breakdown strength of the elastomer at these high fields. The small breakdown strength of air (2–3 V/μm) presents an additional challenge[39] to achieve better material suitable in DEA.

To obtain DEA with better performance the elastomer and the compliant electrodes are introduced in this manuscript to understand the material's properties.

3.1.2.1 Elastomers

To obtain good performance of the applied elastomer material the following conditions need to be achieved to obtain better performance of the DEA.

- The material should have a low stiffness (especially when large strains are required)
- The dielectric constant should be high
- The electrical breakdown strength should be high
  A possibility to enhance the electrical breakdown strength is to prestretch the elastomer film mechanically.
- If the thickness of the film decreases, a lower voltage can be applied to obtain the same electrostatic pressure

- The prestrain of the material avoids compressive stresses in the film plane directions which might be responsible for failure.

Materials for elastomers are based on silicon, polyurethanes and acrylic compounds. In the case of silicon, several fillers improve the material in better cross-linkage, silicone stickiness, increasing hardness and enhancement of mechanical strength[7, 11]. Fillers such as titan dioxide lead to a better dielectric constant. In case of other elastomers such as polyurethanes (TPU) the structure of this material, this includes soft and hard segments of polymer material, leads to high flexibility of this elastomer. Furthermore fillers induce better dielectric properties and dielectric breakdown of this polymer. The most applied materials are acrylic elastomers named under commercial available tape VHB 4910. The properties of the different types of elastomers and their functionality in DEA are shown in Table 4.

Table 4: Comparison of commercial available elastomers in their DEA properties[46]

Material	Prestrain (x,y) (%)	Actuated relative thickness strain (%)	Actuated relative area strain (%)	Field strength (MV/m)	Effective compressive stress (MPa)	Estimated $^1/_2e$ (MJ/m^3)
			Circular strain			
HS3 silicone	(68,68)	48	93	110	0.3	0.098
	(14,14)	41	69	72	0.13	0.034
CF19-2186 silicone	(45,45)	39	64	350	3.0	0.75
	(15,15)	25	33	160	0.6	0.091
VHB 4910 acrylic	(300,300)	61	158	412	7.2	3.4
	(15,15)	29	40	55	0.13	0.022
			Linear strain			
HS3	(280,0)	54	117	128	0.4	0.16
CF19-2186	(100,0)	39	63	181	0.8	0.2
VHB 4910	(540,75)	68	215	239	2.4	1.36

The VHB 4910 (Table 4) did show the best actuation properties although the applied voltage was high. Another type of acrylic tape is named 3M VHB that shows mechanical strain up to 380%, high specific energy density of 3.4 J/g, stress of 8 MPa and theoretical conversion efficiency in the range of 60-90%.
Other important parameters are the compliant electrodes that need certain adjustments to be suitable for this specific actuator.

3.1.2.2 Compliant electrodes

Compliant electrodes are the key to the development of EAP technology because they maintain uniform contact over the entire active region of the elastomer. Therefore the electrodes need to be stretchable without losing too much conductivity to ensure proper functionality of DEA. The most applied electrode material is grease paste (graphite) due to its simple coating procedure and relative cheap price. The main drawback of grease electrodes is the messy handling of this material. New development of electrodes based on carbon nanotubes, conducting polymers and metals will be shortly introduced in this script based on recent publications[47,48]. In some DEA an electrical breakdown can be clearable if the

compliant electrodes have some self-healing effects. In case of grease electrode 20 wt% of reduced graphite C_{20} in form of nanoplatelets are applied and the decrease of resistivity of 28% this material on silicon under stretching of 40 %[47]. Carbon nanotubes electrodes in form of single wall nanotubes (SWNT) are applied on 3M VHB elastomer[48]. To achieve high stretchable and more hydrophilic SWNT (P3-SWNT), the nanotubes are shorten and modified with carboxyl groups over chemical oxidation. The advantages of SWNT to grease electrodes on 3M VHB tape are shown at Figure 18.

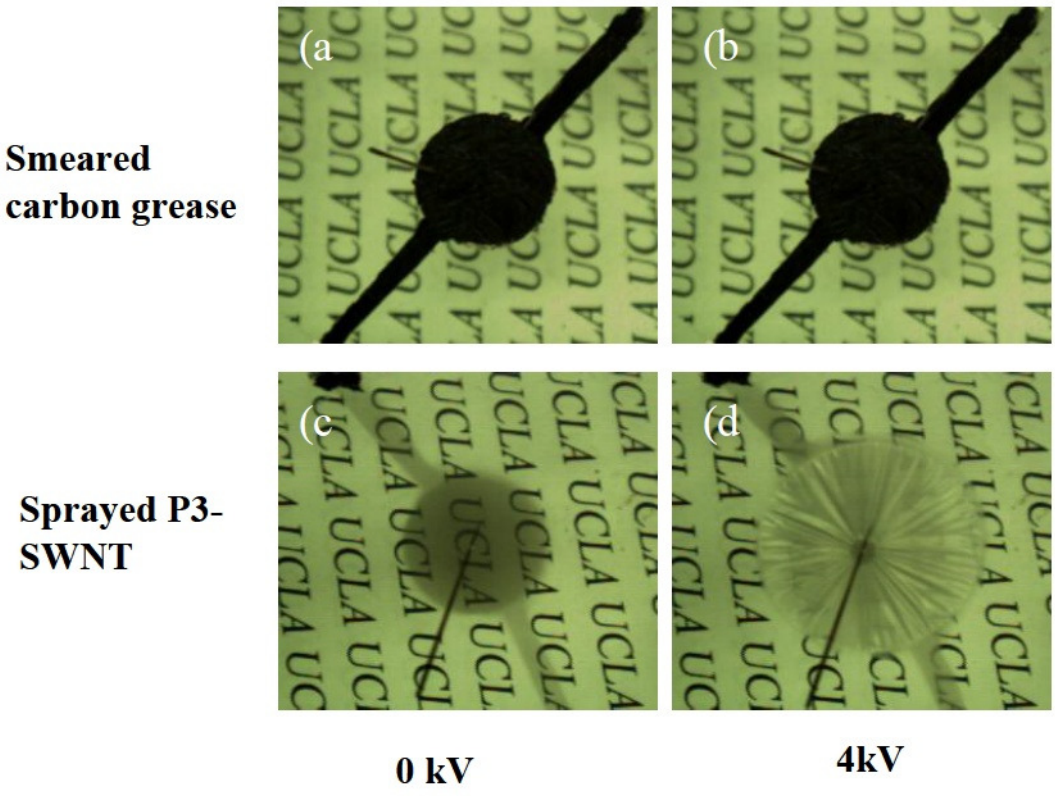


Figure 18: Images of DEA made of 3M VHB tape with electrodes between 0 and 4 kV based on a, b carbon greased and c, d: P3-SWNT[48]

At first it is noticed that the sprayed P3-SWNT enhance the *trans*parency of the DEA and secondly the obtained lateral strain showed only for P3-SWNT on 3M VHB in the range of 200%[48]. It was also discovered that this electrode material obtains self-healing properties after the electrical breakdown, explained by the nature of the CNT to isolate the faults from the rest of the active area that can actuate normally.
Electrodes based on conducting polymers (PPy) on polyurethanes are studied as well, and found comparable to the grease electrodes. Metal based electrodes such as gold, silver and aluminum are also studied and a new zick-zack design of metal layers could increase the stretchability. Danfoss Company applies aluminium electrodes on their already produced DEA materials in several applications.

3.1.2.3 DEA applications

Since 1888 Roentgen found the dielectric elastomer effect there were many developments and application discovered due to the simple actuator mechanism and easy manufacturing. DEA generates large strain and strain rates but for all EAP actuators the reliability for mass production in products need to be improved. Several minor developments such as electroactive fluid pumps, conformal skins for braille screens, insect like robots and an autofocus lens positioner (Figure 19) are shortly introduced[36].

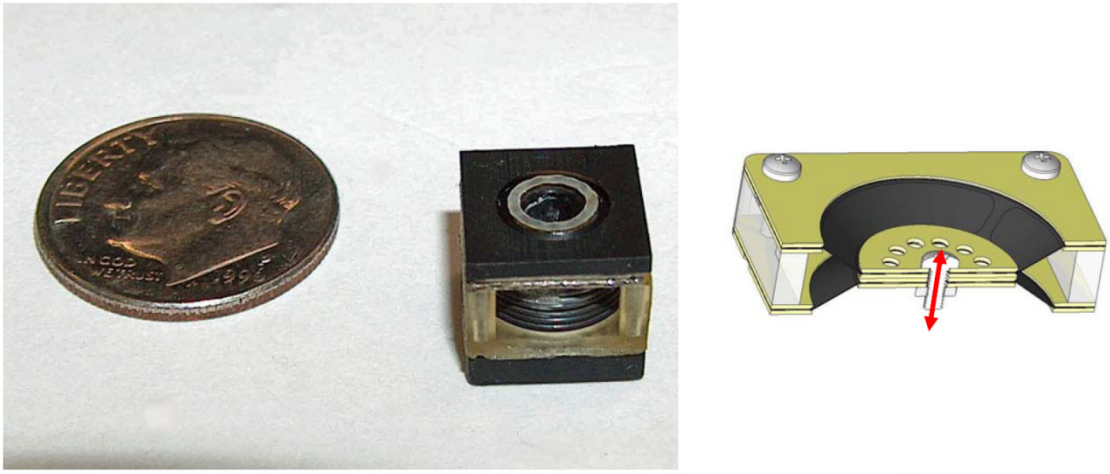


Figure 19: Autofocus lens device with DEA membrane to positioning the lens change[49]

The Autofocus lens positioner can focus a camera by moving the lens in the range of 350 µm[36]. Several other developments are in focus, for example an all plastic engine based on DEA material or to create robotics, touch screens and airships. Besides the many ideas in new applications for actuator material the energy harvesting properties of DE are from great interest. At early stages the first energy harvest device was developed from DARPA (Defense Advanced Research Project Agency) military research in US to use DE material in shoe heels since the energy of the heel strike normally dissipated away as heat[50]. It was found with the first models that energy in the range of 5 J per step can be generated and during walking energy between 1 W – 10 W can be obtained (both feet). If the DE material would replaced by electromagnetic or piezoelectric devices the material would weigh 10 times more. The principle design and functionality of the shoe heel device is presented in Figure 20.

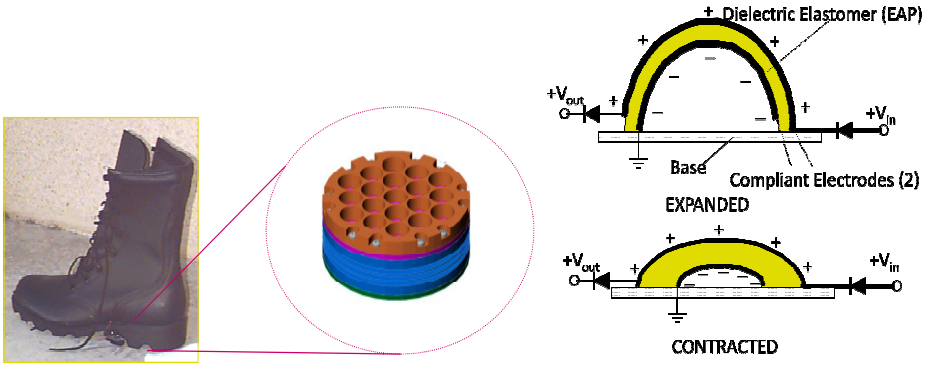


Figure 20: Prototype and functionality of DARPA heel-strike generator[50]

The heel strike of the DARPA generator has thus far produced a maximum of 0.8 J per cycle. The generator was being developed to help soldiers supply more power but the idea of course also has commercial applications. The most recent developments of DEA for commercial application started by Philips to develop an sensitive jacket where 64 actuators placed in the jacket to create a feeling of impact in cinemas or computer games (for example in fighting scenes). Bayer used DEA in cellphones[51] to get an actuation response from the cellphone with future implication to use this technique in a new generation of iPads.

3.1.3 Electrostrictive graft elastomers

The graft elastomers were discovered in 1998 at NASA's Langley Research Center by applying a large electric field to induce strain on materials[52]. The main attributes of these polymers are polar groups attached as side chains and forming polar crystalline regions. If an electric field is applied to those polymers the crystalline regions ranging in other orientations lead to dimensional changes inside the polymer (Figure 21).The electric field needs to be in the range of 10MV/m to obtain strain in the range of 2.5 %. These results are obtained using a chlorotrifluoroethylene and trifluoroethylene backbone having P(VDF-TrFE) polar side chains, producing a comparatively stiff matrix (E = 0.6 GPa).

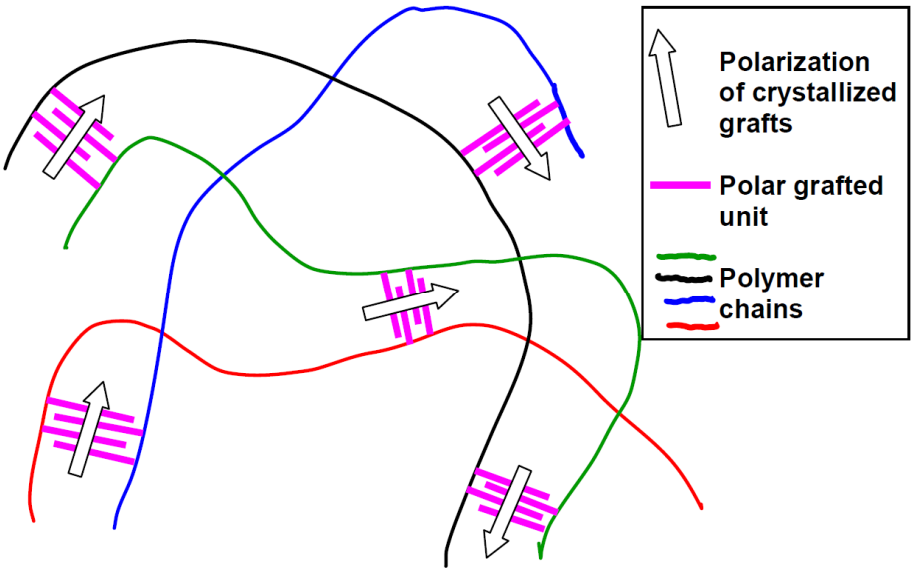


Figure 21: Schematic view of a graft elastomer with no electric field applied. The colored lines shows different regions of flexible polymer backbones

3.1.4 Liquid-Crystal Elastomer (LCE)

The first Liquid-Crystal elastomers were discovered by Finkelmann *et al* in the year of 1981[53]. The reversible actuation mechanism of LCEs based on polymer a material that undergoes a phase transition between the nematic and isotropic phases with actuation speed

under 1s. The reversible process last a bit longer than 10s. The phase transition is activated by inducing joule heating or via light irradiation by including photosensitive groups[54]. The drawback of the thermoresponsive LCE systems is the heat transfer time is controlled by the thermal diffusion in the base material. It is expected that the rate is proportional to the inverse of the square of thickness of the flat films. To get faster reaction time some attempts have been made to decrease the thickness of the film under 1 μm[7]. The simplest ordered phase is the nematic mesophase, in which the mean ordering direction of the rods is uniform. Long polymer chains, which incorporate rigid rod-like units called mesogens, can also order nematically and thus form nematic polymers (Figure 22).

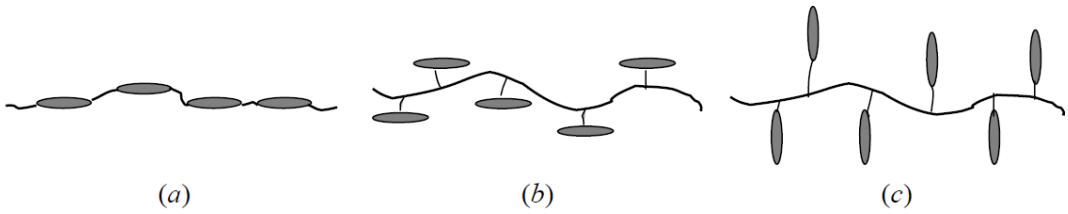


Figure 22: (a) Main-chain LC polymer, (b) side-on side-chain LC polymer and (c) end-on side-chain LC polymer. The small elongated ellipsoid represents the rod-like mesogen[54]

The functionality of liquid crystal nematic elastomer actuator materials have been studied and they are used to mimic muscle performance. In the nematic phase, the orientation of the mesogen forces the polymer backbone to be elongated along the direction of the mesogen. If the isotropic phase is heated, the nematic order is lost, thus allowing the polymer backbone to relax into a coiled conformation. Figure 23 gives a schematic view how the LCEs can work as reversible actuation devices.

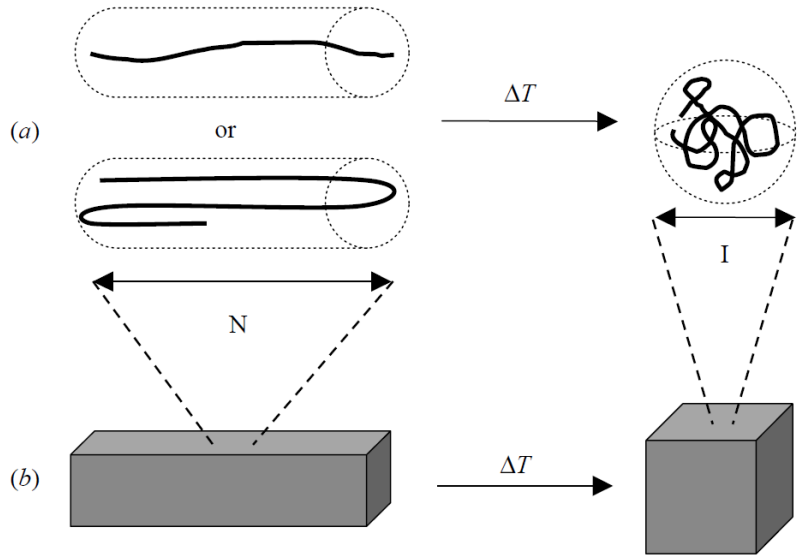


Figure 23: (a) Conformations of main-chain LC polymers in the nematic (N) and isotropic (I) phases. (b) Macroscopic shape change of the single domain sample of main-chain LC elastomer at the nematic–isotropic transition[54].

There are several factors such as structure of the polymer backbone, characteristics of the mesogen and the degree of cross-linking that influence the response time of the LCE. By applying smaller mesogens and a less cross-linked matrix the response time can be shortened[39]. Some LCEs show response times smaller than 10 ms with strains in the range of 45% for electrostatically and thermally driven samples. The LCEs applied electric field was found to be in the range of 1.5 – 25 MV/m. Another induction with light was developed by Tsunami *et al*[55] where azo-compounds were included in the polymer backbone. The light induced phase transition was provoked by a *trans*-to-*cis* photoisomerization of the azo-groups that produced a large change in the shape of the molecules, from a mesogenic rod-like shape for the *trans* isomer to a kinked non-mesogenic shape for the *cis* isomer[54] (Figure 24).

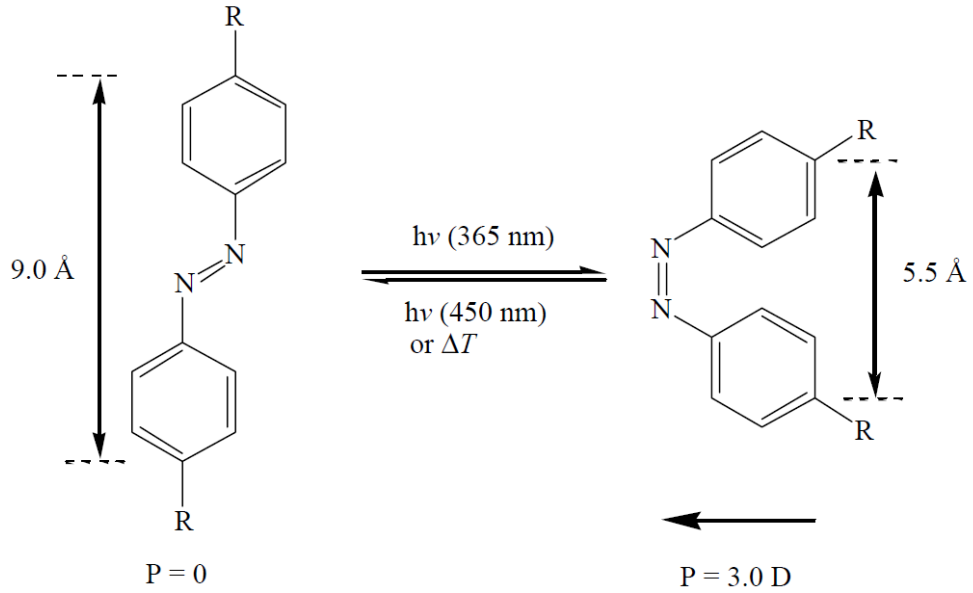


Figure 24: „Photochemical isomerization of azobenzene. The *trans* form is converted into the *cis* form by UV light irradiation, and the resultant *cis* isomer can return to the original *trans* form photochemically upon visible light irradiation or thermally in the dark. The *trans* and *cis* forms are very different in shape, size and polarity“[54]

Nevertheless LCEs are in the early stages of development and a new design in structure and properties of this material can create new applications. LCEs are being studied to develop membranes that can separate right-handed and left-handed forms of drugs in the pharmaceutical industry[56]. Along with applications in artificial muscles and actuators, the elastomers can also be developed to be mechanically tunable optical elements. A swimming motion was obtained when a light was shone on a dye-doped LCE sample floating on water[57]. Another direction is the use of LCEs in piezoelectric application that can be applied since LCEs have through their mesogens change formed polarity that induces piezoelectric properties[7].

3.1.5 Summary electronic EAP

The group of electronic EAPs did show that the applied electric field on the material needs to be several hundred MV/m to get a mechanical response. Ferroelectric polymers based on

modified PVdF material did show that commercial applications are already in the market but the actuation response with relative small strains limits this material in products such as robotic devices. Many new ideas and designs on the other already available electronic EAP based on DEAs has led to different products and application in the market. Table 5 gives an overview of the properties of the electronic EAP group.

Table 5: Actuator properties of electronic EAP, SMA and natural muscles[7]

Actuator	Strain	Actuation Pressure	Density	Efficiency	Speed (fast AND slow)
Natural Muscle	●	●	●	●	●
Electromagnetic	●	●	○	●	○
Piezoelectric	○	●	◐	●	●
Shape Memory Alloy	◐	●	◐	○	○
Magnetostrictive	○	●	○	●	○
Electrostatic	●	○	●	●	●
Dielectric Elastomers	●	●	●	●	●
○ = Poor		◐ = Fair		● = Good	

In comparison with natural muscles only the DE material shows similar performance in strain, pressure, density and efficiency. Nevertheless the main issue to apply DEAs in commercial products is the high electric field that is needed. EAP materials that can run at lower voltages, the so called ionic EAP materials, will be introduced in the next chapter.

3.2 Ionic EAP

Ionic EAPs need electrolytes to obtain actuation in a polymer. The ionic EAP contain different materials[7]:

- Carbon Nanotubes (CNT)
- Conductive Polymers (CP)
- Carbon derived Carbon (CDC)
- Ionic Polymer Metallic Composite (IPMC)
- Electro Rheological Fluids (ERF)
- Ionic Polymer Gels (IPG)

At applied field the motion of the ions with entrained solvent enter or leave the polymer inducing expansion or contraction. In case of the electronic EAP the electric field induces actuation directly, while for ionic EAPs the electric field or applied voltage induces charging

of the electrolyte embedded in the ionic EAP. The charging of the ionic EAP leads to a secondary reaction, where ions and solvent enter the polymer and lead to a change in volume. If the polymer phase is electronically conducting (as in conducting polymers and carbon nanotubes) then ions serve to balance charge generated on these conductors as potential is changed, creating very strong local fields (but overall low voltage). The voltages employed in these materials are low (1 – 7 V) but the energies are nonetheless high because the high charge density of the electrodes[36]. To apply the ionic EAP in products the low voltage is one of their main advantage but the need for electrolytes reduces the range of their applications. In recent years many developments have been made to use solid electrolytes or ionic liquids (instead of wet electrolytes), and with encapsulation the ionic EAP actuators can operate in air. The next chapters will introduce the ionic EAPs, their actuation mechanism, challenges, applications and recent research published in the field.

3.2.1 Carbon nanotubes (CNT)

CNTs are allotropes of carbon. They are tubular in shape, made of graphite. CNTs possess various novel properties that make them useful in the field of nanotechnology and pharmaceuticals. They are nanometers in diameter and several millimeters in length and have a very broad range of electronic, thermal, and structural properties. These properties vary depending on the type of nanotubes, defined by their diameter, length, chirality or twist and wall nature[58].Carbon nanotubes were first discovered in 1952 by Radushkevich and Lukyanovich, where a 50 nm tube made of carbon was presented[59]. A large percentage of academic and popular literature attributes Sumio Iijima for the discovery of hollow, nanometer sized tubes named as multi wall nanotubes composed of graphitic carbon in 1991.[60] SWNT were discovered by Benning *et al* in 1993[61]. „The bonding in carbon nanotubes is sp^2, with each atom joined to three their unique strength. Under high pressure, nanotubes can merge together, trading some sp^2 bonds for sp^3 bonds, giving the possibility of producing strong, unlimited length wires through high-pressure nanotube linking“[58]. The principle structure and differences between multiwall (MWNT) and single wall nanotubes (SWNT) are presented in Figure 25.

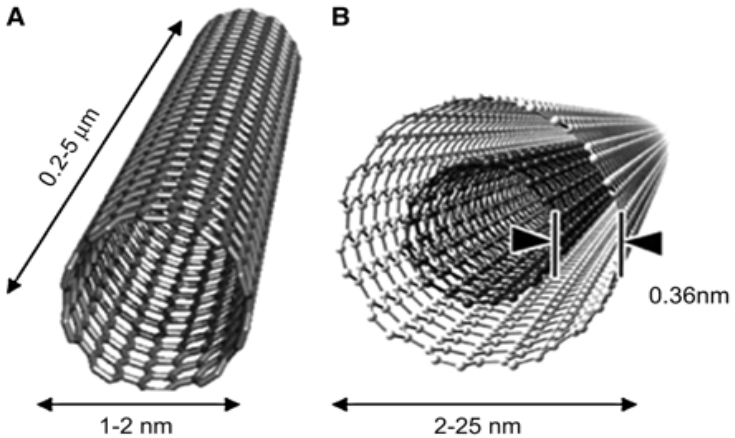


Figure 25: Carbon nanotubes rolled from graphene layer into tubes. A: SWNT and B: MWNT[62]

The difference between MWNT and SWNT can be find in their physical properties and their applications. Table 6 shows the main differences between SWNT and MWNT.

Table 6: Properties of SWNT and MWNT[58]

Sr. No.	SWNT	MWNT
1.	Single layer of graphene.	Multiple layer of grapheme
2.	Catalyst is required for synthesis.	Can be produced without catalyst.
3.	Bulk synthesis is difficult as it requires proper control over growth and atmospheric condition.	Bulk synthesis is easy.
4.	Purity is poor.	Purity is high.
5.	A chance of defect is more during functionalization.	A chance of defect is less but once occurred it's difficult to improve.
6.	Less accumulation in body.	More accumulation in body.
7.	Characterization and evaluation is easy.	It has very complex structure.
8.	It can be easily twisted and are more pliable.	It can not be easily twisted.

CNTs can be synthesized and then cut by sonication in concentrated nitric acid to the desired length, ranging from 1µm to a few micrometers. Several production methods have been developed over the years by researchers to obtain CNT material. The main CNT production method is based on the arc discharge method[7].

In this method, nanotubes are synthesized through arc vaporization of two carbon rods placed end to end with a distance of 1mm in an environment of inert gas such as helium, argon at a pressure between 50 to 700 mbar. Carbon rods are evaporated by a direct current of 50 to 100 amps driven by 20 V which creates a high temperature discharge between the two electrodes. Due to this, the anode will get evaporated and rod shaped tubes will be deposited on the cathode[58]. To produce SWNT with the arc discharge method different metal catalysts, inert gas and optical plasma control are applied. In case of MWNT synthesis the reaction can take place in liquid nitrogen, under magnetic field and plasma rotating arc discharge. Other methods to synthesize CNT are named as laser ablation method, chemical vapor deposition method (CVD), flame synthesis and silane solution method. The purification of CNT is based on air oxidation, acid refluxing and sonication process. CNT material has been researched over the last 20 years and many applications have already been discovered, including pharmaceutical products, electrode materials, biosensors, drug delivery, nano-electronic,

yarns, transistors, batteries, hydrogen storage and actuators. The field of CNT actuator will be discussed in-depth in the next chapter since this manuscript deems the materials to be suitable for "artificial muscles".

3.2.1.1 CNT actuators

Baughman *et al.*[63] was the first who discovered that CNT (SWNT) form bundles due to van der Waals forces with diameter of 10 nm and align via filtration (Bucky paper). These CNT sheets can be applied for actuators. The actuation of CNT depends on the surface charging; therefore, multiwalled carbon nanotubes (MWCNTs) are considered inefficient because of their less accessible surface area[39]. To achieve actuation of CNT they need to be placed in a electrolyte. „The actuation of CNT revealed that ionic current flow is responsible for deforming of the CNT. The applied electrolyte forms electric double layer around nanotubes (Figure 26 A), creating an ionic imbalance between nanotubes and electrolytes. The C-C bond length also increases because of the repulsion between positively charged carbon atoms formed by electron removal. These dimensional changes are translated into a macroscopic deformation in a network of entangled nanotubes (Figure 26 B). When this network is used, the bond length changes translate into macroscopic deformation"[7]. On low and moderate charging coulombic forces dominate and there excists a parabolic relationship between strain and the applied potential. If the potential increases the ions and solvent start to exchange electrons with nanotubes and the double layer discharges.

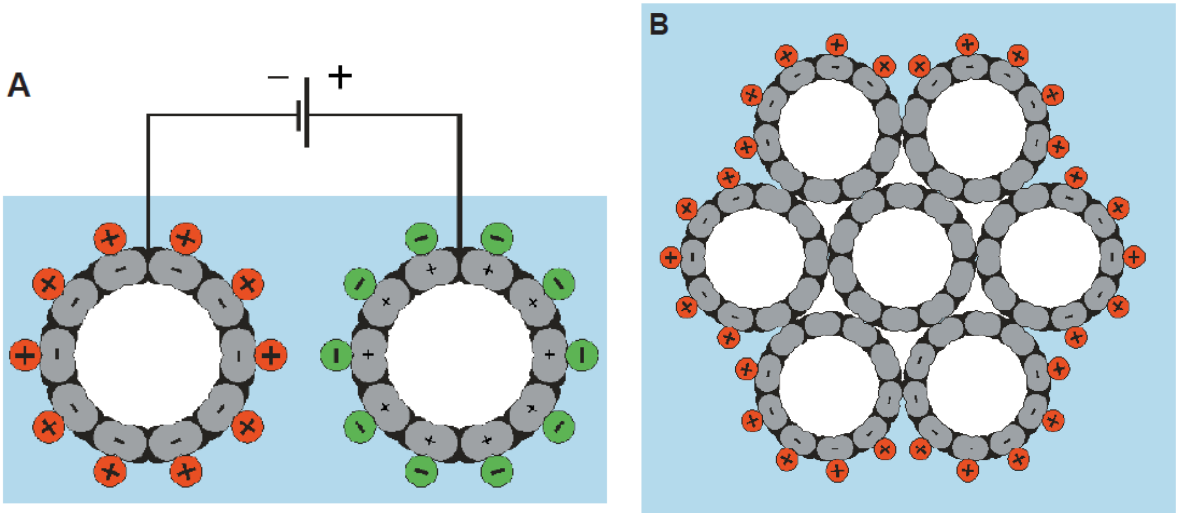


Figure 26: „Schematic illustration of charge injection in a nanotube-based electromechanical actuator and the effect of nanotube bundling. (A) An applied potential injects charge of opposite sign in the two pictured nanotube electrodes, which are in a liquid or solid electrolyte (blue background). Depending on the potential and the relative number of nanotubes in each electrode, the opposite electrodes can provide either in-phase or out-of-phase mechanical deformations. (B) Charge injection at the surface of a nanotube bundle is illustrated, which is balanced by the pictured surface layer of electrolyte cations. Although penetration of electrolyte and gases into interstitial sites and nanotube cores might occur for the investigated bundled nanotubes, this has no noticeable effect on the observed surface area or the measured electrode capacitance"[63].

To obtain bending beam CNT trilayer devices the Bucky paper was fixed between double sited Scotch tape. At applied potential in 1.0 M NaCl and at frequency of 15 Hz the trilayer device bent several centimeters (Figure 27).

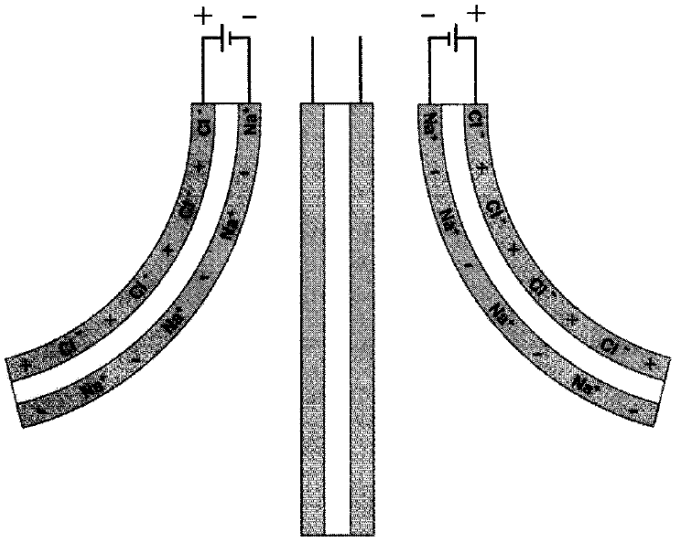


Figure 27: „Schematic edgeview of a cantilever-based actuator operated in aqueous NaCl, which consists of two strips of SWNTs (shaded) that are laminated together with an intermediate layer of double-sided Scotch tape (white)“[63].

Similar operation was observed for this type of actuator made from nanotube paper that had been annealed at 1100°C for 1 hour in flowing argon. The CNT actuator research started at 1999 and until now a lot of progress has been made to obtain CNT actuators in different design and with higher efficiency and functionality. The advantages and disadvantages of CNT actuators are given in Table 7.

Table 7: Advantages and disadvantages of CNT actuators[7]

Actuator type	Principle	Advantages	Disadvantages	Reported types
Carbon Nanotubes (CNT)	The carbon-carbon bond of nanotubes (NT) suspended in an electrolyte changes length as a result of charge injection that affects the ionic charge balance between the NT and the electrolyte.	• Potentially provide superior work/cycle and mechanical stresses • Carbon offers high thermal stability at high temperatures <1000°C	• Expensive • Difficult to mass produce	SWCNT and MWCNT

The goals for most actuators in the ionic EAP group are the implementation of ionic liquids. To obtain CNT based actuators the „Bucky gel“(BGA, bucky gel actuator) was first introduced of Tokyo University. The principle assemblies of this actuator type consist of 10% SWNT with ionic liquids ($EMIBF_4$) that forms together a gel[64]. It is fabricated by hot-pressing

the prepared electrode and electrolyte layers together. BGA is a tri-layered bimorph nano-composite system consisting of an electrolyte layer sandwiched between two identical electrode layers (Figure 28).

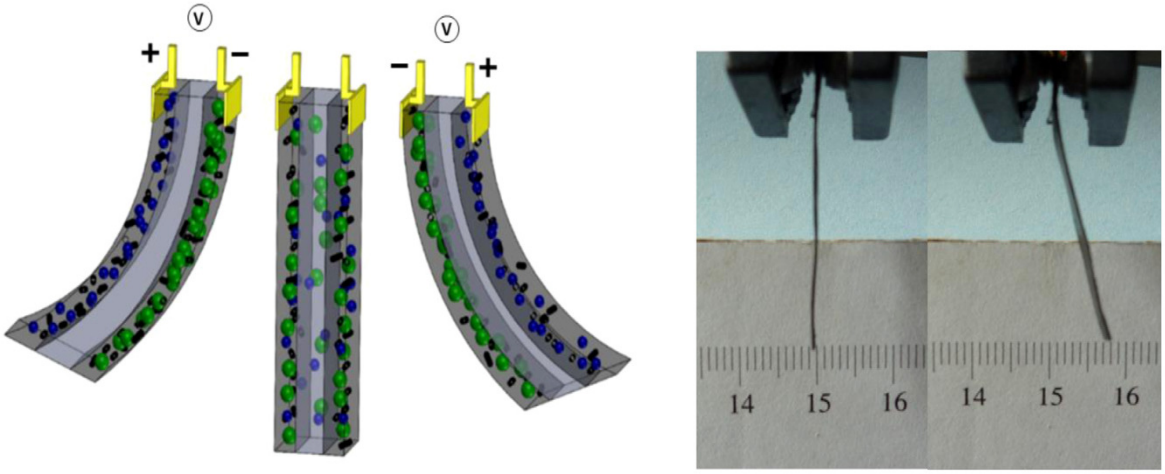


Figure 28: Schema of BGA and displacement under applied voltage[64]

The reason behind the BGA bending motion is not fully understood and two different mechanisms are discussed[65].

The charge injection model states that when a voltage is applied to the electrodes, there will be a change in carbon–carbon bond length in carbon nanotubes that leads to the expansion and contraction of the opposite electrodes. Change in electrode size causes the actuator to bend toward one side, since the layers are bound together. The second proposed mechanism states that the bending motion is the result of ion transfer between BGA layers. According to this hypothesis, bending motion occurs when positive and negative ions are separately accumulated on the opposite electrodes. Therefore, one electrode layer would swell while the other one shrinks as a result of the size difference of the positive and negative ions. This change in the electrode size will cause BGA to bend toward the anode.

It is also possible to make MWNT actuators, which have new applications in many fields[66]. To obtain yarns from CNT (MWNT) they can be drawn from forest spinning and due their high stiffness of 357 GPa and strength of 8.8 GPa they are comparable with carbon fiber material or even can replace commercially available Kevlar[67] (Figure 29).

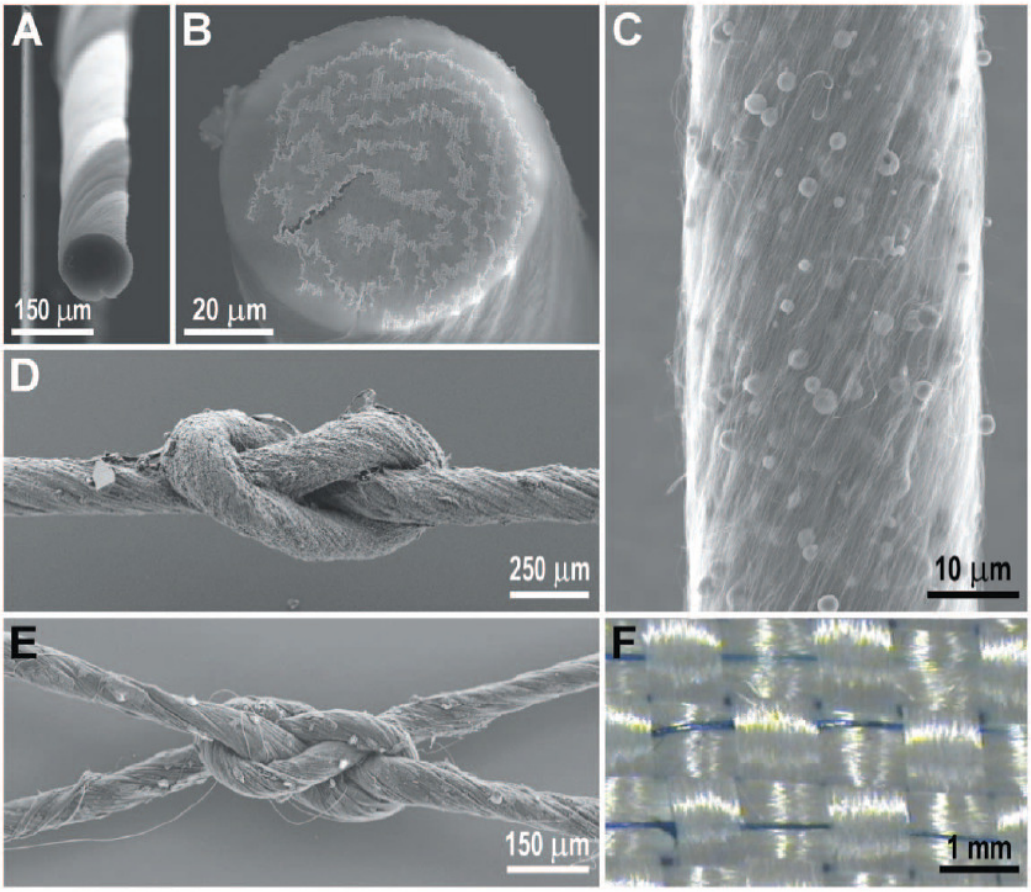


Figure 29: „(A and B) SEM images of Si3N4NT@MWNT0,2 biscrolled yarn that was twist spun in air. The brighter areas correspond to MWNTs. (C) SEM image of TiO2@MWNT1,0 yarn made by aerosol-based guest deposition and twist insertion in air. (D) SEM image of overhand knot in 95%LiFePO4@MWNT3,3 yarn. (E) SEM image of carrick bend knot between two 88% SiO2@MWNT3,0 yarns. (F) Photograph of 85% TiO2@MWNT3,0 yarn that has been hand sewn into Kevlar (DuPont) textile“[66].

Other application for the CNT yarn were recently published and showed that MWNT in form of carbon nanotubes aerogel muscles obtained giant elongations and elongation rates of 220% and (3.7×10^4) % per second[68]. The densities of the carbon aerogel sheets drawn from forest in speed of 2 m/s have a density of 1.5 mg/cm^3 with a thickness of 20 µm. The aerogel sheets act as a low-modulus rubber when stretched in the sheet width direction by up to 300%. Figure 29 shows the aerogel sheet in actuation mode at RT and high temperatures up to 1500 K.

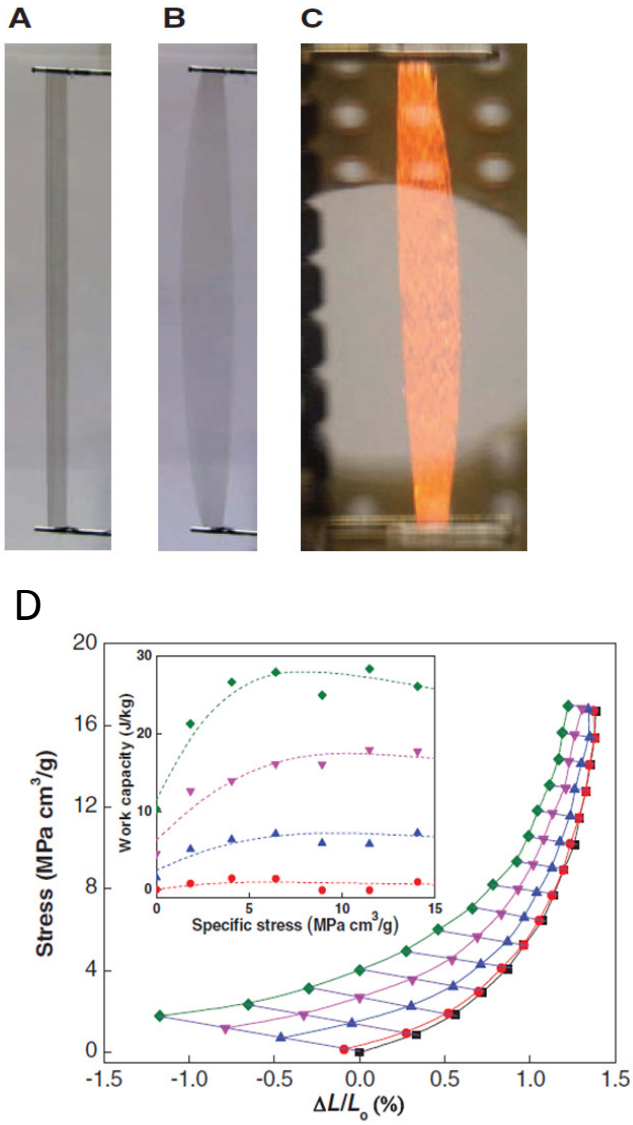


Figure 30: „(A and B) Photograph of a rigidly end-supported 50-mm-long by 2-mm-wide nanotube sheet strip (A) and the same sheet strip expanded in width by applying 5 kV with respect to ground (B). (C) Photograph of a 25-mm-long nanotube sheet strip actuated at 1500 K by applying 3 kV. (D) Specific stress versus length-direction strain at constant applied voltage (curves rising to the right) and for increasing voltage for a given tensile stress applied before actuation“[68].

Due to the constant electrostatically generated stress acting against the elastic modulus, which leads to an actuator stroke (Figure 30 A, B), it was observed that even at high temperatures (Figure 29 C) of nearly 1500 K actuation properties could be obtained. Therefore in this publication[68] it was proposed that the nanotube sheet modulus is independent from temperature. As seen in Figure 30 D the lengthwise actuation generates an isometric specific stress up to 4.0 MPa cm^3/g.

“In addition to extending the capabilities of artificial muscles to giant strokes and strain rates at extreme temperatures, the present actuator mechanism provides other application possibilities that relate to the structural change of the nanotube sheets during large-stroke actuation. The nanotubes diffract light perpendicular to the alignment direction, which can be

dynamically modulated at over kilohertz frequencies for optical applications[68]. The ability to tune the density of nanotube sheets and then freeze this actuation is being used for optimizing nanotube electrodes for organic light-emitting displays, solar cells, charge stripping from ion beams, and cold electron field emission"[68].

3.2.2 Carbide-derived carbons (CDCs)

CDC materials are mostly applied in supercapacitors due to their nanoporous structure. The principle synthesis of CDC starts from carbon materials derived from carbide precursors that are transformed into pure carbon over physical or chemical processes. Depending of the synthesis, CDCs can range structurally from amorphous carbon to graphite, CNT or graphene[69]. Some examples of CDC structures obtained from chemical process (carbide chlorination) are presented in Figure 31.

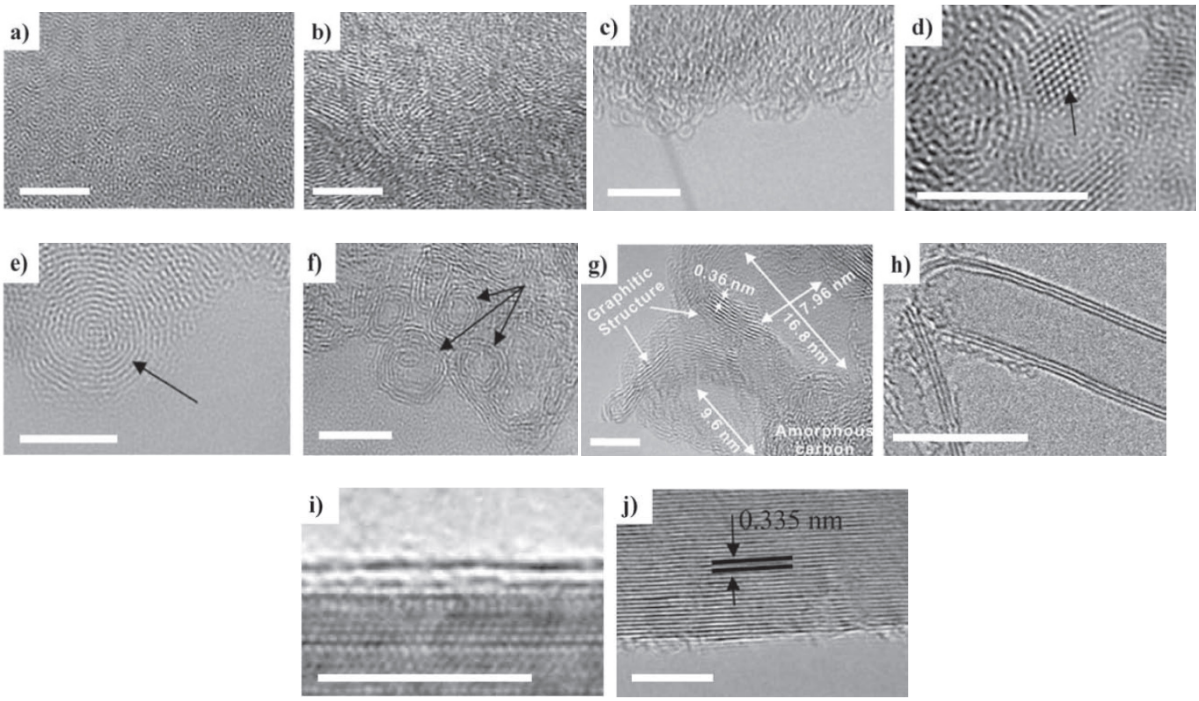


Figure 31: TEM images of various CDC structures obtained from carbide chlorination a) amorphous porous carbon, b) turbostratic carbon, c) fullerene-like carbon, d) nano-diamond, e) onion-like carbon, f) carbon nano-barrels, g) mesoporous carbon, h) CNT, i) epitaxial graphene and j) graphite[69]

All CDC synthesis methods have one aspect in common that the carbon is formed by selective extraction of the metal or metalloid atoms while transforming the carbide structure in pure carbon. The main synthesis to obtain CDC is the halogenations, hydrothermal treatment and thermal deposition of carbides[69]. Halogenations is defined as the most common method, discovered in 1918 by Otis Hutchins in his patent, where he exposed hot silicon carbide to dry chlorine gas ($SiC(s) + 2Cl_2(g) \rightarrow SiCl_4(g) + C(s)$)[70]. This method was a bit modified 1954 for $SiCl_4$ production. Later it was discovered that CDC is a new class of carbon material. More

and more research was performed and it was discovered that the applied temperature, pressure and choice of carbide precursors (SiC, W_2C, TiC, etc) determine which carbon structure can be obtained, as seen in Figure 32 where TiC-CDC structures are obtained after chlorination at 600^0C.

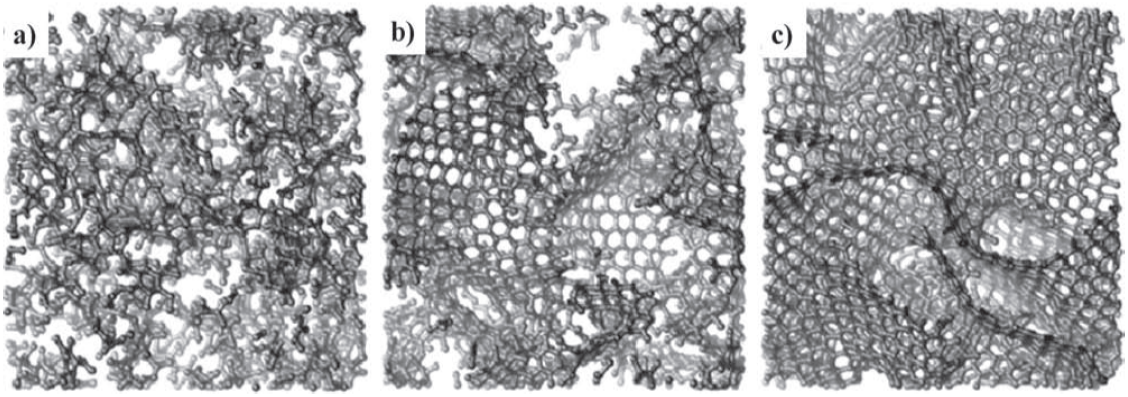


Figure 32: Simulated TiC-CDC structures (chlorination at 600 °C) of a) fast quenching, b) 800 °C; medium rate and c) 1200 °C; slow quenching[69]

At low temperatures low SiC crystallinity is observed but with higher temperatures graphene sheets and graphite ribbons are formed. The temperature of chlorination also determines the pore size of the CDC material. At higher temperatures, there is an increase in pore size due to self-organization and higher carbon mobility along with increased crystallinity of the carbon material (Figure 33).

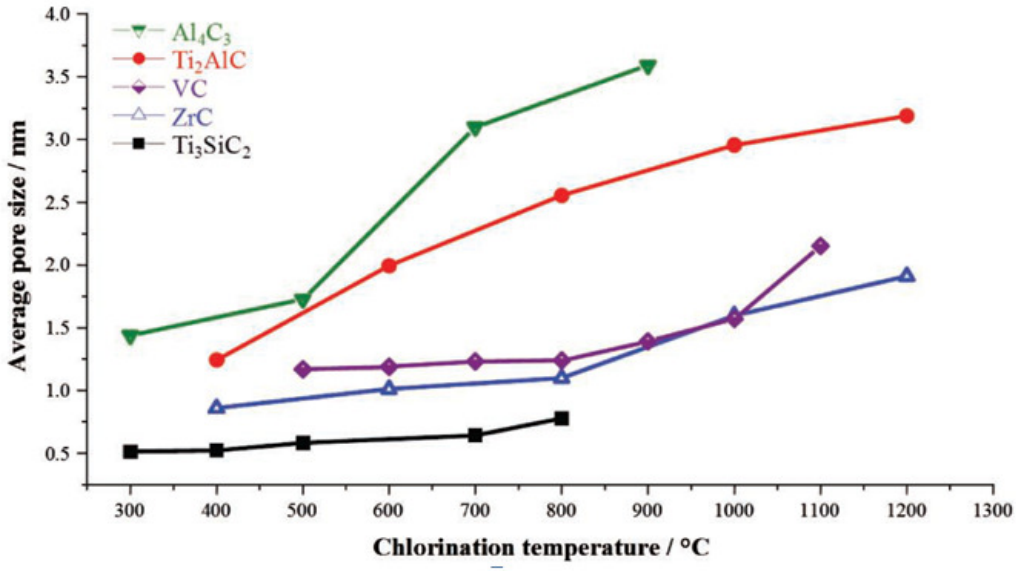


Figure 33: Average pore sizes for selected binary and ternary carbides[69]

For many carbide precursors, we find a direct correlation between the halogenation temperature and the resulting pore size with smaller pore sizes at lower temperatures[69]. With controlling the temperature it is possible to tune the pore size in sub-Ångstrom accuracy. It was found that the pore size distribution is even smaller than for SWNT.

CDC materials have many application due to their nano-porous structure, such as purification of noble gases or removal of toxins, catalyst in fuel cells, electrodes for Li-air or Li-ion batteries, electrical energy storage and gas storage, tribological (reduction of friction) usage and supercapacitor electrodes. The main usage of CDC materials are as supercapacitors due to their properties in physical charge separation on high surface electrodes, their charging/discharging is fast and completely reversible with more than 1 million recharge cycles (lifetime > 10 years) and efficiency in the range of 99%. The capacitance of CDC materials depend on what precursors are applied during synthesis and in case for TiC-CDC the gravimetric capacitance was found to be in the range of 150 F/g while with Al_3C_4-CDC the capacitance increased to 280 F/g. The supercapacitor storage principle is based on the Electrochemical Double Layer Capacitors (EDLCs). „In a conventional capacitor, energy is stored by moving charge carriers, typically electrons, from one metal plate to another. This charge separation creates a potential between the two plates, which can be harnessed in an external circuit. The total energy stored in this fashion increases with both the amount of charge stored and the potential between the plates. The amount of charge stored per unit voltage is essentially a function of the size, the distance and the material properties of the plates and the material in between the plates (the dielectric), while the potential between the plates is limited by the breakdown field strength of the dielectric. The dielectric controls the capacitor's voltage. Optimizing the material leads to higher energy density for a given size. EDLCs do not have a conventional dielectric. Instead of two plates separated by an intervening insulator, these capacitors use virtual plates made of two layers of the same substrate. Their electrochemical properties, the so-called "electrical double layer"[69], result in the effective separation of charge despite the vanishingly thin (on the order of nanometers) physical separation of the layers. The lack of need for a bulky layer of dielectric and the porosity of the material used permits the packing of plates with much larger surface area into a given volume, resulting in high capacitances in small packages. In an electrical double layer, each layer is quite conductive, but the physics at the interface between them means that no significant current can flow between the layers. The double layer can withstand only a low voltage, which means that higher voltages are achieved by matched series-connected individual EDLCs, much like series-connected cells in higher-voltage batteries. EDLCs have much higher power density than batteries. Power density combines the energy density with the speed at which the energy can be delivered to the load. Batteries, which are based on the movement of charge carriers in a liquid electrolyte, have relatively slow charge and discharge times. Capacitors can be charged or discharged at a rate that is typically limited by the heat tolerance of the electrodes“[71]. A recently discovered new application based on CDC materials in actuator devices will be introduced in the next chapter.

3.2.2.1 CDC based actuators

The actuation phenomenon of nanoporous carbon was discovered in an earlier research.[72] Since then new developments have been made to obtain CDC polymeric actuators with different design. The following procedure gives an example to obtain CDC polymeric actuators (Figure 34) by combining the CDC porous particles with a binder.

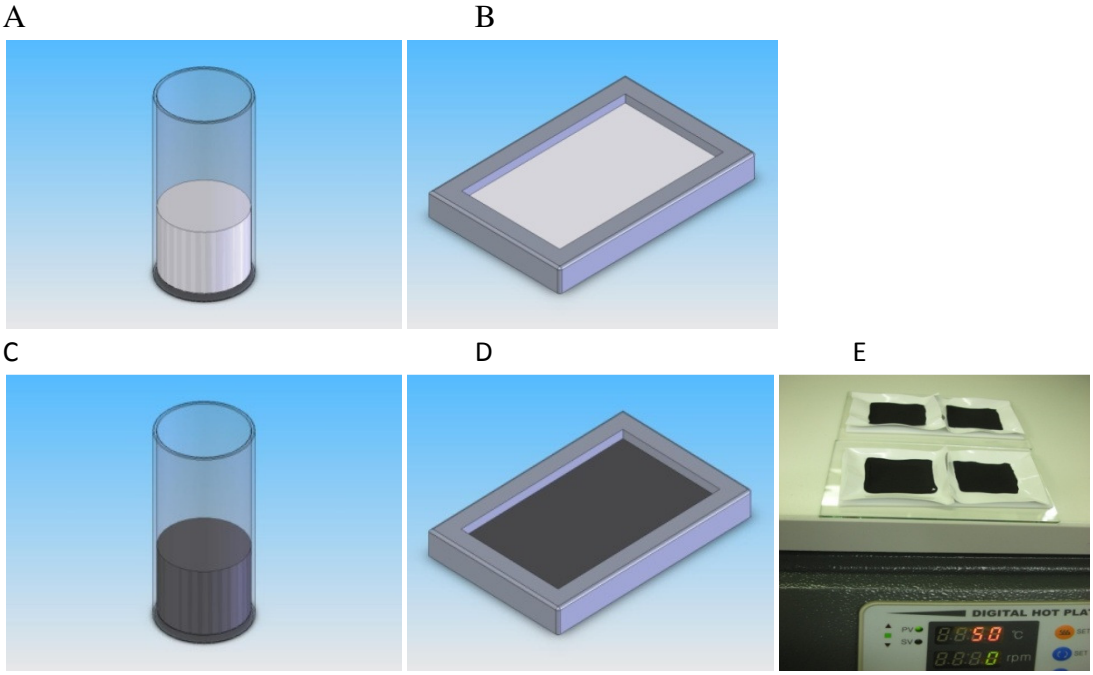


Figure 34: Assembling of CDC polymeric layer. A, B: PVdF(HFP) polymer solving and mixing with ionic liquid and casting, C,D: Sonication of CDC powder, PVdF, ionic liquid and solvent and cast to form a film. E: CDC polymeric layers[73]

The CDC polymeric layer is then hot-pressed in trilayer arrangement in different designs to obtain bending or linear (volume change) actuation (Figure 35).

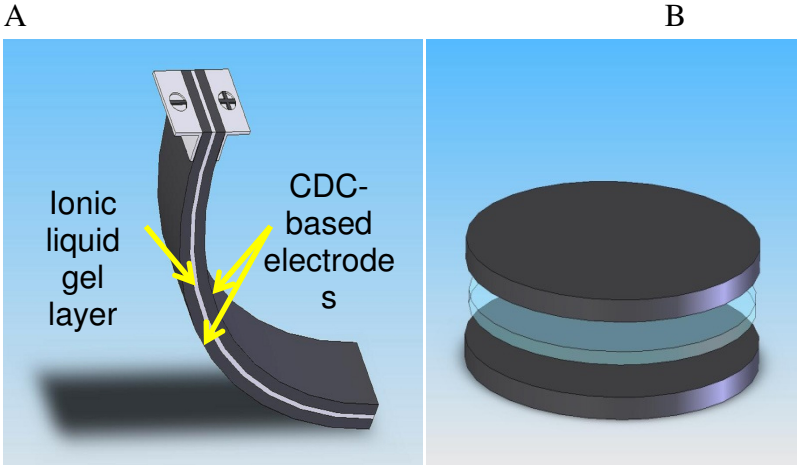


Figure 35: CDC polymeric actuators in A: bending beam and B: volume change induced linear strain[73]

For all CDC polymeric actuators the capacitance properties determine the actuation response and several investigation been made to prove the correlation of pore size distribution to displacement and strain[73]. The actuation mechanism of the CDC polymeric actuators is not completely understood. The CDC is also often applied for supercapacitor devices that are

famous for their high power density and energy conversion efficiency up to 98% at charging/discharging cycles. The CDC polymeric device consists of two CDC layers with high surface areas separated by a permeable membrane. The actuation mechanism of CDC material can be described by the electrochemical double layer capacitance (EDLC) model that is explained by charge injection forming an electrical double-layer and by charge distribution induced by ion migration and accumulations[74]. Actuator measurements of CDC based polymeric actuators revealed that the strain is directly dependent on the specific surface area of CDC material and therefore also dependent of the pore size distribution[75]. To find comparable materials similar to CDC, it was found that well known CNT actuators were similar in strain but the speed was faster[76], which could be the results of the better conductive CNT layer. To improve CDC conductivity, additional gold foil was laminated on top of the three layered sandwich CDC actuator (Figure 36) and the actuation strain was compared to those without gold foil.

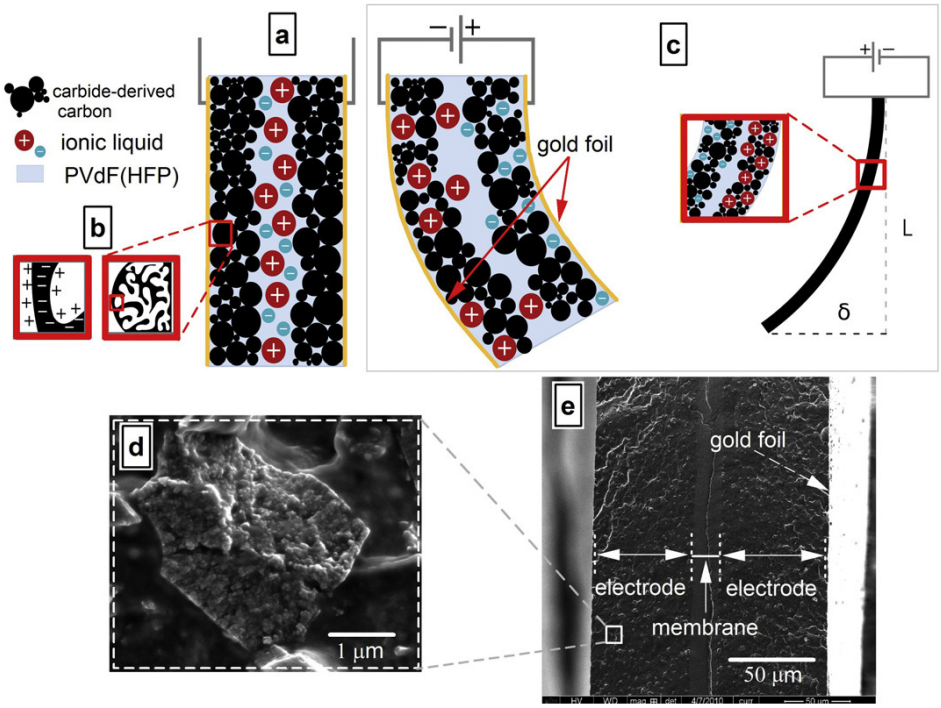


Figure 36: „(a) Schematic depiction of nanoporous carbide-derived carbon based actuator modified with gold foil (CDC/gold). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.) (b) Simplified notation of electrical double-layer formation inside porous CDC media. (c) Displacement of actuator under applied voltage. (d, e) SEM images of cross-section of actuators with polymer supported and gold-foil-modified CDC electrodes“[75].

The experiments of gold foiled CDC polymeric actuators showed (Figure 37) an improvement in actuation strain, reduced voltage (until ± 0.25 V) and higher actuation speed (frequency below 0.1 Hz)

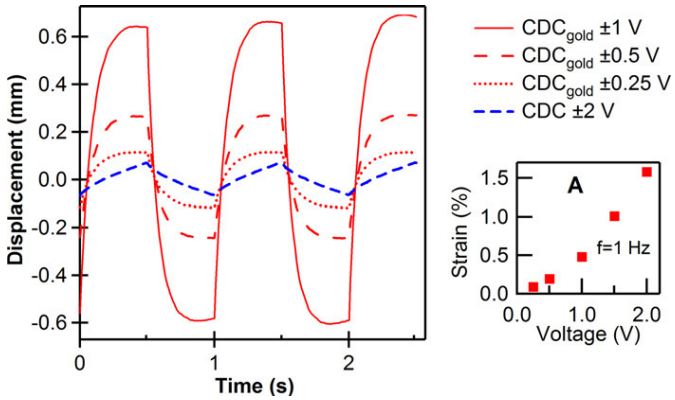


Figure 36: Tip displacements of CDC and CDC/gold actuators (measured at 5 mm distance from clamp) when different excitation voltages with frequency of 1 Hz were applied. Inset A represents strain as a function of applied voltage[75].

The developments of CDC polymeric actuators are still at an early stage and many modifications and research needs to be made to optimize and understand the mechanism behind it. The low actuation speed may be related to the conductivity of the material or it might be related to the pore size and ion channels, which need further investigations.

3.2.3 Ionic polymer metal composites (IPMC)

IPMC actuators are constructed in simple arrangements. It consists of a polyelectrolyte, which is between two high-surface-area flexible metallic electrodes that interpenetrate the polyelectrolyte. The polyelectrolyte acts as an ion-conducting layer, where the polymer chains provide one ion type and the opposite ion types are mobile solvated ions[7, 11]. Some polyelectrolyte examples are Nafion® (perfluorinated alkenes with short side-chains terminated with ionic groups, such as SO_3^-), Flemion® (ionic groups COO^-) and styrene/divinylbenzene-based polymers in which the ionic groups substituted on the phenyl rings[77]. Applying a voltage between the two electrodes, the solvated mobile cations start to move towards the oppositely charged electrode, resulting in swelling near the negative electrode and shrinkage near the positive electrode, which in turn bends the actuator tri-layer (Figure 37)[11].

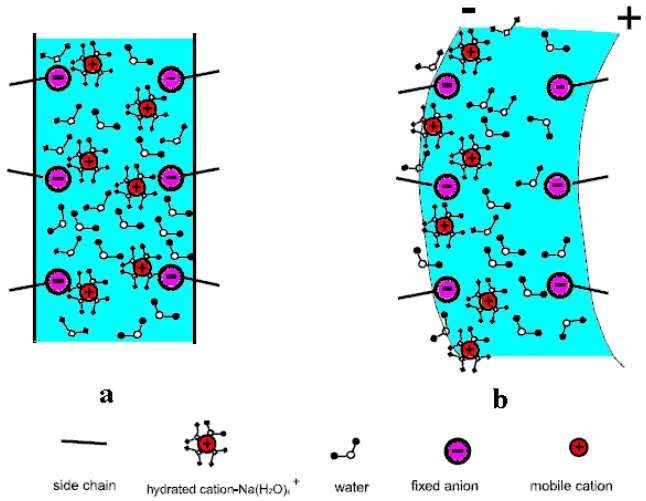


Figure 37: Actuation model for IPMCs (adapted from reference 59) (a) before the voltage is applied and (b) after the application of the voltage[11].

Beside the fast actuation speed of IPMC actuators an additional phenomenon occurs which starts directly after the actuation and is named back relaxation resulting at applied voltage to a decrease in bending strain. There are two main explanations in the literature[7], the first one refers to the amount of water molecules that are being carried of the cation's solvation shell while migrating into the cathode side[78]. The other explanation refers to the reorganization of ions in cation rich clusters leading to changes in the corresponding electrostatic interaction forces[79]. Due to the back relaxation, the application of IPMC actuators is limited and only actuation at high frequencies up to 1 Hz are suitable. Figure 38 gives the effect of actuation strain of IPMC at different frequencies.

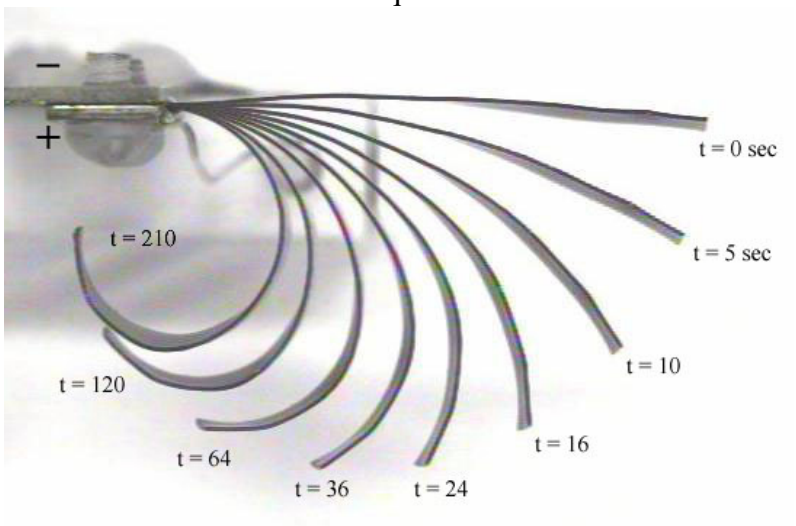


Figure 38: Flemion® based IPMC actuator in function of time[36]

„It is not uncommon that IPMCs drift in position after initial displacement and require some steady current to maintain a fixed position. This, along with the gradual leakage of water (the solvating species) from the surface of the device reduces efficiency, as well as degrading performance. One method of greatly reducing leakage and relaxation is to use highly inert, non-volatile ionic liquid electrolytes. IPMCs have been actuated at up to 100 Hz, with the fast transport being achieved due to the ease of transport though the highly porous polyelectrolyte"[36]. The properties of IPMC material are given in Table 8.

Table 8: Material and actuation properties of IPMC

Young's Modulus, E	Up to 2 GPa
Shear Modulus, G	Up to 1 GPa
Poisson's ratio, ν	Typical: 0.3-0.4
Power density (W/mass)	Up to 100 J/kg
Max force density (Cantilever Mode)	Up to 40 Kgf/Kg
Max displacement/strain	Up to 4% linear strain
Bandwidth (speed)	Up to 1 kHz in cantilever vibratory mode for actuations Up to 1 MHz for sensing
Resolution (force and displacement control)	Displacement accuracy down to 1 micron Force resolution down to 1 mg
Efficiency (electromechanical)	Up to 6 % (frequency dependent) for actuation Up to 90% for sensing
Density	Down to 1.8 g/cm^3

Application for IPMC actuators are devices that need fast actuation strain such as mechanical grippers, metering valves, diaphragm pumps, sensors, fins for robotic fish and an IPMC-operated artificial eye[80,36]. Several researches are made to combine IPMC actuators in biomimetic applications[7].

The advantages and disadvantages of IPMC actuator materials are listed in Table 9.

Table 9: IPMC actuator advantages and disadvantages[7]

Actuator type	Principle	Advantages	Disadvantages	Reported types
Ionomeric Polymer-Metal Composites (IPMC)	The base polymer provides channels for mobility of positive ions in a fixed network of negative ions on interconnected clusters. Electrostatic forces and mobile cations are responsible for the bending.	• Require low voltage (1–5 V) • Provide significant bending	response (in the range of 1 Hz) • Extremely sensitive to dehydration • dc causes permanent deformation • Subject to hydrolysis above 1.23V • Displacement drift under dc voltage.	Base polymer: • Nafion® • Flemion® **Cations:** • tetra-n-butylammonium, Li+, and Na+ • Metal: Pt and Gold

3.2.4 Conducting polymers (CP)

Conducting polymers were discovered in 1977 from a mistake of a PhD student in Heegers group in applying a catalyst in acetylene powder. The obtained metallic looking material was then investigated additionally by McDiarmid and Shirakawa. In the year 2000 the three professors shared the Nobel prize for discovering conducting polymers (polyacetylene). It was discovered that the material is conductive because of conjugated double bounds. In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localized “sigma” (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localized “pi” (π) bond which is weaker. Electronic hopping does lead to the conductive nature, but in the conductivity range of semiconductors (Figure 39).

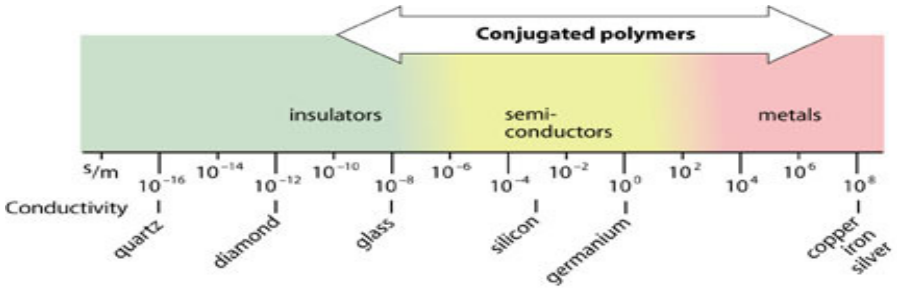


Figure 39: Comparison of conductive materials[7]

The second condition is that the plastic has to be disturbed - either by removing electrons from (oxidation) or inserting them into (reduction) the material. This process is known as doping where the first doping is named as p-doping e.g. the polymer is oxidized with halogens:

$$(CH_n) + \frac{3x}{2} I \rightarrow (CH_n)^+ + I_3^-$$

The iodine molecule attracts an electron from the polyacetylene chain and becomes I_3^-. The polyacetylene molecule, now positively charged, is termed a radical cation, or *polaron*. The lone electron of the double bond, from which an electron was removed, can move easily. As a consequence, the double bond successively moves along the molecule. The positive charge, on the other hand, is fixed by electrostatic attraction to the iodide ion, which does not move so readily.

The second doping is the n-doping, where the polymer is reduced with an alkali metal:

$$(CH_n) + xNa \rightarrow (CH_n)^{x-} + xNa^+$$

The redox doping of organic conductors is analogous to the doping of silicon semiconductors, whereby a small fraction of silicon atoms are replaced by electron-rich (e.g. phosphorus) or electron-poor (e.g. boron) atoms to create n-type and p-type semiconductors, respectively.

Undoped conjugated polymers can be semiconductors or insulators. In such compounds, the energy gap can be > 2 eV, which is too great for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes only have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. Even at a very low level of doping (< 1%), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 0.1–10 kS/cm for different polymers. The highest values reported up to now are for the conductivity of stretch oriented polyacetylene with confirmed values of about 80 kS/cm[81].

The effect of p- and n-doping plays a big role in recent developed new light electrochemical cells (LECs) based on conducting polymers to replace the light emitted diodes (LED) to achieve better performance.

Light-emitting electrochemical cells (LECs)

In light-emitting electrochemical cells (LECs) the distributions of ions assist the injection of electronic carriers and lead to light emission. In 1995 Pei *et al.*[82] introduced the light emitting electrochemical cell as an electrochemical device based on two electrodes (Indium titan oxide, ITO) connected by a blend of an electroluminescent polymer with a polymeric electrolyte, where cations and anions move in opposite directions. Its working principle based on the possibility of doping a conducting polymer as both p- and n-type. The polymer side to the anode is oxidized and p-type carriers are introduced. The polymer side closer to the cathode is reduced with providing n-type carriers. If the applied potential is greater than the energy gap of the polymer, electrochemical doping will appear forming an in-situ p-n junction[83], presented at Figure 40.

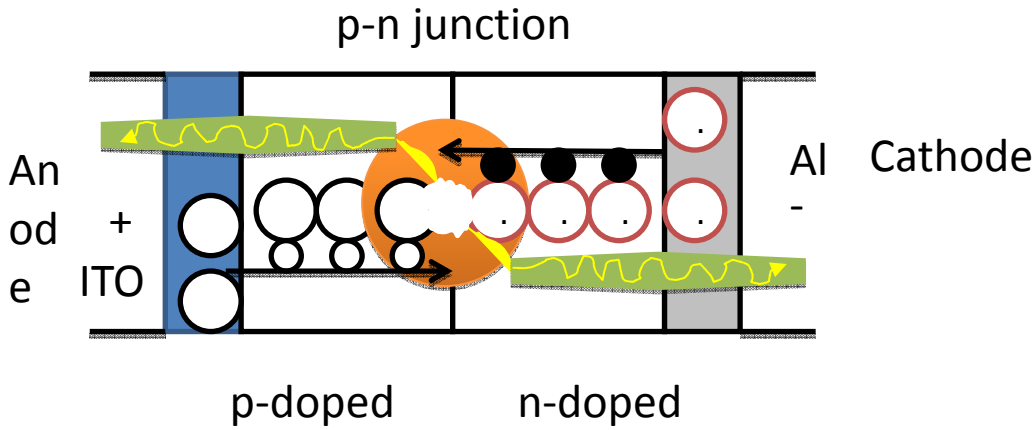


Figure 40: Principle operation of LEC with Anode (ITO or PEDOT-PSS) and Catode (Al) connected by an active layer based on PEO, KCF3SO3 and SY (phenyl-substituted poly(paraphenylenevinylene) co-polymer termed "superyellow") forming the p-n junction on applied voltage at steady state conditions of SY ($V_{DC} \geq E_g / e$). The small open circles represent holes and the small solid circles represent electrons. The light emission (green with yellow) appeared from an in-situ formed p-n junction at steady state conditions[82].

In the central undoped region where the carriers meet, injected electrons and holes recombine to form excitons, which can decay under the emission of light (Figure 40). The charge balance in this process is given by cation and anion mobility. The active layer consist in this example of a mixture of the light emitting polymer "superyellow" (SY-PPV), an electrolyte consisting of poly(ethylene oxide) (PEO) and the salt potassium triflate (KCF3SO3). To increase the life-time and efficiency of LEC devices (efficiency 2.5 % similar to LED devices) several modifications are made concentrating on encapsulation[84], improved ion-conductivity[85] and a new printing technology for large scale fabrications[86].

Other recent developments are made to apply conducting polymers in composites (chitosan-polypyrrole) to obtain reversible antioxidant properties[87]. The conducting polymers were combined with chitosan over a chemical oxidation process and it was found that the obtained composite material can be dissolved as stable suspension in light acetic acids[87]. To obtain conducting polymer powder a chemical oxidation needs to take place and once the powder is obtained it is very difficult to bring these particles back into the solution. The composite chitosan-PPy is very useful as a coating material on different fabrics. The antioxidant

properties of the chitosan-PPy films did show that under electrochemical reduction the antioxidant properties can be renewed[87]. By applying different oxidants in the formation process it was revealed that porphyrine moieties can be obtained in the chitosan matrix that can be applied in sensing materials[88].

Since the discovery of the novel material there has been many research and developments done to apply conducting polymers in many applications including anticorrosive coatings, electromagnetic shielding, organic light emitted displays (OLED), light emitted electrochemical cells (LECs), displays, solar cells, capacitors, transistors, sensors, actuators and several more[7,11].

3.2.4.1 Conducting polymer actuators

Conducting polymers such as Polypyrrole (PPy), Poly-3,4-ethylenedioxythiophene (PEDOT), polyaniline (PANi) and others (Figure 41) are often applied in actuator applications[89,90,91]. The preparation of conducting polymers is based on radical polymerization.

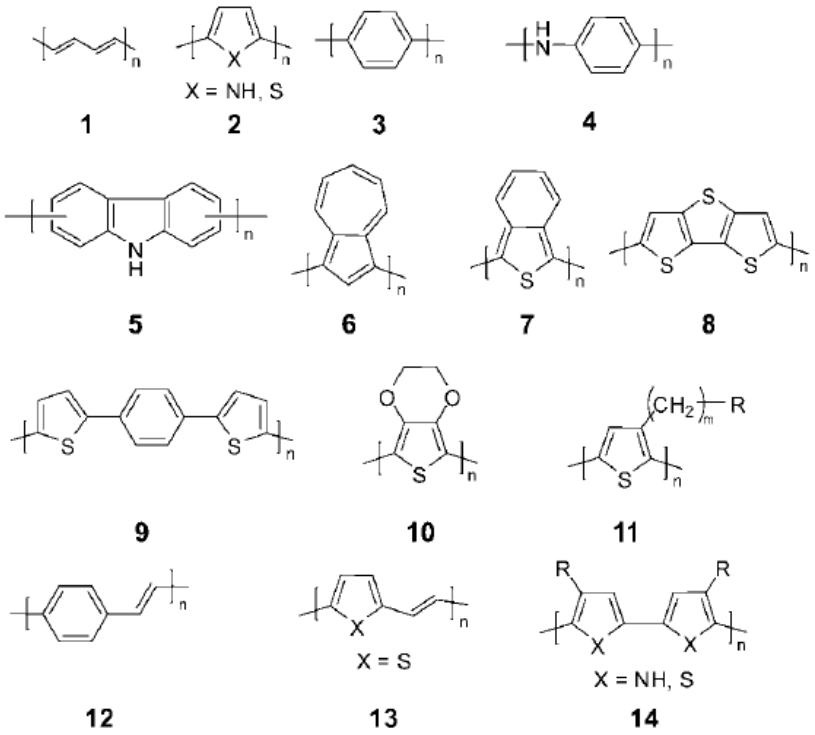


Figure 41: Selected building units of conducting polymers: 1, polyacetylene (PA); 2, polypyrrole (PPy), polythiophene (PTh); 3, poly-p-phenylene (PPP); 4, polyaniline (PANI); 5, polycarbazole; 6, polyazulene; 7, poly(isothionaphthalene); 8, poly(dithienothiophene); 9, poly(dithienylbenzene); 10, poly(ethylenedioxythiophene) (PEDOT); 11, poly(3-alkylthiophene); 12, poly(phenylenevinylene) (PPV) ;13, poly(thienylenevinylene) ;14, poly(bipyrrole), poly(bithiophene)[92].

Polymerization

The preparation of conductive polymers can be divided in electrochemical polymerization and chemical polymerization. From the theoretical point of view lead the radical polymerization of monomer units over cascade different steps to insoluble conducting polymer chains (12-16 monomer units) which forms a polymer network[93].

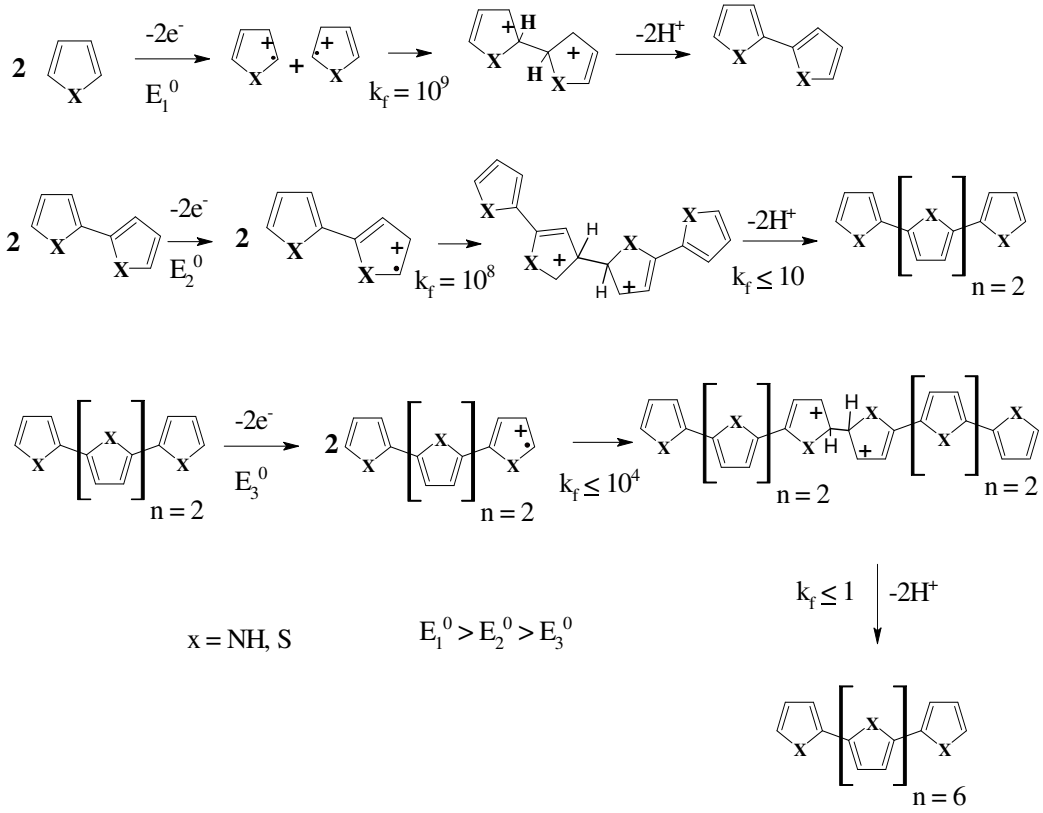


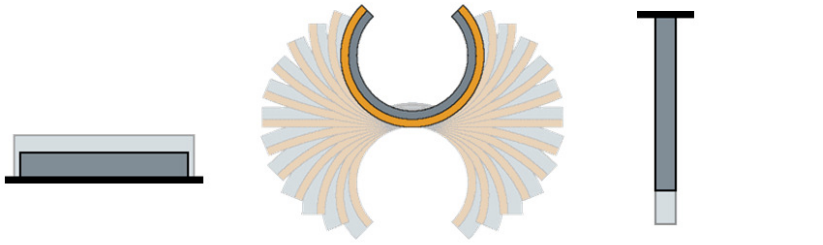
Figure 42: Mechanism of Dimerization and Oligimerization of Monomers (Pyrrole, Thiophens) in solution. Eo (standard potentials), kf (speed constant)[92]

The mechanism behind the formation of the conducting polymer units is based on formation of dimer, tetramer and octamer units where the speed formation constant k_f shows which chain lengths are preferred. The speed constant of the deprotonation becomes lower if longer chain lengths are produced, which can be explained with the higher stabilization of the previously formed cations over the conjugated monomer units. If the chain length is higher than 12-16 monomer units it becomes insoluble and deposits via electropolymerization on the working electrode. Several parameters (electrolyte and monomer concentration, temperature, electrolyte type, solvent type, electrochemical polymerization conditions, thickness of CP layer) can be changed to obtain conducting polymer networks with different actuator responses.

Actuator devices

The electrochemical polymerization of the conducting polymer (CP) takes place in a three electrode cell with an electrolyte with a reference electrode (mainly Ag/AgCl electrode), a

counter electrode (Pt-sheet) and the working electrode which is the actuator device (Figure 43).



Volume change
CP deposited on
Pt or Au surface
Working in electrolyte

Bilayer, Trilayer,
Hinge, Helix fiber
CP deposited on flexible foil
with Pt layer
Working in air
or electrolyte

Free standing CP film
Linear length change
Working in electrolyte

Figure 43: CP deposited on electrode (volume change), deposited on flexible foil (bilayer, trilayer or fiber) and deposited on stainless steel and peeled off for free standing CP

For Bilayer and Trilayer devices a non-conductive polymer such as PVDF, PET or other plastics must be coated with a thin conductive metal layer such as Pt or Au. In case of a bilayer only one side is coated and for a trilayer both sides are coated. The metal layer such as Pt or Au needs to be vaporize or sputtered on the plastics, which limits the choice of heat resistance (~ 180^{o}C) materials. The conductive plastics behave as working electrodes where the conducting polymer is deposited in form of a polymer network. The replacement of the metal coatings were applied in a recent research[94] with a chemically oxidized conducting polymer layer such as PPy or PEDOT on PVdF membranes or with conductive coatings based on MWNT/PEDOT-PSS[95]. In both alternative coatings the deposited conducting polymer in bilayer or trilayer design did show comparable actuation strain to those, which were deposited on inert metals. The advantages and disadvantages of chemical and electrochemical polymerization are presented in Table 10.

Table 10: Comparison of chemical and electrochemical polymerization

Polymerization approach	Advantages	Disadvantages
Chemical polymerization	• Larger-scale production possible • Post-covalent modification of bulk CP possible • More options to modify CP backbone covalently	• Cannot make thin films • Synthesis more complicated
Electrochemical polymerization	• Thin film synthesis possible • Ease of synthesis • Entrapment of molecules in CP • Doping is simultaneous	• Difficult to remove film from electrode surface • Post-covalent modification of bulk CP is difficult

Bilayer, Trilayer devices

On the conductive cantilever the conductive polymer is deposited in a three electrode compartment and is actuated in an aqueous or organic electrolyte under applied voltage. The basis for conducting polymer actuation is considered to be largely involved in swelling of the polymer from ion and solvent ingress during oxidation and reduction cycles (Figure 43), achieved at low operating voltages.

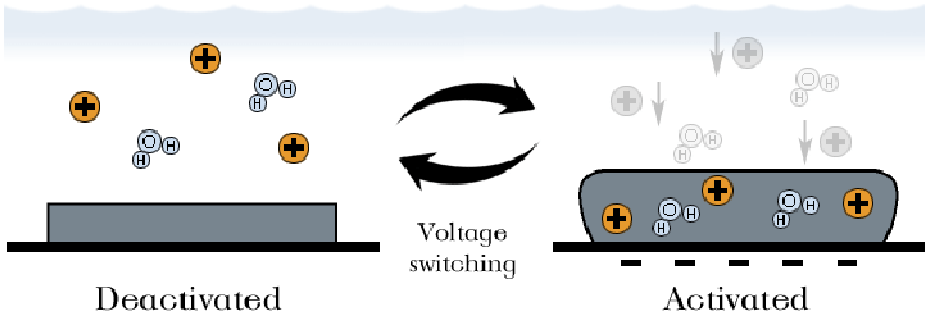


Figure 44: Charging/discharging with reversible volume change

To balance the charge neutrality, ions from surrounding electrolytes either enter or exit the polymer. It is this ion movement, accompanied by the solvent, which is primarily responsible for the swelling or contraction of the material.

Small anions can be used to balance the positive charges created in the polymer backbone during oxidative doping and anions enter the conducting polymer inducing a volume change (4).

$$PPy + A^- \leftrightarrow PPy^+(A^-) + e^- \quad (4)$$

$$PPy^+(A^-) + C^+ + e^- \leftrightarrow PPy(A^-)(C^+) \quad (5)$$

The ion movement can be cation-driven (5) instead, when a large immobile anion, such as dodecylbenzene sulfonate (DBS^-) in PPy, is included during electropolymerization, with mixed-modes of actuation also possible. Such cation effects are discovered also for CP bilayer actuators where mainly anion mobility is expected[96].

The equation (4, 5) shows that to maintain charge balance, a change of electronic charge must be accompanied by an equivalent change of the ionic charge, which requires mass transport between the polymer and electrolyte.

Goals in the area of conducting polymer actuator research are to find out the right conditions to achieve high actuation. Less ground research has been made to understand the mechanism of charging/discharging and resulting actuation. Three different models are introduced in the literature based on different assumption and experimental results.

1. Polaron/Bipolaron model

The polaron/bipolaron model describes the charging of polymer chains with three redox steps starting from neutral to the polaron state, from the polaron to the bipolaron state and from the bipolaron to the metallic state at different potentials[97] (Figure 44).

A B

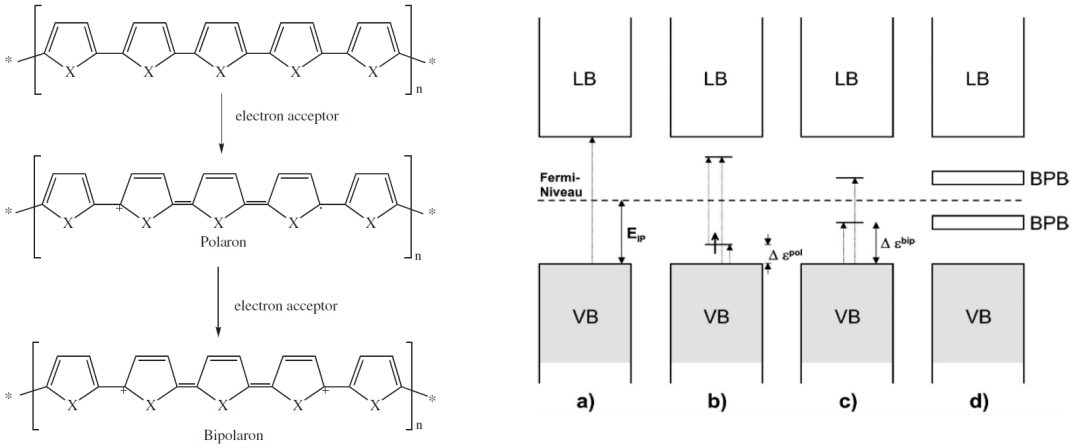


Figure 45: A: Formation of polaron and bipolaron at oxidation of CP[98], B: band structure of conducting polymer at oxidation with valence band (VB), bipolaron band (BPB), conductance band (LB); a) neutral state, b) polaron (S=1/2), c) bipolaron (S=0) and d) bipolaron band[96].

The polaron/bipolaron model was developed from inorganic crystals and it was proposed (Figure 44A) that a polaron or radical cation is introduced into the conjugated backbone after the loss of an electron. When oxidation of the same segment of the conjugated backbone occurs, the unpaired electron of the polaron is lost and a di-cation (i.e., bipolaron) is formed. The band structure of the conducting polymer did show during the oxidation (charging) process that the first step induces a radical (spin S=1/2, unpaired spin) where the polaron formed with further oxidation to a bipolaron (S=0, paired spin). To overcome the Fermi level (border between conductor and non-conductor) the formation of the bipolaron needs an energy of 45eV to reach this point. Further oxidation leads to the BPB and 1.4 eV of energy is necessary. It was found that the bipolaron is not more stable than the polaron and that with increasing oxidation in theory the conductivity must also increase. But with increasing oxidation the conductivity of the CP decreases.

2. Electrochemically stimulated conformational relaxation (ESCR) Model[99]

The ESCR model implements that the applied ions (anions) at oxidation are the main reason for the change in volume. The structure of the polymer film is influence by the anions that enter and leave the polymer film causing the volume change. A schematical model of the reaction of the CP during charging/discharging is presented at Figure 45.

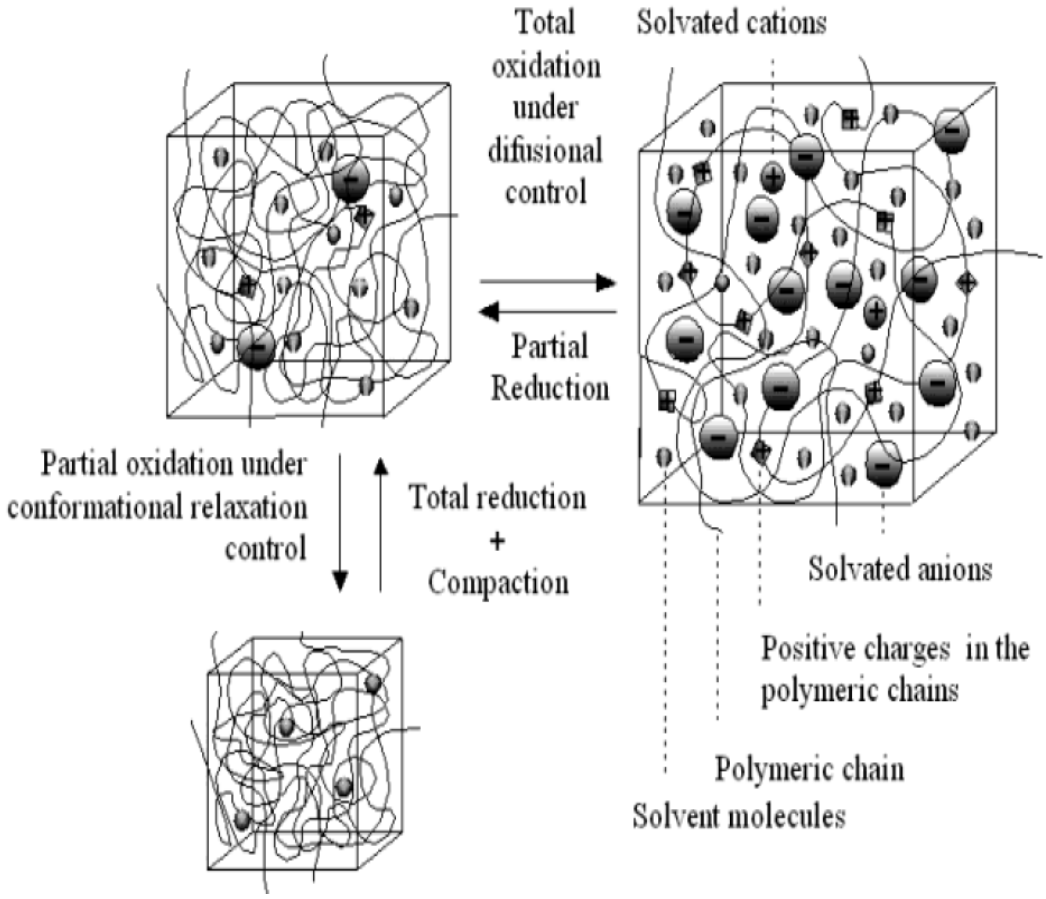


Figure 46: ESCR model of CP film during charging/discharging[96]

During oxidation electrons are extracted from the polymeric chains of conducting polymers while the positive polarons and bipolarons are formed. Between the monomeric units of the conducting polymer the double bonds are reorganized and give rise to conformational changes. To prove that the volume change is mainly dependent on the ions that move in and out during charging/discharging several studies have been made and have shown, in several cases, consistency with the ESCR model[100,101]. The ESCR and polaron/bipolaron models are the most accepted models for the conducting polymer actuation mechanism nowadays. Nevertheless both models can't explain cationic effects at reduction and other effects that take place during charging/discharging cycles.

3. Model of reversible σ-dimerization[92, 93]

The model of reversible σ-dimerization was introduced by Heinze *et al.*[92] and was based on simulation and electrochemical methods to obtain the electronic nature of the conducting polymer at electropolymerization and at charging/discharging cycles (Figure 46).

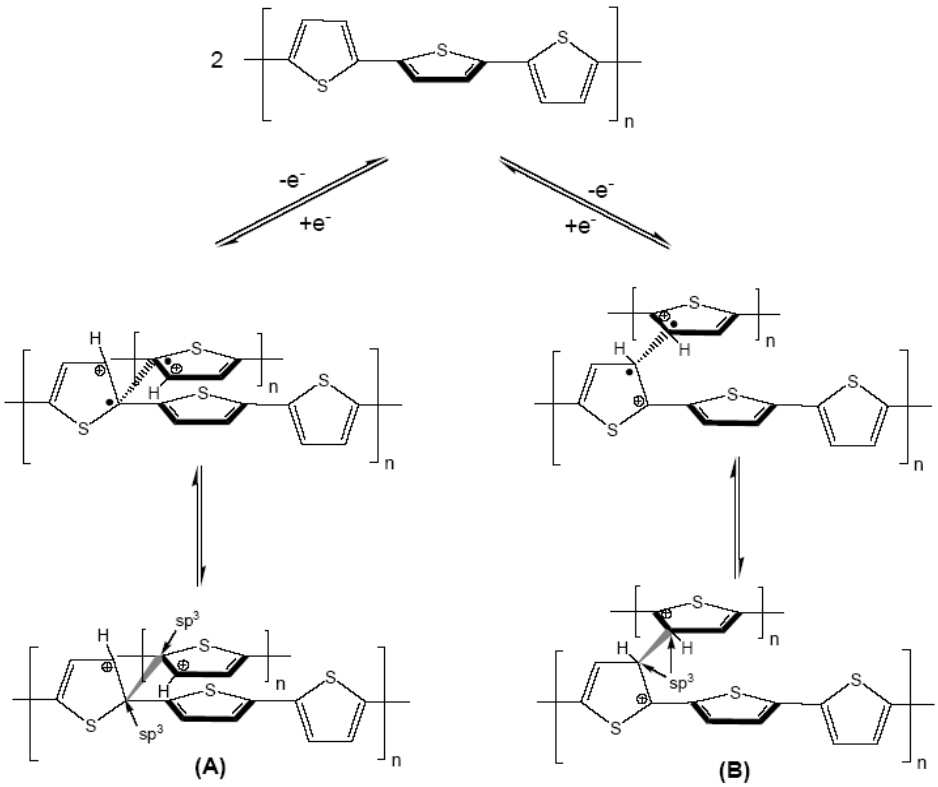


Figure 47: Proposed electronic state of oxidized polythiophene chains forming sp^3 centers with localized charges (A and B)[92].

During electropolymerization it was proposed that "σ-dimers" are formed and over intermoleculare coupling of α, α'(Figure 45 A) or β, β'(Figure 45 B) units at the sp^3 centers localized charge is obtained. At chain length of 12-16 monomer units the elimination of H^+ is forming a neutral fully conjugated system. The connection of the model of reversible σ-dimerization and actuation behavior of PPy/TBAPF6 deposited on Pt coated PET flexible plastic foil (PPy-bilayer) did show that during reversible redox cycles different PPy structures formed at different polymerization potentials influencing the actuation properties[96].

The introduced models of the mechanism of conducting polymers are insufficient in explaining all phenomena observed in actuator studies. More ground research has to be made and new methods must be applied to look inside\ the polymer during actuation to obtain more knowledge of the charging/discharging and induced volume change properties. Another very critical factor is the efficiency of actuation that was found to be under 0.1% and leads to the conclusion that 99.9% of the energy is somehow emitted as heat or lost in other reactions. Nowadays the focus of conducting polymers is based on applications. To assure a proper functionality of this material for reliable industrial products the increase in ground research must be emphasized.

Applications of conducting polymer actuators

Application of conducting polymers can be found in macro and micro devices targeting micro pumps, valves or smart structures in biomaterials or medicine[90, 91] and many more. Several

attempts have been made to attain robots or lab-on-chip devices with conducting polymer actuator implementation. The biggest challenge is to obtain actuators with high force, high strain, strain rate and no degradation of this material over a long reaction time. The advantages and disadvantages of conducting polymer actuators are concluded in Table 11.

Table 11: Advantages and disadvantages of conducting polymer actuators

Actuator type	Principle	Advantages	Disadvantages	Reported types
Conductive Polymers (CP)	Materials that swell in response to an applied voltage as a result of oxidation or reduction, depending on the polarity causing insertion or de-insertion of (possibly solvated) ions.	• Require relatively low voltage • Induce relatively large force • Extensive body of knowledge • Biologically compatible	• Exhibit slow deterioration under cyclic actuation • Suffer fatigue after repeated activation. • Slow response (<40 Hz)	PPy, PEDOT, Poly(p-phenylene vinylene)s, Polyaniline, and PTh

A macro device based on an artificial fish construction with conducting polymer actuator tail will be shortly introduced in the following section[102].

For this project we chose to prepare PPy in dodecylbenzene sulfonate (DBS) on Au-coated PVDF membranes, to produce films that were largely unidirectional and cation-driven in their actuation, for potential use in sea water. The performance of the trilayers at a range of actuator lengths (1.0 to 2.5 cm), PPy thicknesses (5 to 20 μm), frequency of actuation (0.03 to 10 Hz) and NaCl concentration (0.1 to 0.5 M) have been examined in the presence of either the large tetramethylammonium cation or with Na+. The trilayer configuration was found to give the best overall performance, which was then used to construct the caudal fin tail of a self-contained robotic fish (Figure 48) with control elements and energy supply integrated in the body.

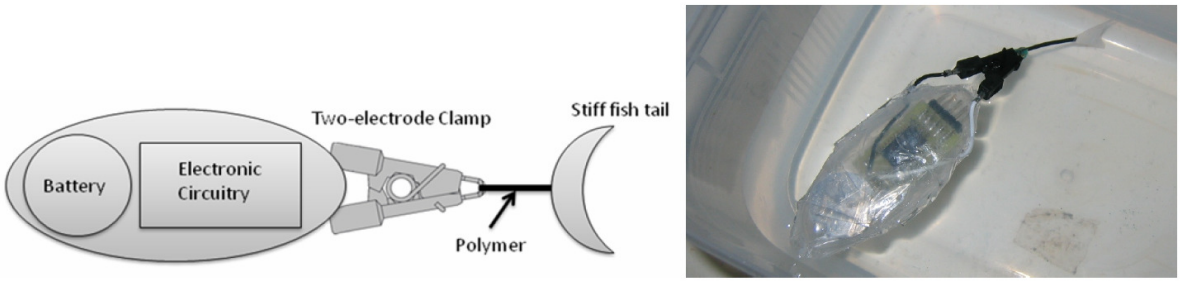


Figure 48: Conceptual design and photograph of the robotic fish. Overall dimensions 9 cm × 3.5 cm × 1 cm, plus tail [102]

A completely self-contained robotic fish was constructed in which a swimming motion was achieved for 10-12 hours in 0.2 M NaCl, using the PPy(DBS) trilayer actuator as the caudal fin. It was recognized that more efficient fish movement will require polymers with stronger and larger actuation, which might be achieved by using more powerful PPy actuator films, even if some form of encapsulation needs to be considered. Further improvements are envisaged through the addition of sensors to the fish, along with a more sophisticated control system[102].

New studies of polypyrrole combined with polyol-borate polymers (Figure 49) did show that polymer composites are obtained with actuator functionality driven by water gradients. The film actuator can generate contractile stress up to 27 MPa, lift objects 380 times heavier and transport cargo 10 times heavier than itself. Combination of this new material with piezoelectric elements did show that driven by water gradients, this generator outputs alternating electricity at ~0.3 Hz with peak voltage of 1.0 V[103].

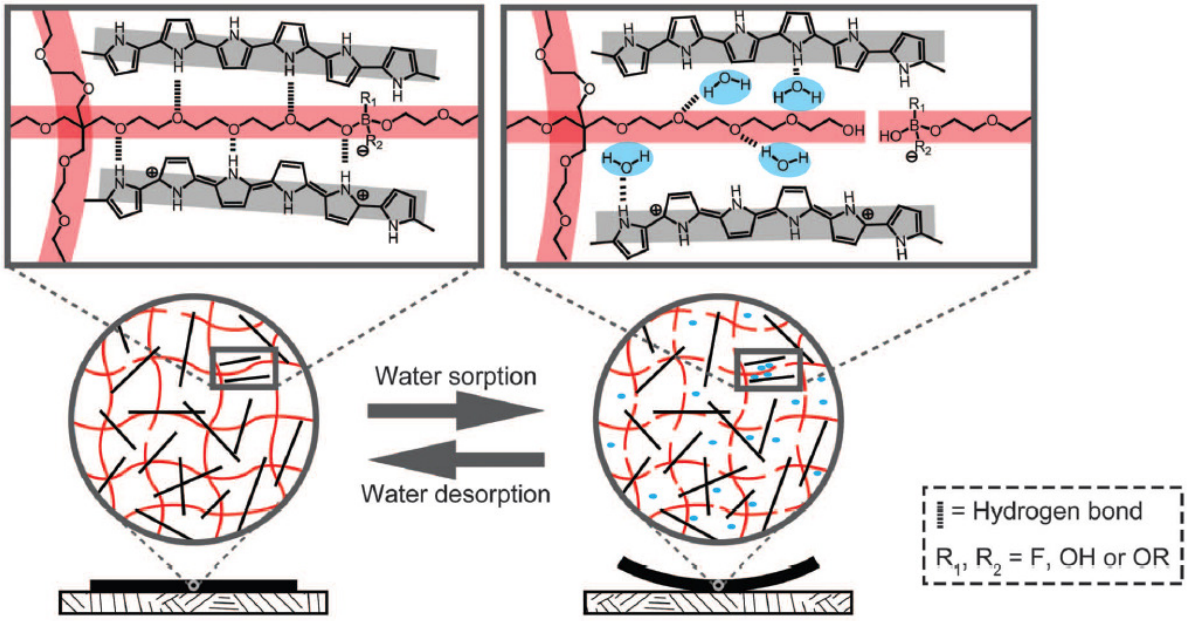


Figure 49: PEE-PPy composite film (black) is composed of PPy polymer chains (gray lines) and a PEE-borate network (red lines). The structure changes (involving H bonds and borate ester bonds) in response to water (blue dots) sorption and desorption[103].

„The dynamic polyol-borate network formed within the PPy matrix also serves as a macromolecular counterion for PPy. The polyolborate network is sensitive to water by means of hydrolysis and reforming of the borate ester crosslinking hub upon water sorption and desorption, which changes the mechanical properties of the composite (Figure 49). Intermolecular hydrogen bonding between the polyol-borate network and PPy also modulates intermolecular packing of the polymer composite to alter its mechanical properties in response to water. Therefore, the polymer composite exhibits fast, reversible and dramatic mechanical deformation and recovery in response to environmental moisture, visually reminiscent of “fast twitch” muscle activity“[103]. The activation cycle and intermediate curlings of the composites are presented at Figure 50.

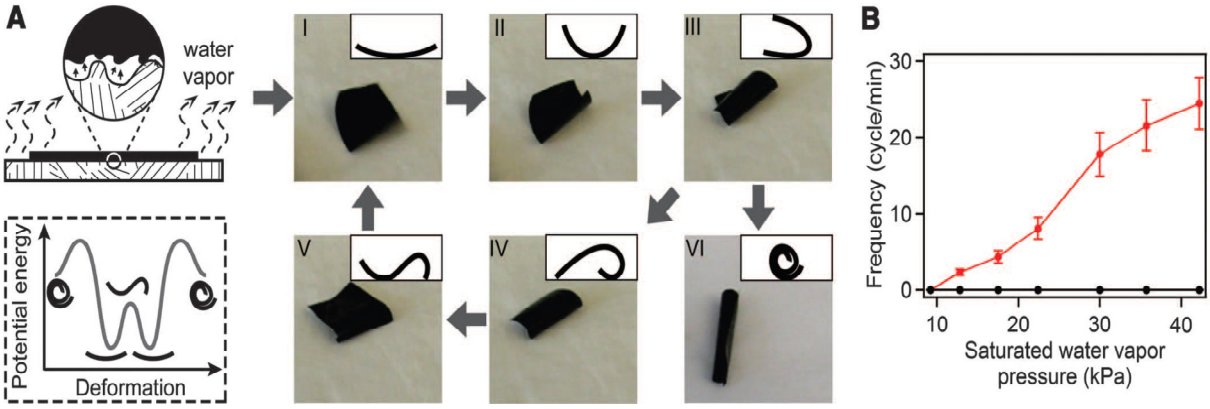


Figure 50: Locomotion of a PEE-PPy film on a moist substrate. (A) Representative images and sketches of the film's multistage locomotion and a schematic diagram of the film's elastic potential energy. (B) Flipping frequency of PEE-PPy (red) and PPy (black) films correlated with saturated water vapor pressure at each substrate temperature (n = 5). One flipping cycle refers to a motion process starting from stage I through stage V and back to stage I[103].

It was discovered that the PPy-PEE composite system features an interpenetrating network of a rigid polymer with a soft, hydrolytically sensitive polymer that can perform water-gradient–induced displacement, converting the chemical potential energy in water gradients to mechanical work. Besides mechanical vibration energy, the generator based on this powerful actuator can use at low temperature water gradients as its energy source. The water-gradient–driven actuator and generator demonstrated potential applications as sensors, switches, and power sources for ultralow-power devices[103].

3.2.5 Ionic polymer gels (IPG)

The best known example for ionic polymer gels is based on polyacrylnitrile, which is activated by a chemical reaction, changing the gel volume by applying different pH (from acid to alkaline environment). The disadvantage of the chemical reaction from acid to alkaline is the formation of salt that can be attached to the polymer surfaces and blocking the contact between the polymer chains and therefore slowing down the response time. The chemical activation of the gel has only limited application and the developments to activate the gel electrically were made by Calvert *et al.*[104]. If the gel bends to the cathode side it becomes alkaline and inversely more acidic to the anode side. Furthermore the response time is far too low to find application in robotic devices. The advantages and disadvantages of IPGs are presented in Table 12.

Table 12: Advantages and Disadvantages of IPGs

Actuator type	Principle	Advantages	Disadvantages	Reported types
Ionic Gels (IGL)	Application of voltage causes movement of hydrogen ions in or out of the gel. The effect is a simulation of the chemical analogue of reaction with acid and alkaline.	• Potentially capable of matching the force and energy density of biological muscles • Require low voltage	Operate very slowly —it would require very thin layers and new type of electrodes to become practical	Examples include: • PAMPS, Poly(vinylalcohol) gel with dimethyl sulfoxide • Polyacrylonitrile (PAN) with conductive fibers

Efforts are made to improve the response characteristics utilizing submicron-diameter electrospun PAN fibers. Actuation of ionic polymer gels is slow due to the required diffusion of ions, and the large displacement produced by electrodes deposited on the gel surface causing damage. Better performance can be obtained by using thin layers and robust electroding techniques (Figure 51)[11].

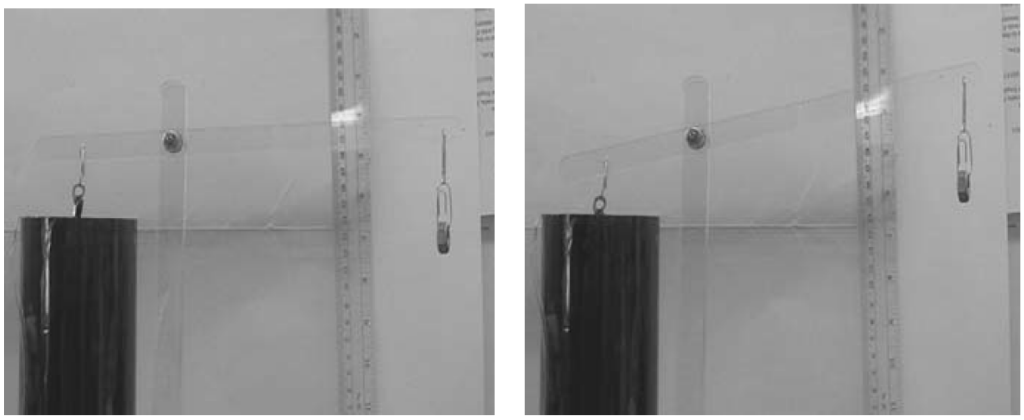


Figure 51: Working of PAN Crane with electrochemically driven actuation system (left) before and (right) after 20minutes[11]

The applications of IPGs are limited and a lot more developments have to be made to apply those ionic EAP in robotics or actuator devices.

3.2.6 Electrorheological Fluids (ERFs)

Electrorheological Fluids (ERFs) are composed of dielectric particles suspended in insulating oil, which can change their viscosity under applied electric fields. The phenomena of this effect was first discovered in 1940 and named "Winslow Effect"[105]. Under the electric field, electrorheological fluids form fibrous structures which are parallel to the applied field and can increase in viscosity (Figure 52) by a factor of up to 10^5.

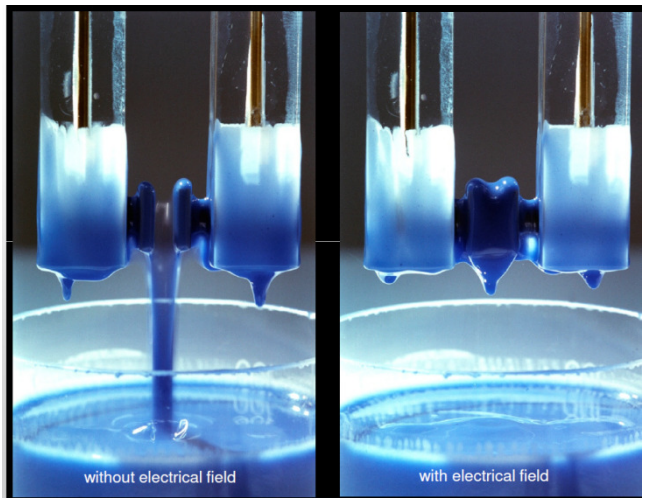


Figure 52: ERF without and with electric field with increasing viscosity

Under the application of an external electric field the change in viscosity take places in 10ms. If the electric field is sufficiently strong (> 2kV/mm) the ERF can solidify into an anisotropic solid. “There are two main theories to explain the effect: the interfacial tension or 'water bridge' theory and the electrostatic theory. The water bridge theory assumes a three phase system; the particles contain the third phase which is another liquid (e.g. water) immiscible with the main phase liquid (e.g. oil). With no applied electric field the third phase is strongly attracted to and held within the particles. This means the ER fluid is a suspension of particles, which behaves as a liquid. When an electric field is applied the third phase is driven to one side of the particles by electro osmosis and binds adjacent particles together to form chains. This chain structure means the ER fluid has become a solid. The electrostatic theory assumes just a two phase system, with dielectric particles forming chains aligned with an electric field in an analogous way to how magnetorheological fluid (MR) fluids work”[106].

ERFs are made from suspensions of an insulating base fluid (silicon oil) and particles (0.1 - 100 µm) that can be Cr-doped titanoxide (TiO_2) with fibrous structure or urea-coated nanoparticles of barium titanate oxalate (Figure 53).

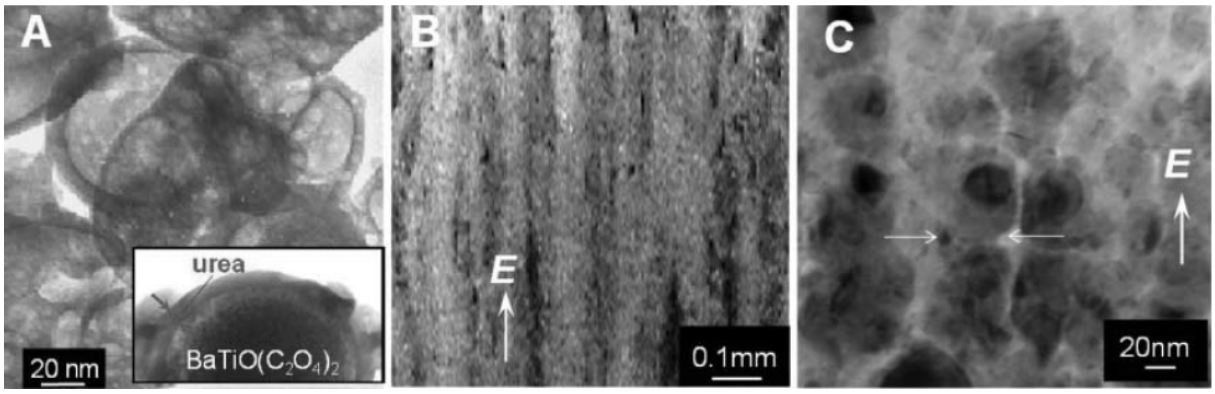


Figure 53: A: urea-coated nanoparticles of barium titanate oxalate, B, C: chains forming of nanoparticles under an applied electric field (2 kV/mm)[107]

It was discovered a Giant ERF (GERF) could be obtained where the applied field was reduced to 500 V/mm from particles with improved dielectric properties (Figure 53). The advantages and disadvantages of ERF are given in Table 13.

Table 13: Advantages and disadvantages of ERF

Actuator type	Principle	Advantages	Disadvantages	Reported types
Electro-rheological fluids (ERF)	ERFs experience dramatic viscosity change when subjected to electric field causing induced dipole moment in the suspended particles to form chains along the field lines	• Viscosity control for virtual valves • Enable haptic mechanisms with high spatial resolution	• Requires high voltage	Polymer particles in fluorosilicone base oil

Despite the relative high electric field requirements there are many applications for ERFs already in industrial products. They are in devices where forces need to be transmitted for example shock absorbers, active dampers, clutches, adaptive gripping devices, variable flow pumps and more[108]. The adaptation of ERF to typical EAP application was recently developed for Active Knee Rehabilitation Device Human Trials (Figure 54).

Figure 54: In the container attached to the leg the ERF smart fluid contains. Voltage is applied to the cylinders; the liquid inside the gap turns solid in less than a millisecond, creating resistance on a healing joint with the turn of a dial.

4. Summary of non-EAP and EAP material

The topic of this manuscript based on „artificial muscles“shows a wide variety of materials that are compared to natural muscles. It is not yet possible to achieve the efficacy and durability of natural muscles with any material introduced here. The main targets of the new smart materials are to achieve muscle work or actuation strain that's near as possible to the natural muscle's performance. The non-EAP materials do not use electric energy to activate the material. Air pressure for pneumatic artificial muscles (PAM or McKibben) is used where a high pressure induces volume changes in a flexible bladder. This principle was developed and applied earlier in several robotics and artificial limbs because the performance is similar to the natural muscle. Other materials are based on shape memory alloys showing reversible volume change by thermal activation while some other polymers can be activated by light or magnetic impulses. Since the demand of flexible electronics, the EAP group of materials is introduced in this manuscript to show the high potential of this new class of smart materials. The EAPs are divided into ionic and electronic subgroups with the difference that electronic EAPs need an electric field and ionic EAPs need an electrolyte to operate. The electronic EAP group includes Ferroelectric Polymers, Dielectric Elastomers (DE), Electrostrictive Graft Elastomers and Liquid Crystal Elastomers (LCE). The broadest applications in real products can be found in ferroelectric elastomers (piezoelectric effect) because of their controllability and reproducible actuation properties and long-term studied piezoelectric effects. The most popular are dielectric elastomers (DE), which are just entering the stage of being implemented in real products and many companies have started to introduce this material in their products. The greatest disadvantages of the electronic EAP is the need for a high electric field (0.5 - 10 kV/m), which limits their potential application range. On the other hand the ionic EAP group that includes CNT, CP, IPMC, CDC, IPG and ERF need only low voltages (1-7 V) to achieve sufficient muscle work, but the limitation and processability that depend of electrolytes is the biggest challenge to make this group reliable for industrial products. Many research and optimization to replace the electrolyte with ionic liquids and solid electrolytes has shown good improvements and many new ideas and innovations have taken place over the last 30 years. The main challenge for all „artificial muscles“is the actuator's performance, which for the electronic and ionic EAP is that a high actuator force generally follows with low displacements. The actuation speed and the creep during actuation creates another limitation in real applications. For the ionic EAP a lot of additional ground research has to be made to understand which actuation mechanism can explain all actuation properties. As an example the electric double layer capacitance in CDC or IPMC, the charging/discharging in CNT and CP rely on specific mechanisms that are still not fully understood. In comparison the mechanism of ferroelectric polymers or dielectric elastomers are understood quite well. Recent research shows a tendency to combine different EAP materials together and many useful properties could be obtained that might also be interesting in energy-harvesting applications. The next generation of electronic products needs to be smart materials used in the next generation of flexible cell phones, cameras, iPads, e-newspapers, smart shirts and many more. Some of these product developments have already started and more R&D made in controllable and reliable EAP can help to design new products. Doing research and

development in EAP („artificial muscle“) covers many different topics (chemistry, physics, IT, technology, etc.) and has a bright future with many fresh applications every year.

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