Recent advances in the 3D printing of ionic electroactive polymers and core ionomeric materials

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Abstract:

In this paper, we present a review of the recent advances in the 3D printing, or additive manufacturing, of ionic electroactive polymers (EAP) and their future applications. Ionic EAPs are a promising field of study that has only recently seen a shift towards additive manufacture with advances in more sophisticated 3D printing technologies. Several current ionic EAP additive manufacturing processes and reported applications are discussed. This paper reviews explicitly ionic EAPs, over their dielectric counterparts, due to their potential applications as artificial muscles and the possibility to produce them through recent additive manufacturing developments. The mechanisms of actuation behind these recent developments and known material examples are also examined. We also discuss the merits of additive manufacturing and its potential in the field of electroactive polymer production and application. References have been provided to further cement the growing interest in this field and provide an in-depth explanation of the essential concepts and mechanisms.

1.0 Introduction:

Emerging in 1880, with Wilhelm Röntgen's pioneering research into the effect of an electrostatic field on a strip of natural rubber[1, 2], the field of research into EAPs and soft robotics was formed[3-17]. Polymers that are electrochemically responsive are known as electroactive polymers (EAPs). They respond to an electric field or current with a physical deformation or, with the reverse effect, converting movement into an electrical signal. Polymers are an attractive field of research due to their lightweight, inherent mechanical flexibility, and durability[18-20]. It is these appealing properties that draw the attention of both chemists and material engineers alike. These properties give EAPs an almost human-like range of motion and have accelerated the development of soft actuators, soft robots, and soft sensors that have an array of applications, from protheses to micro-robots[21-25]. Often described as "soft" actuators, EAPs fulfil the criteria of having their actuation, sensing, and motion transmission elements being seamlessly applied to a continuous singular body[26].

The 3D printing of soft and programmable materials is a valuable tool as it allows the more complex geometries required by an idealised "soft robot". By making use of their ability to emulate natural muscles and having a considerable actuation strain, EAPs are often applied to the production of artificial muscles and

smart prosthetic devices that can be external or internal to the human body[14, 15, 21, 27-29]. Recently the use of EAPs to produce refreshable Braille displays has also been shown[30, 31]. These tactile displays use an array of EAP actuators that can be individually activated to raise or lower the Braille dots on the display. These displays can be used to develop so called "artificial skin", in which a visual change can be created by utilising the tactile impressions on a high resolution tactile display[32]. These materials also display a great capacity for microfluidics, with both diffusion micropump and displacement micropump applications being known[33]. Aside from these microfluidic pump applications, they also show promise as chemical sensors and chemical transistors[34]. Lastly, with their potential application into microelectromechanical systems (MEMS) as smart actuators, it is easy to understand the interest around EAPs.

This paper has a particular focus on ionic EAP and their actuators due to their biomimetic potential in artificial muscles development. Ionic EAP actuators have garnered much interest in recent years as potential alternatives to dielectric EAPs, and conventional hard bodied actuators and sensors due to their low electrical energy consumption, biocompatibility, durability, and some have displayed an ability to operate in both air and aquatic environments[27, 35-39]. Due to their bi-directional actuation and low voltage requirements, they show potential as grippers and multiple degrees of freedom (MDOF) actuator systems[5, 40, 41]. Additionally, recent research has uncovered novel additive manufacturing techniques to allow for the extrusion of ionic EAP actuators [5, 7, 16, 17, 40, 42].

A review article by Zolfagharian *et al* 2016[43] extensively reviewed the standard 3D printing processes of soft actuators. In this review, the likes of shape memory polymers, photopolymers or light activated polymers, hydraulic and pneumatic actuators were all covered in detail. However, ionically driven EAPs were not the main focus in this review, and few examples were given or detailed. Bar-Cohen and Anderson also published a review article in 2019[9]. Covering a great depth of EAP actuator knowledge, they discuss the fields of dielectric EAP actuators and ionic EAP actuators in detail. Additionally, by providing descriptions and examples of EAP actuators, categorised into the several subgroups of these two fields, the attractive properties of EAPs are emphasised. However, the examples of 3D printed ionic EAP actuators are limited. A review by Martins *et al* in 2020[8] once again provides great knowledge into the working principles, applications and limitations of EAP actuators. However, once again, examples of 3D printed ionic EAP actuators were limited.

Because of the scarcity of current literature explicitly focussed on the additive manufacturing of ionic EAPs, this review places more focus on this aspect of ionic EAPs, in which the core ionomeric materials are shown to be 3D printable. That is to say, where the core ionomeric material responsible for ion transport through the bulk of the sample has been shown to be explicitly reproducible by additive manufacture. The reason that interest is given to the core ionomeric materials printability is that this forms the backbone of the actuator and, by being printable, allows more complex geometries to be formed, for example, multiarmed grippers and walkers. Additionally, by focussing on the printability of the core ionomeric material, time in post-production assembly can be saved, and new exciting applications can also be discussed.

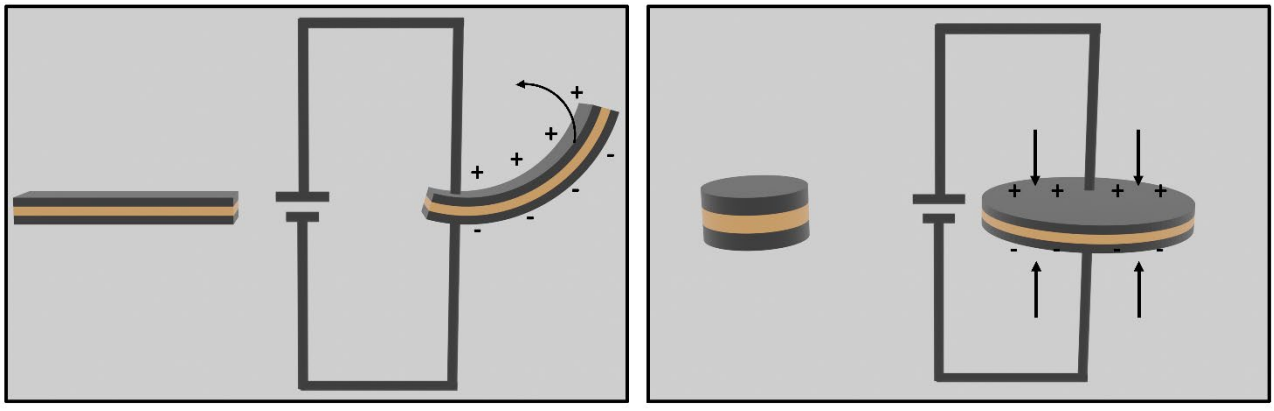

Figure 1: The two types of EAP actuators and a depiction of their actuation.

2.0 Ionic and Dielectric Electroactive Polymers Overview:

Ionic EAPs generally consist of two electrodes and an ionomeric core material capable of ion exchange. Upon activation, ionic EAPs can be used to produce bending phenomena due to their specific ion movements in an electrical field[27, 36, 44-48]. Several types of ionic EAPs have been developed, such as ionic polymer gels[48-52], ionic polymer-metal composites (IPMCs)[40, 41, 53-62], nanocarbon EAPs [30, 63-69] and conductive polymer EAPs[28, 70]. Their flexible nature and bending mechanism garner much interest in the development of artificial muscles, soft robots and flexible/wearable sensors[29, 47, 53, 71].

Ionic EAPs are not without their areas of weakness and have great potential for improvement (as seen in Table 1)[9, 43]. The force exerted is weaker than in their dielectric counterparts in part due to their ionic displacement mechanism. As a result of their relatively lower electrochemical coupling coefficient, their efficiency is also comparatively low, typically less than 30%[38, 47, 71]. These low forces do not mean that the polymer samples themselves are weak, as ionic EAPs have been shown to lift masses several times their own, as well as to produce grippers and arms capable of locomotion[5, 47]. As a result, these areas of improvement are of key interest for the development of more efficient ionic EAPs.

Dielectric EAPs are driven by the columbic attraction of parallel plate electrodes[22, 25, 39]. Structurally unique from their ionic counterparts, the core elastomeric material contained in dielectric EAPs is utilised for its elastic behaviour under traction and contraction forces[4]. As such, the core elastomer defines much of the forces generated and the magnitude of the operating voltages required for successful contraction. Due to the monodirectional nature of the actuation produced by dielectric devices, dielectric actuators struggle to produce the natural bending motions observed in their ionic counterparts. However, these limitations can be overcome through careful device design[72, 73]. Dielectric actuators are often utilised as soft pumping devices, wearable sensors and oscillators due to their expansive/contractive actuation mechanism, [12, 25, 31, 32, 74].

Table 1: Comparison of Ionic and Dielectric Electroactive Polymers

Type of EAP	Advantages	Areas for improvement
Ionic	▪ Low operating voltage ▪ Natural bidirectional bending is driven by voltage polarity ▪ Large bending displacement	▪ Low bending actuation force ▪ In air operation requires electrolyte; consideration to lessen the impact of evaporation ▪ Aqueous systems suffer from hydrolysis at >1.23V ▪ Low electrochemical coupling coefficient, hence lower efficiency ▪ Do not hold strain using DC voltage (except for Nano-carbon and Conducting polymer EAPs)
Dielectric	▪ Room temperature stability	▪ Require large operation voltages

	▪ Hold strain using DC voltage ▪ Large activation forces ▪ Rapid response times	▪ Electrostriction actuation results in monodirectional actuation irrespective of voltage polarity ▪ Pre-straining required during fabrication

3.0 Ionomeric Materials for Ionic Electroactive Polymer Actuator Fabrication

The physical diffusion of ionic species through the ionic EAP actuator is what drives actuation. Ion choice in ionic EAPs is vital as the various ion mobilities are affected by hydration volumes, charge and ion size[44, 45, 75]. Additionally, interactions with the ionomeric polymer network[46, 76-79] also defines the operational capabilities of the actuator in terms of actuation rate, degree of movement and force generated[37, 78]. Ion hydration volume has, perhaps, the most significant effect on an actuator's performance, as ions with larger hydration volumes would suffer from decreased mobility but at the same time generate more strain for actuation. Therefore, there exists a balance between the actuator tip force generated and the rate at which actuation occurs. Additionally, ion–polymer interactions within the network will lead to additional mobility factors such as the movement of identically charged species past each other will result in drag[38, 80].

Therefore, since ion transport through the actuator is of great importance, material choice for the core ionomeric material is paramount. Several examples of acrylate and vinyl based polymer gel networks have been utilised to facilitate ion transport[48, 49]. These include the likes of poly(methacrylic acid) gel and poly(acrylamide-co-acrylic acid) gel in an electrolyte solution of sodium chloride. By nature, these gels have high affinities to aqueous solutions, and hence they help facilitate the transport of hydrated cations through the polymer network. Easily obtained and easy to work with, these acrylate and vinyl networks make a good choice for ionic polymer gel actuators.

At the forefront of ion exchange materials development, and also bearing an iconic name, DuPont's Nafion™ perfluorinated polymer membranes have seen a wide range of academic and materials research[81-83]. Due to its popularity as a highly cationic conductive membrane, several analogues have been developed. These include Flemion™ of Asahi Glass, Aquivion™ of the Solvay Group, as well as various other fluorinated polymer networks[84-86]. Well known for its physical robustness, chemical inertness, and high-water permeability, Nafion™ is a prime candidate for ionic EAP actuators. Additionally, through the use of ionic liquids as electrolytes, IPMC actuators of higher performance are produced[87]. By tuning the binding energy and diffusion coefficients of these ionic liquids, the bending strain and charging time of the IPMC actuators can be controlled[88].

The synthesis of numerous block copolymer ionomeric materials has been shown by groups such as Watanabe *et al*[41, 89], Long *et al*[90-92] and several others[93, 94]. These block copolymers self-assemble into ionic phase regions and non-ionic phase regions, with the ionic regions providing diffusion pathways through the bulk of the sample. Several Interpenetrating Polymer Network (IPN) ionic EAP actuators have been shown using poly(ethylene oxide) interlaced with other polymer network blends[95-97]. The concatenation of different polymer networks forms an IPN that cannot be separated without the cleavage of chemical bonds. They possess good thermo-mechanical properties, and with consideration given to the free volume available for ion migration, the ionic conductivity can be tailored[98-101].

Conducting polymer actuators can be formed via electrochemical polymerisation of an inert electrode and can be actuated either in contact with said electrode or as a free-standing film[102]. Actuation is performed using small mobile anions and the expansion upon oxidation and contraction upon reduction. This is often referred to as anion driven actuation, with the reverse being confirmed in the case of larger anions being immobilised within the conduction polymer network and the subsequent movement of smaller cations to

maintain charge balance. This cation driven actuation causes an expansion upon reduction to occur. Several conducting polymers have been utilised in actuator production, with Poly(aniline), Poly(3,4-ethylenedioxythiophene) and Poly(pyrrole) being some of the best documented[103-106].

3.1 Electrode Materials for Ionic Electroactive Polymer Actuator Fabrication

Brought forward by Oguro *et al* 1993[107], the electroless plating of highly conductive platinum nanoparticles can be directed onto the surface ionic membranes allowing for the production of highly conductive Nafion™ and similar soft IPMC actuators. The plating of conductive precious metals such as platinum and gold provides an efficient and straightforward electrode production method[38, 108]. However, the formation cracks in the electrode surface can form regions free of metal nanoparticles and result in increased resistance or electrode failure[109]. As such, the development of conducting polymer reinforced electrodes has been shown to lengthen precious metal electrode lifetime as well as prevent electrolyte evaporation.

Conducting polymers such as poly(aniline) and poly(pyrrole) display the necessary features for soft electrode production due to their flexible nature. Continued research into the additive manufacture of conducting polymers also makes these soft actuators a very exciting area of research[28, 70, 110, 111]. Additionally, due to their unique redox cycling mechanism conducting polymer EAPs are also capable of sustaining strain under an applied DC potential. Nano-sized carbonaceous materials such as carbon nanotubes and buckyballs have been extensively researched for their structural properties in composite materials[112-114]. However, by utilising polymer/nanocarbon composite materials, the electrically conductive carbon materials can be utilised as effective electrodes for actuator production. Additionally, the mechanism of charge injection affecting the length of the carbon-carbon bonds in the nano-sized carbonaceous electrodes allows for sustained strain under applied DC voltage, overcoming a key drawback of ionic EAP actuators.

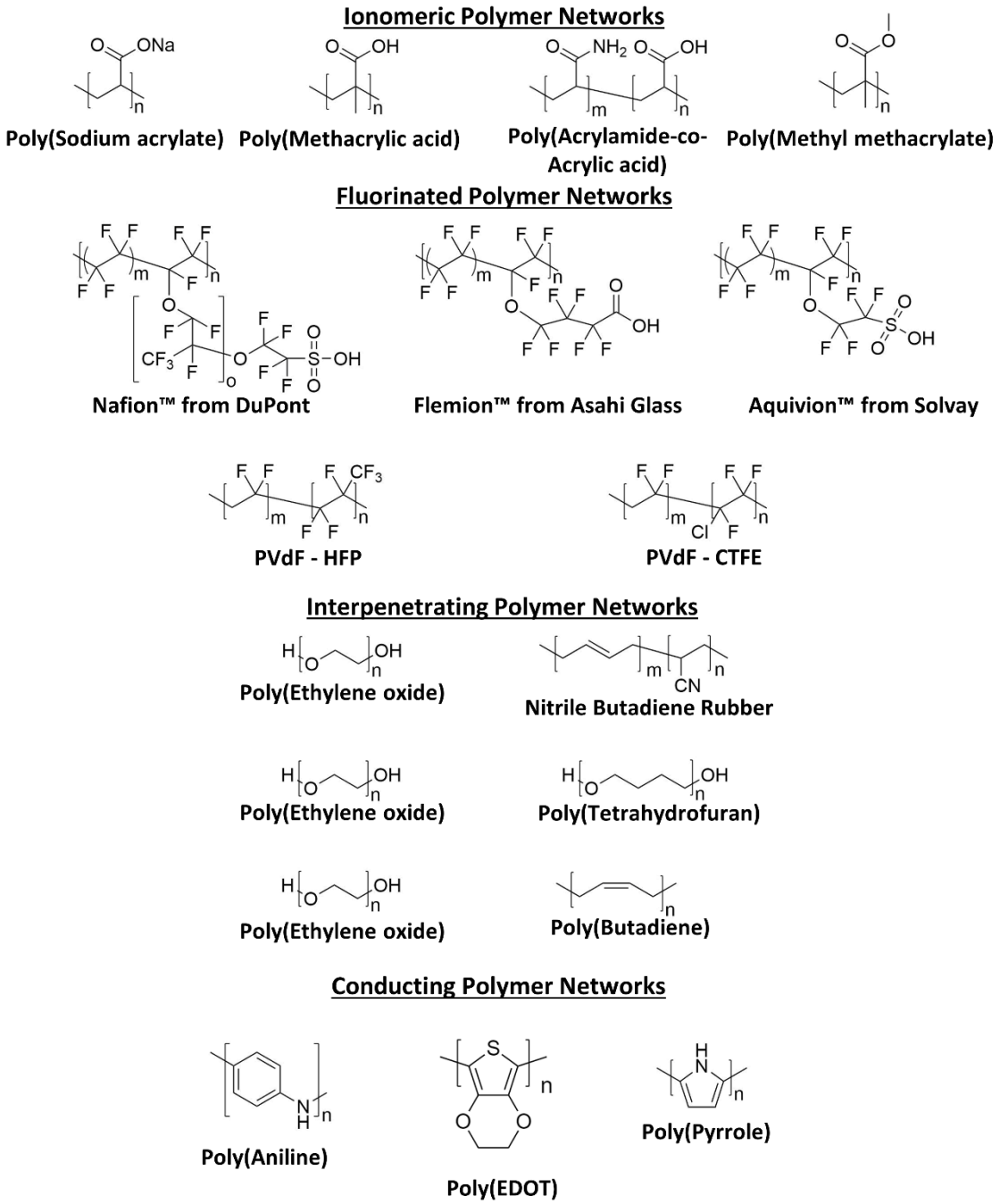

Figure 2: Chemical structures of several commonly used polymer networks for ionic EAP actuator production.

3.2 Mechanisms of Ionic Electroactive Polymer Actuation

The following section details the mechanisms by which the four main types of ionic EAP actuators are driven. The movement of ionic species constrained in the polymer matrix is the driving force of the electro actuation. The application of electric potential and the subsequent migration of charged species result in a nonuniform build-up of stress in the polymer sample. The result is a physical deformation to relieve this stress. The ionic species interaction with the polymeric core material and the electrode layers helps define the different mechanisms of operation. As such, the four sections below briefly summarise the chemical and physical effects that occur during actuator operation and the resulting physical deformation.

3.2.1 Ionic Polymer Gel Actuators

A polymer gel actuator is composed of mobile ions and fixed anions within the polymer network. Initially, all charges are in equilibrium until an electric field is applied (Figure 3). With the application of an electric field,

mobile cations migrate towards the cathode at a faster rate than mobile anions migrate to the anode. This is due to the fixed anions within the polymer network[48]. Due to the difference of ion concentrations at the opposite gel surfaces and the difference in respective ion concentrations within the solution and the gel, osmotic pressure is developed on the surface of the gels[52]. It is this difference in osmotic pressure that causes the bending phenomenon of the gel with its anodic side concave. Consequently, these ionic polymer gel actuators are expected to bend in the reverse direction (cathodic side concave) if the gel is in contact with the anode[48]. Initially reported in 1955 by Katchalsky *et al* [115], ionic polymer gels have seen extensive attention in regards to EAP actuator production. In recent years the use of new ionic liquids and macromolecules for more efficient in-air operation has been significant [9, 24, 116].

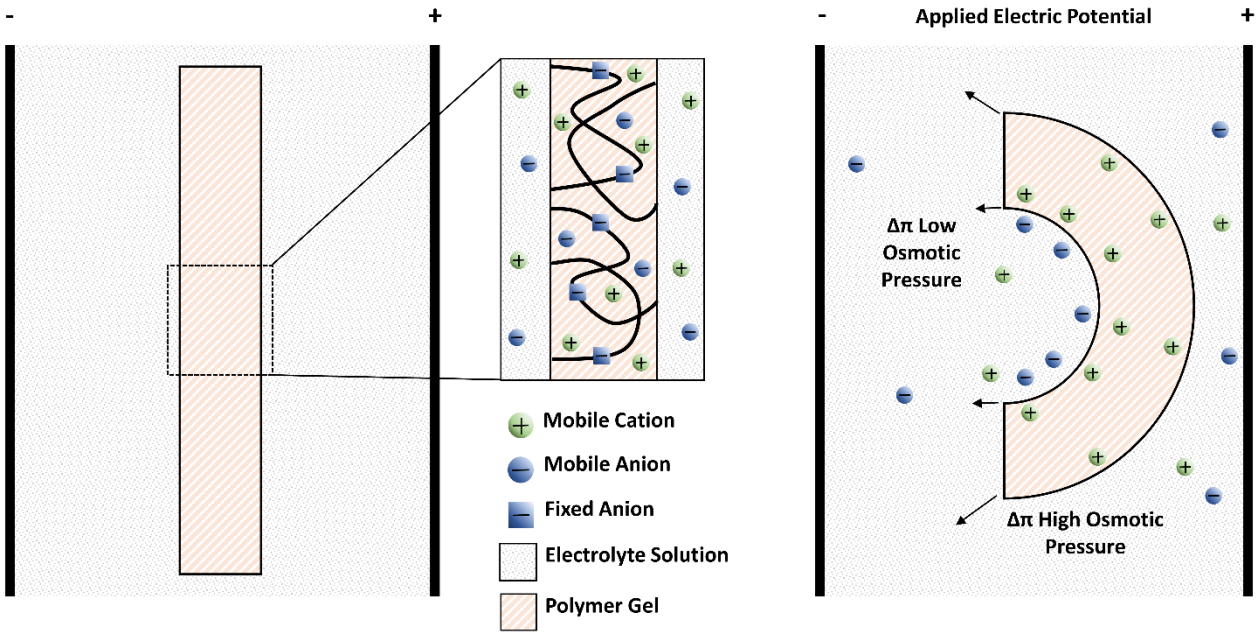

Figure 3:Ionic polymer gel actuator in a single electrolyte system (adapted from Jo and Kwon 2011[48]).

3.2.2 Ionic Polymer-Metal Composite Actuators

IPMCs are a widely studied ionic EAP material. Initially reported by three groups in 1992, the primary attraction to IPMC actuators are their characteristically low operational voltages[62, 117, 118]. In IPMCs, metal electrodes on the surface of an ionomeric polymer backbone drive the production of an electric field through the sample[38, 107, 108]. These backbone materials are ionic conductors that, through the anionic species fixed in the network, allow for the transport of cations at a high rate[76, 78, 79, 119]. As seen in Figure 4, the ion transport of hydrated cations to the cathode is facilitated by the sulfonic acid ionomeric polymer backbone. The increased build-up of cations on the cathodic side of the sample produces a strain that causes the sample to bend towards the anodic side[47, 71]. With the development of cation grafted perfluorinated polymers such as poly(vinylidene fluoride-co-hexafluoropropylene) (aka PVdF – HFP), the transport of anions is possible, and hence the opposite bending direction is achieved[56].

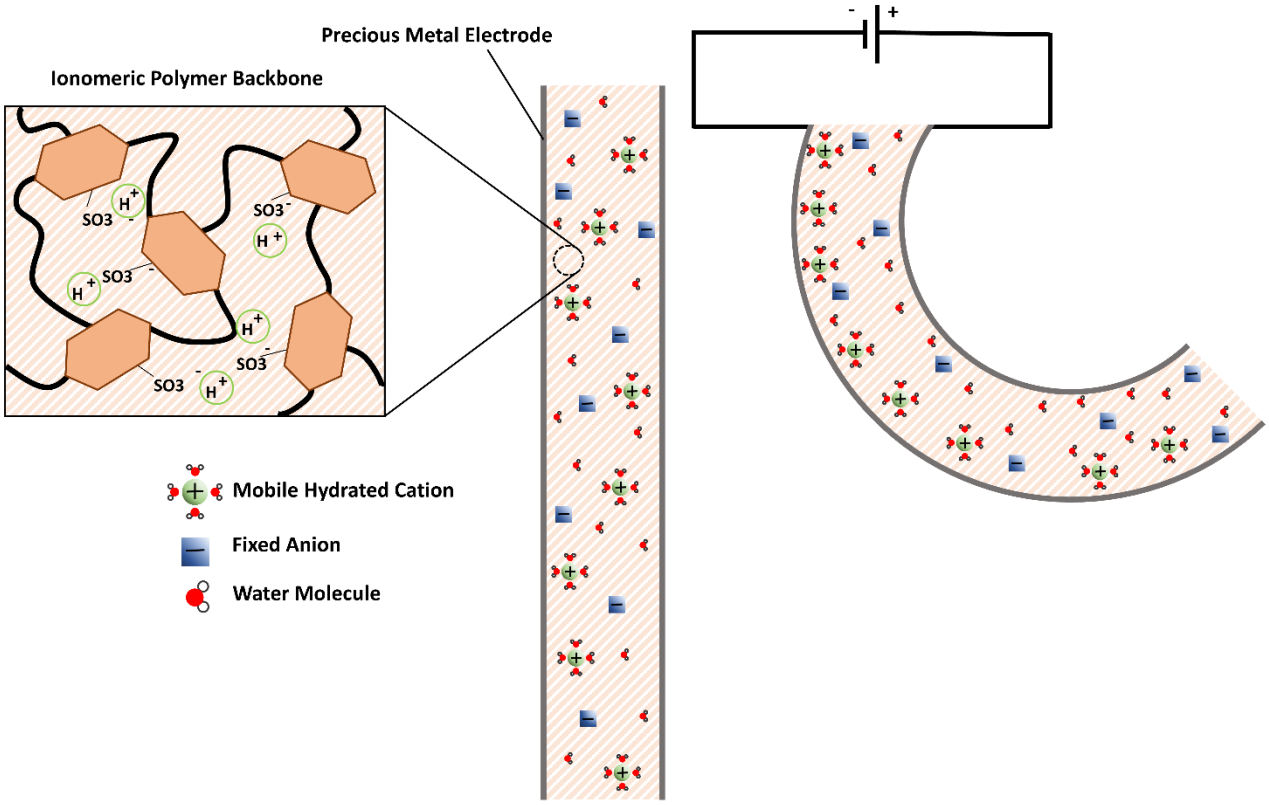

Figure 4: Ionic polymer-metal composite actuator with a single electrolyte solution (adapted from Bar-Cohen and Zhang 2008, and Bhandari *et al* 2012[29, 71])

3.2.3 Nanocarbon Actuators

Carbon nanotubes were first reported in 1999 to construct an EAP actuator[65]. Actuation in nanocarbon actuators is driven by the electrolyte forming an electric double layer with the nanocarbon structures. This double layer allows for the injection of charges that affect the ionic charge balance between the nanocarbon structure and the electrolyte, with larger charge injections resulting in more significant dimensional changes. These changes in dimension can be explained due to changes in the carbon-carbon bond length[65]. The removal of electrons in the nanocarbon structures cause them to carry a net positive charge. This net charge results in the repulsion of the adjacent carbon nuclei and hence increasing the carbon-carbon bond length[9]. These nano-scale size changes lead to the expansion and contraction of the nanocarbon gel electrodes on the macroscale[30]. This leads to the bending motion of the actuator, as seen in Figure 5.

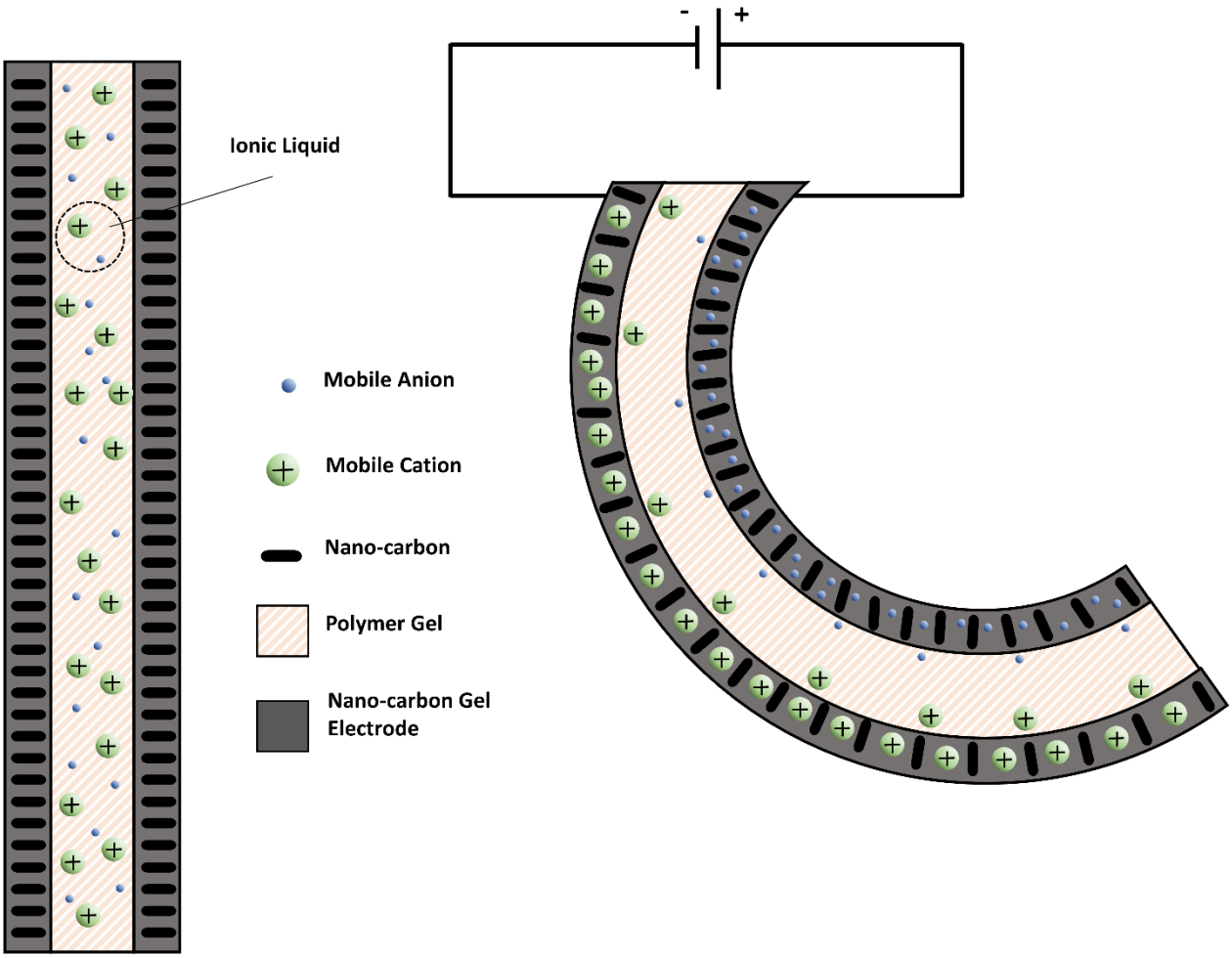

Figure 5: Nanocarbon actuator with an ionic liquid electrolyte (adapted from Asaka *et al* 2013[30]).

3.2.4 Conducting Polymer Actuators

Conducting polymer actuators function via a reversible counter-ion insertion/expulsion process during redox cycling[111, 120-122]. An applied voltage supplies the cathode of the actuator with electrons for reduction while oxidation occurs at the anode (Figure 6). An exchange of ions from the electrolyte causes swelling of the conducting polymer, which can occur upon oxidation (for anion movement to balance positive charges on the conducting polymer) or upon reduction (for cation movement, where bulky immovable anions are employed). A combination of both actuation types accentuates the bending of the actuator shown in Figure 6. Finally, the migration of ions via the ionomeric polymer backbone allows for the charge to be balanced between the electrodes[9]. Conducting polymer actuators are an attractive field of research, including trilayer designs that are alternatives to electrostatic and piezoelectric polymer actuators, with large strains being generated[123].

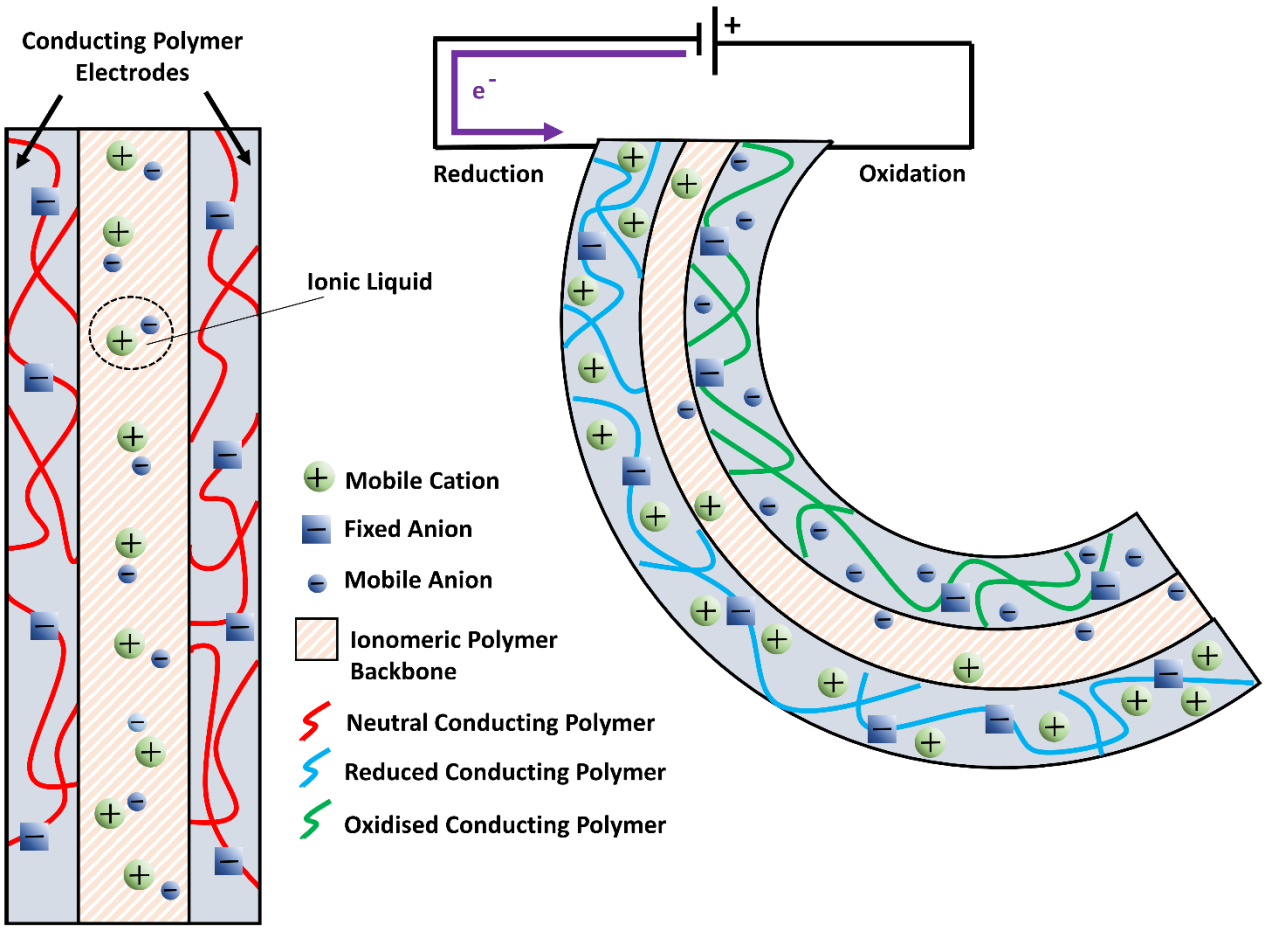

Figure 6: Conducting polymer actuator with an ionic liquid electrolyte, cation driven actuation method (adapted from Kim *et al* 2013[110])

3.2.5 Comparison of Ionic Electroactive Polymer Actuator Structure-Property Relationships

While all ionic EAP actuator mechanisms operate on the principle of migration of mobile charged species in the presence of an electric field, the specific chemical structures and electrode materials defines the four operational mechanisms presented above.

As the defining feature of ionic EAP is their lower operational voltages, the electrochemical properties of the core polymer materials are of great importance. Highly conductive materials such as Nafion™ and other anion grafted perfluorinated polymers are often used in IPMC, nanocarbon and conducting polymer actuator production[59, 109, 124]. These conducting membrane materials are robust and durable but also have significant negative environmental impacts due to their synthesis and long lifetimes[125, 126]. From an application standpoint, these materials can be formed to shape using various casting and moulding techniques[127, 128]. These membrane materials are best applied to extrusion-based additive manufacturing[7].

The implementation of ionic liquid electrolyte trapped within a polymer gel allows for the development of efficient ionic EAP actuators that have good air-stability[24, 116]. These ionic gels have been used in nanocarbon as well as conducting polymer actuators[51, 129]. Additionally, these ionic gels have been shown to be fabricated using conventional casting and moulding methods as well as photocuring[51]. As such, these forming methods could be applied to both extrusion and light-based additive manufacturing[130]. Therefore, for future 3D printing applications, these ionic gel systems show great potential.

The choice of electrode material in ionic actuators plays a key role in the performance of devices, as it interacts directly with core ionomeric material. Electrically conductive precious metals such as gold and platinum are often used in IPMC production[60, 131]. However, composite materials of electro-grafted PEDOT on top of metal electrodes has been shown to improve actuator performance and lifetime[109]. Finally, for additive manufacture, electrodes made of nanocarbon and conducting polymers have already shown promising results[16, 132].

Table 2: Summary of Recent Ionic Electroactive Polymer Actuator Materials and Applications

Material Types	Mechanism	Example Materials	Reported and Potential Applications
Ionic Polymer Gel Actuator	Movement of Hydrogen cations in and out of the gel due to an applied voltage. This movement of ions results in the reversible bending of the sample	Poly(Sodium acrylate) gel in sodium carbonate, Poly(Methacrylic acid) in sodium chloride solution and Poly(Acrylamide-co-Acrylic acid) gel in sodium chloride solution [48]	Bending actuators, shrinking actuators and artificial muscles[48, 49]
Ionic Polymer-Metal Composite Actuators	A material capable of ion exchange provides areas of local negative charge. These clusters allow for the movement of mobile cations from the anode through a series of channels or holes. These mobile cations are responsible for the bending phenomenon	Ionomers: Nafion™ (sulfonated tetrafluoroethylene made by DuPont)[5, 6, 124] Flemion™ (Nafion™ analogue of Asahi Glass)[55] Cation/Anion – grafted PVdF-HFP[56] PVdF-CTFE[133] Charge carriers: Various cations and anions Electrodes: Various precious metals[38, 107]	Bending actuators, twisting actuators, soft robots, crawling/walking motions, multiple degrees of freedom actuators and artificial muscles[5, 7, 40]
Nanocarbon Actuators	Charge injection and the changing of carbon-carbon lengths in the nanocarbon structures Affect the charge balance between the nanocarbon electrodes and the electrolyte.	Single or multiwalled Carbon nanotubes[64-68] Bucky gels[30, 63]	Bending actuators, soft robots, biomimetics, artificial muscles and micro braille display[30]
Conductive Polymer Actuators	Oxidation and reduction occur in conductive polymer materials due to an applied voltage. This oxidation and	Poly(Aniline)[103], Poly(3,4-ethylenedioxythiophene)[104], and Poly(Pyrrole)[28, 70]	Bending actuator, folding actuators, hinges, micro pumps and potential for artificial muscles[28]

	reduction cause insertion or de-insertion of ions into or from the polymer network. This results in a swelling or shrinking effect.

4.0 The Current State of Electroactive Polymer Actuator Fabrication:

Traditional methods of EAP production requires slow, often manual, production of devices and lengthy post processing and assembly[43]. A dominance in casting, moulding, and pressing techniques, as well as a reliance on prefabricated, commercially available materials, creates issues that are addressed by a shift to additive manufacturing. Unfortunately, some EAP production techniques also require complex and time-consuming synthesis procedures that cannot easily be applied to additive manufacturing. These include electrochemical polymerisation procedures[134] and other emulsion polymerisation techniques that require high pressures and temperatures[135].

A review of current literature indicates that the current state of ionic EAP production has untapped potential in synthetic and polymer chemistry research. On the other hand, groups that produce novel EAP networks tend to focus more on the ion exchange and conductivity capacities of their novel networks and not the potential applications as soft ionic EAP actuators[136-138]. Therefore, a shift to additive manufacturing will require an overlapping interest between the fields of polymer chemistry, materials engineering, as well as having a great depth of additive manufacturing understanding. However, should more methods based on 3D printing be developed, the time spent in post-production and assembly could be lessened and also help make actuator fabrication simpler. By incorporating these manufacturing techniques, the number of discrete parts and the need for housings and fittings could be lowered. As a result, the time spent in post-processing and assembly would be reduced and simplified. Additionally, 3D printing can facilitate batch production of EAP samples and eventually even the mass production of samples[139]. For example, batch production could facilitate the testing of several actuators or soft robot elements in a faster time frame. Considering these factors, a shift towards 3D printing is both desired and beneficial.

5.0 Additive Manufacturing for Ionic EAP Soft Actuator Production:

Several examples of 3D printed soft actuators have been developed, including the likes of shape memory polymers[140, 141], light activated polymers[42] and dielectric[22, 74] EAPs. Examples of ionic EAP actuators that make use of 3D printing technology can also be readily found[41, 142, 143]. However, they often employ the use of additive manufacturing to produce electrodes, moulds, fixings, and other components rather than the core ionomeric material that is the backbone of the actuator. This section will focus exclusively on the additive manufacturing of core ionomeric materials for use in ionic EAP actuators.

Material extrusion (MEX) additive manufacturing is a popular 3D printing technique. The principle extrusion method is simple to understand and apply, and as such several research teams have developed their own MEX 3D printers[7, 144]. By vectoring across the surface of the build plate, individual layers are laid down from the print head, initially on top of the build plate and then on each other, until the desired shape is achieved (Figure 7a). Fused deposition moulding (FDM) is a key extrusion 3D printing technique that makes use of melt-processable polymer filaments to produce intricate objects.

On the other hand, vat photo-polymerisation (VPP) methods make use of photo-curable resins to produce printed objects. There are two subgroups of VPP, namely Digital Light Projection (DLP) and Stereolithography Apparatus (SLA). DLP makes use of either and liquid crystal display (LCD) screen, liquid

crystal on silicon (LcoS) or a digital micromirror device (DMD) to produce a photomask[145]. This mask creates the outline of each individual layer. Each layer is then cured using an inbuilt light source to form the desired shape from the build plate (Figure 7b). Lastly, SLA makes use of a laser beam to direct light onto the build plate using mirrors with controllable angles. This laser beam spot then vectors across the surface of the plate to build up the desired shape (Figure 7c).

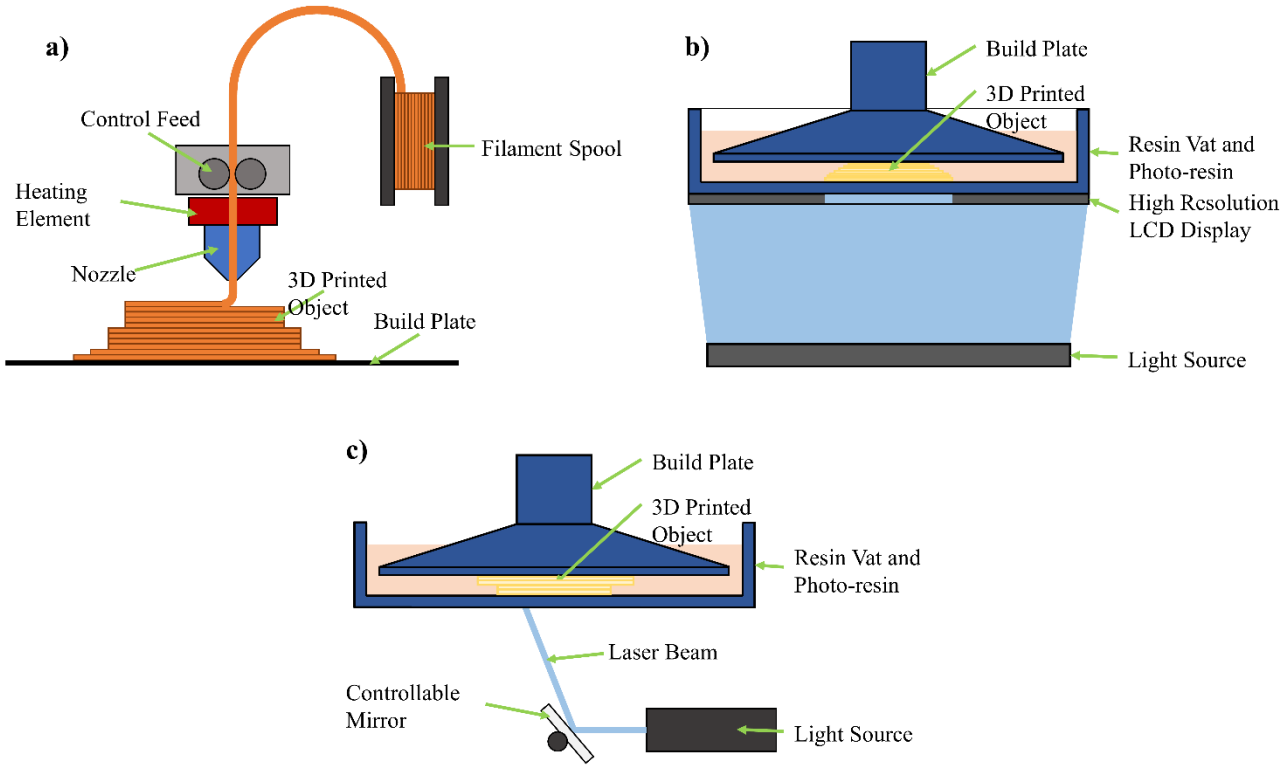

Figure 7: Overview of the mechanisms of 3D printing. a) FDM printing process. b) DLP printing process. c) SLA printing process

The use of additive manufacturing to produce ionic EAP soft actuators continues to be an appealing but elusive prospect for many. In particular, 3D printing with vat photo-polymerisation (VPP) methods, such as Digital Light Projection (DLP) and Stereolithography Apparatus (SLA), remain primarily open for investigation. These light-based printing approaches hold great potential for the production of soft actuators as they commonly display faster build speeds and higher layer-by-layer resolution than their counterparts and have already shown good use in a wide range of applications[146-154]. Faster build speed allows for more efficient use of time in development and prototyping. A higher resolution allows for smaller and more precise soft actuators to be produced.

There are certain difficulties in overcoming the limitations inherent to 3D printers that are primarily designed for commercial applications (Table 3). These include challenges due to the large volumes of material required, a focus on primarily MEX techniques, as well as having an accessible melting point for these thermoset extrusion techniques.

Photo-polymerisation, on the other hand, poses challenging requirements of the liquid starting materials, and a suitable rate of curing for the layer-by-layer printing process is needed. Ultimately, a faster rate of sample production, compared to manual preparation, is a major point in favour of 3D printing. Consideration must be taken in monomer and photo-initiator choice[155, 156]. These challenges limit the number of monomeric materials suitable for vat-based additive manufacturing. As such, few truly 3D printed examples of ionic EAPs have been shown, in which the core ionomeric polymer material has been produced via additive manufacture.

Fortunately, FDM and other material extrusion-based printing techniques have shown successful soft actuator production. Notably, the research conducted by Carrico and his colleagues has demonstrated the application of 3D printed IPMC actuators by making use of a modified FDM method[5-7, 40, 54]. Additionally, other examples

of 3D printed ionic actuators, such as the layer-by-layer casting of bucky-gel actuators[16, 63] and a direct writing technique of Nafion™ solution and single-walled carbon nanotubes (SWCNT)[17], are also reviewed here.

Table 3: Limitations Affecting the 3D Printing Methods of Ionic EAPs Actuators

Type of 3D Printing	Advantages	Limitations
Material Extrusion (MEX)	▪ Simple working principle ▪ Low cost and easily accessible	▪ Filament requires an accessible melting point ▪ Filament requires suitable rheological properties for extrusion ▪ Difficulty printing fine detailed items
Stereolithography Apparatus (SLA)	▪ High precision due to small laser spot size ▪ Smoother surface finish over counterparts	▪ Requires a photosensitive resin for curing ▪ Longer print times due to having to vector across the print surface
Digital Light Projection (DLP)	▪ High precision due to small pixel size ▪ Fast print time due to each layer curing in full as a raster	▪ Requires a photosensitive resin for curing ▪ Rougher surface finished compared to SLA

5.1 Material Extrusion of Nafion™ Precursor for IPMC Soft Robot Fabrication:

IPMC devices have been used in a variety of applications ranging from underwater propulsion systems[157-159], micro pumps[160-162] and sensors[163, 164]. However, these have made use of conventional fabrication techniques. Recent Ionic EAP research using MEX 3D printing has led to the production of IPMC soft robots that can display linear movement[40].

In 2015 Carrico *et al* developed a novel approach for the additive manufacturing of Nafion™ IPMCs[7]. By utilising a MEX technique, the production of 3D IMPC structures with sub-millimetre scale resolution and at a fast rate was achieved. Impressively, their 3D printing technology can also incorporate other thermoplastics such as acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA). This would allow for the construction of composite structures with inert and active regions.

In its conventional form, Nafion™ is not capable of being melt processed[165]. To overcome these limitations, melt processable Nafion™ sulfonyl fluoride precursor had to be obtained and extruded into a filament for 3D printing. Therefore, after being formed to the desired geometry, the 3D printed object could be activated via hydrolysis. Finally, electrode surfaces of platinum were deposited using an electroless plating process, as described by Oguro *et al* 1993[107]. Using their custom extrusion setup, Carrico *et al* were able to produce 3D printed IPMC actuators that performed on par with their conventional Nafion™ IPMC counterparts[7]. They also demonstrated that their 3D printed IPMC displayed superior responses at lower frequencies (Figure 8a).

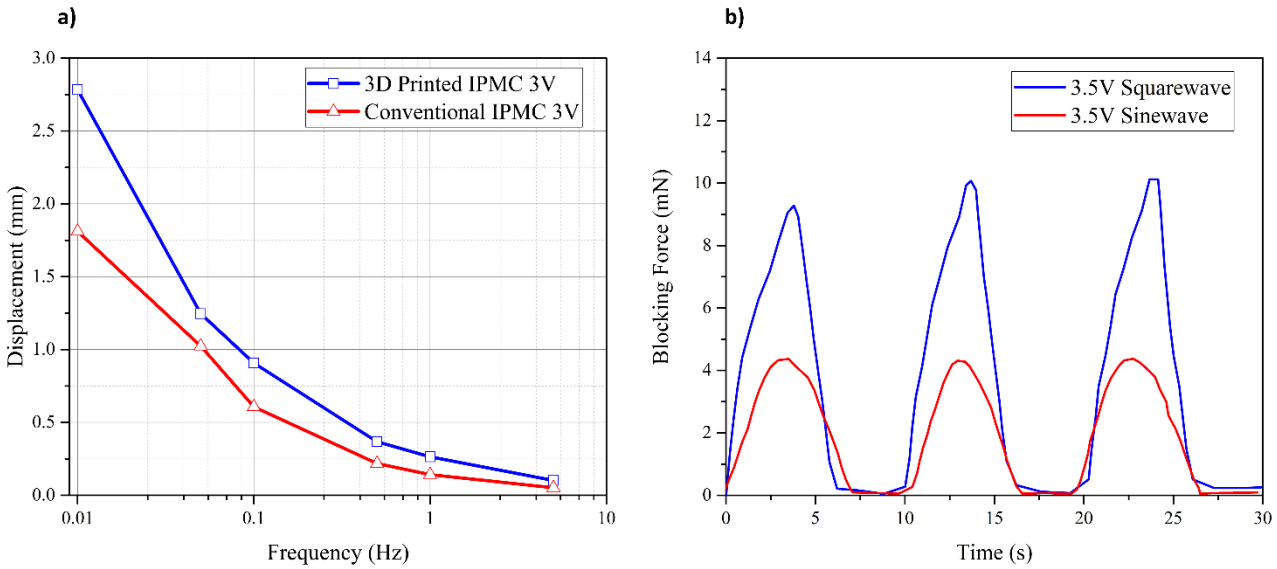

Figure 8: a) Comparison between Carrico *et al* 2015 3D printed Nafion™ IPMC actuator and a convention sheet based Nafion™ IPMC actuator and adapted from Carrico *et al* 2015[7]. b) Blocking forces generated by the 3D printed ionic EAP actuators, showing the effect of the waveform on blocking force generated and adapted from Yin *et al.* 2021[166].

Using this custom built 3D printer, Carrico *et al* 2017 were able to produce 3D printed IPMC actuators with various functions, and in structures that would be difficult and time-consuming to reproduce using more conventional methods[5]. These additive manufacturing techniques were used to produce a single actuator capable of multiple actuation directions without the need of additional parts or complicated setup procedures, as well as actuators capable of rotational and gripping motions. These actuator examples showed that, with correct design and application, the restriction of ionic EAPs being limited to bending motions could be circumvented. By using purposeful computer aided design (CAD), actuator examples with a variety of potential applications could be manufactured. A publication by Yin *et al* 2021[166] further developed the MEX technique of Carrico *et al*. In this paper, they further explored the additive manufacturing techniques of IPMC production and highlighted the balance required in material extrusion for adequate printing quality. They further characterise their printed IPMC actuators in terms of blocking force. These actuators, produced using 3D printing, developed blocking forces of up to 10.5 mN, where the input waveform shape affected the blocking force (Figure 8b)[166]. Furthermore, these AM produced IPMCs showed comparable ion exchange capacity to conventional Nafion™ membrane materials, showing that the novel extrusion techniques and subsequent hydrolysis did not limit the material's ionic capabilities.

Additionally, Carrico *et al* 2017 were able to combine these novel actuators to produce a 3D printed artificial "caterpillar" or a soft crawling robot, which combined both gripping and linear actuation to produce a controllable walking motion (Figure 9)[40]. Made up of "body segments" and "leg segments", the soft robot walks using an expansion /contraction motion of the body segments and a gripping motion of the leg segments. These soft robots were capable of linear movement of up to 15.5 centimetres in the span of 9 minutes. Finally, by implementing Bayesian optimisation as a learning-based control approach, challenges in existing methods where continuous sensor feedback is required could be addressed[54]. Unfortunately, degradation of the IPMCs over time resulted in successive experiments being unable to replicate the same performance[54] and highlighting one of the areas of improvement needed in IPMC production.

Overall, Carrico *et al* successfully brought a well-known IPMC production technique into the realm of additive manufacturing. In doing so, they could overcome the difficulties of conventional post-processing and assembly to produce actuators and a soft crawling robot. This highlights that the additive manufacturing of IPMC structures has many benefits.

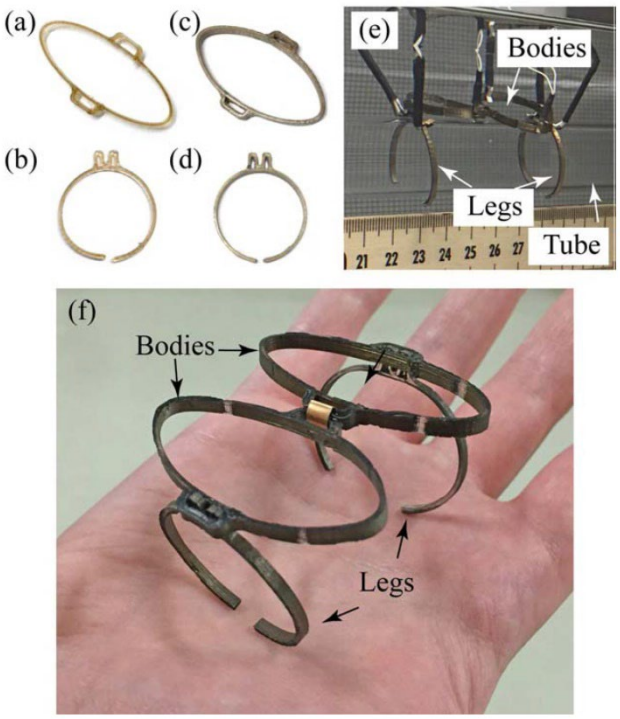

Figure 9: Fabricated soft crawling robot from additive manufacture, reproduced with permission from Carrico *et al.* [40]. Original (a and b) and platinum plated (c and d) bodies and legs. e) Assembled soft robot attached to a clear tube underwater. f) Closer view of the assembled soft crawling robot.

5.2 Layer-by-layer casting of Bucky-gel Actuators and Sensors:

In 2003, Fukushima *et al* developed a thermally stable ionic liquid / SWCNT gel with high electroconductivity[130]. Room-temperature ionic liquids of imidazolium ions could be ground with SWCNT to form physically crosslinked gels, also known as bucky-gels. This gelation process exfoliates the heavily entangled SWCNTs by a possible cation-π interaction when ground in imidazolium ionic liquids[167] to form finer bundles. Additionally, thermal polymerisation of molten salts such as 1-(4-acryloyloxybutyl)-3-methylimidazolium hexafluorophosphate ($ABMIPF_6$) could be performed to produce homogeneous polymer composites of exfoliated SWCNT[130]. These composites were shown to have increased dynamic hardness as well as being electrically conductive.

Further expanding upon the ionic liquid / SWCNT gel synthesis techniques developed in 2003, Fukushima *et al* 2005[63] were able to develop a novel dry actuator through the layer-by-layer casting of the electrode and ionomeric core components. Electrode composites consisting of exfoliated SWCNT, room-temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$) and PVdF – HFP were cast in a simple three-layer configuration over an internal layer of $BMIBF_4$ and PVdF – HFP[63]. Using this process, they did not require the deposition of a metallic layer electrode or the electrochemical polymerisation of conducting polymer electrodes. They had developed a programmable AM casting method in which the electrode surfaces and core ionomeric material is seamlessly connected, facilitating both intra and inter-layer ion transport necessary for rapid response.

Incorporating the techniques developed by Fukushima *et al*, Kamamichi *et al* 2008[16] were able to successfully develop a novel MEX additive manufacturing process in which the layer-by-layer casting of bucky-gel actuators could be realised. A custom dispenser apparatus was developed to facilitate the extrusion of the gelatinous mixtures of the electrode and ionomeric core. The 3D patterning of electrodes was used to construct various complex 3D models, including the likes of a linear actuator via a reversing electrode connection (Figure 10b and c)[16]. These linear actuators provided an optimal pathway to convert the mechanistically driven bending motion of ionic EAPs to useful linear locomotion by means of an “S” shaped bend.

Overall, by adopting this additive manufacturing technique, the conventional manual casting could be replaced with a true automatic forming process, and the construction of parallel or stacked sensor and actuator devices could be realised as a true one step printing process in which all components can be printed.

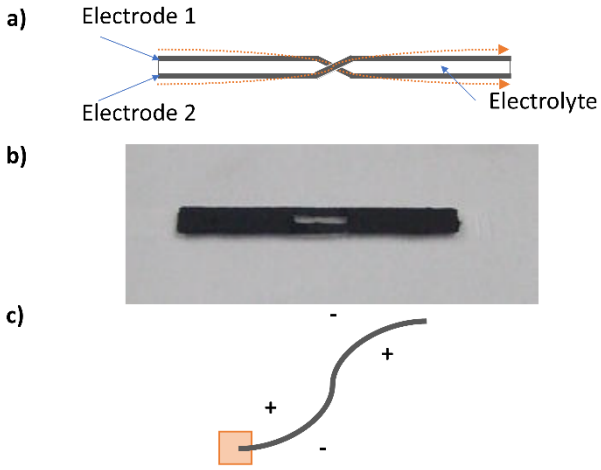

Figure 10: Bucky gel additive manufactured reversing actuators, reproduced with permission from Kamamichi *et al.* [16]. a) Reversing connection printing pattern. b) Fabricated Bucky-gel reversing actuator. c) Bending produced from these reversing actuators.

5.3 Direct Writing of Single-Walled Carbon Nanotube / Nafion™ Composites

Using customised direct writing equipment to print their novel SWCNT / Nafion™ composites, Luo *et al* 2018[17] were able to extrude layer-by-layer actuator structures. Critical challenges they needed to overcome were that the ink needed to have both the desired rheological properties for printing and shape retention as well as being able to solidify without cracking. After careful characterisation of ink viscosity and adhesive bonding strengths, the viscoelastic behaviours of their composite inks were adapted for extrusion printability. They were therefore able to show that with Nafion™ concentrations between 20-70wt% and as long as the extrusion pressure was above a certain threshold, the printing of the core Nafion™ ionomeric material was feasible[17]. Using a SWCNT slurry as an electrode material, the initial electrode layers could then be printed onto a glass substrate. This was followed by subsequent layers of Nafion™ material and finally SWCNT to sandwich the structure (Figure 11). They therefore showed a proper multi-material 3D printing process of their novel SWCNT / Nafion™ composites. Cyclic voltammetry of the composite sample revealed that the electrode system could be considered quasi-reversible. Additionally, the sensory performance of their printed structure was analysed and showed that as pressure was exerted along with the printed matrix, a corresponding varying output voltage could be determined[17]. This shows promising evidence that individual areas of their printed sample can be utilised for their sensory effect, with potential application in flexible sensors and artificial skin.

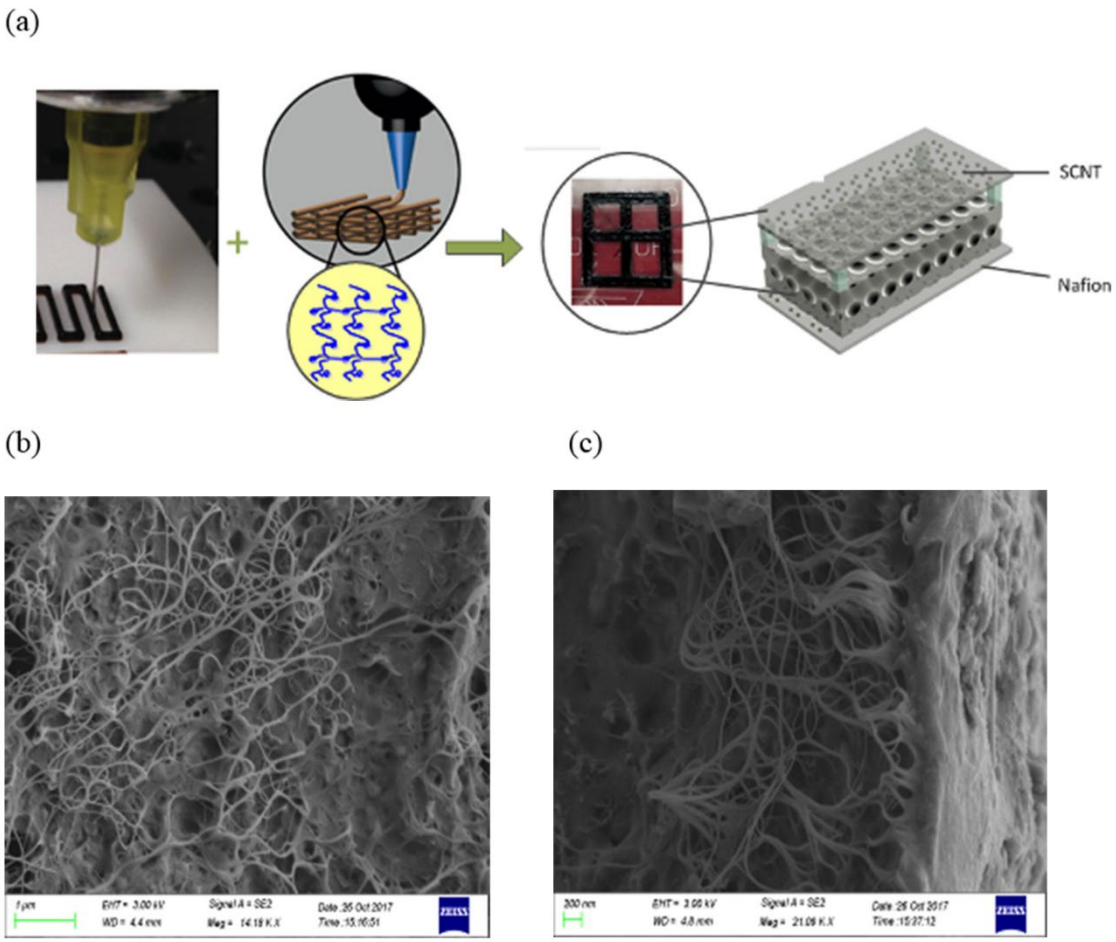

Figure 11) a) Multi-material printing process, reproduced with permission from Luo *et al.* [17], showing the printability of the novel SWCNT / Nafion™ composites. b) SEM image of the SWCNT electrode surface, scale bar to 1 pm. c) SEM image of the cross-section of the composite, scale bar to 200 nm.

5.4 Additive manufacture of Ionic Liquids and Ionic Liquid/Polymer Blends

By utilising MEX additive manufacturing technologies, research teams have been able to extrude ionic liquid (IL)/polymer blends into an array of different electronic devices. Notable applications include soft sensors[50], soft actuators[168] and energy harvesting[169]. Due to the large array of potential ionic liquids at disposal, these possess inherent flexibility and tunability. ILs can be tailored to the specific requirements of a project and, as such, have a great opportunity to be implemented in additive manufacturing. Blends of ILs and perfluorinated polymers such as PVdF are often used in MEX 3D printing of devices[16, 169]. One of the very attractive aspects of ILs is their enhanced room temperature stability compared to aqueous electrolytes. As a result, they can improve the operational ranges of the devices[170]. By utilising the room temperature stability and conductivity of ILs and the robustness and durability of perfluorinated polymers, soft devices could be prepared for actuator and sensing purposes.

First shown by Long *et al* 2014[171], the photo-polymerisation of ionic liquid monomer and diacrylates was utilised using SLA techniques to produce 3D printed complex objects. Additionally, by tuning the IL ratios, the glass transition temperature could be tuned to directly affect the ionic conductivity of the devices. These results show the additive manufacturing opportunity that ILs possess, as they have been successful with not only extrusion methods but also photocuring techniques.

6.0 Prospects for Ionic Electroactive Polymers and their Additive Manufacturing:

An attractive prospect for ionic EAP actuators is in the production of biomimetic artificial muscles. Indeed several examples of successful biological like movements have been recorded[40, 172]. However, to draw closer to biological movements, ionic EAPs have to be able to produce both powerful and rapid movements to simulate fast and slow twitch muscle fibers[173]. Additionally, with the recent and continued development of

air-operating ionic actuators, the limitations and boundaries of a challenging aspect of ionic EAP operation are steadily being pushed back[174-176]. The additive manufacture of soft actuators is an exciting area of research, with considerable prospects for the development of true one-step production processes where housing or fittings, ionomeric polymer core and electrode surfaces can all be printed in one project (Figure 12).

These one-step processes would allow for ease of assembly and save time in post-production. As additive manufacturing techniques continue to evolve in resolution and size, so too should ionic soft actuator production. The development of smaller and more resolved actuators can push the boundaries of lifelike artificial muscles, should bundles of additive manufactured EAP artificial muscle fibres be produced.

While vat photo-polymerisation driven by additive manufacturing systems such as DLP and SLA pose several hurdles to overcome in terms of monomer material phase and curing speed, light-based 3D printing boasts a higher resolution with producing finer details due to the small laser spot/pixel size used. Additionally, build rates of DLP 3D printers are typically faster for larger prints when compared to more conventional extrusion-based 3D printing techniques. This is due to the process of DLP curing entire layers at once. Therefore, it presents a significant opportunity for the continued development of ionic actuator production.

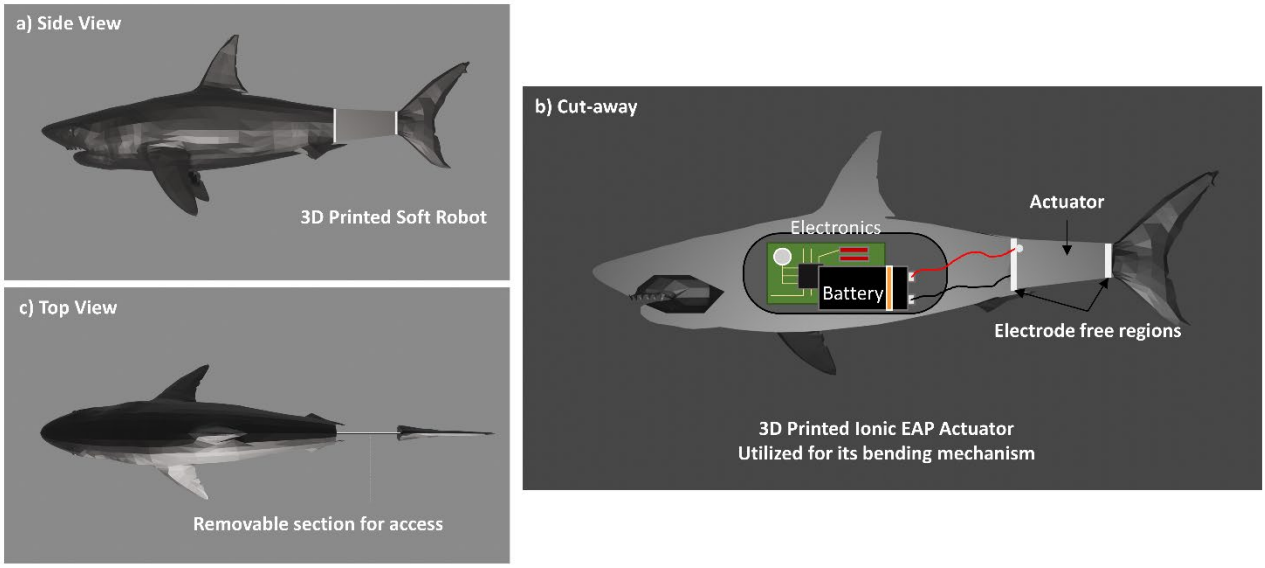

Figure 12) Prospective 3D printed soft robot, in which the ionic EAP actuator and robot body can be printed using a single printing process.

7.0 Conclusion:

In recent years new research into the additive manufacture of electroactive polymers has been performed, and the results are exciting. This paper presents a summary of the recent developments in ionic EAPs in which the core ionomeric polymer material is 3D printable. The four primary materials that have been utilised for ionic EAP actuator production and their corresponding ionic actuation mechanisms are also reviewed.

While several examples of successful ionic EAP production have been recorded, few applications are mentioned, and fewer still have shifted production towards additive manufacturing. Fortunately, as additive manufacturing processes and understanding continue to evolve, more opportunities for the one step production of EAP actuators present themselves.

Ionic EAPs hold great potential in the development of soft robotics and sensors. The examples of ionic EAP additive manufacturing shown here also help to emphasise that, with a shift to 3D printing, soft robots that would be difficult to produce using manual techniques can be fabricated. Finally, the vat photo-polymerisation based additive manufacturing fields of SLA and DLP have not been as deeply investigated as material extrusion-based techniques such as FDM. Therefore, these additive manufacturing techniques may hold future potential.

We hope that this paper helps to portray the value of additive manufacturing as well as the future potential for the additive manufacturing of ionic EAP actuators and sensors.

Author Contributions:

Kyle Edward Engel: Conceptualisation, Investigation, Validation, Visualisation, Writing-Original Draft, Writing-Review and Editing

Paul A. Kilmartin: Supervision, Validation, Visualisation, Writing-Review and Editing

Olaf Diegel: Supervision, Validation, Visualisation, Writing-Review and Editing

Conflicts of Interest:

There are no conflicts to declare

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References:

1. W. Roentgen, *Ann. Phys. Chem*, 1880, **11**, 771-786.
2. C. Keplinger, M. Kaltenbrunner, N. Arnold and S. Bauer, *Proceedings of the National Academy of Sciences*, 2010, **107**, 4505-4510.
3. E. Saleh, in *3D and 4D Printing of Polymer Nanocomposite Materials*, Elsevier, 2020, pp. 505-525.
4. D. Gonzalez, J. Garcia and B. Newell, *Sensors and Actuators A: Physical*, 2019, **297**, 111565.
5. J. D. Carrico and K. K. Leang, 2017.
6. J. D. Carrico, J. M. Erickson and K. K. Leang, 2016.
7. J. D. Carrico, N. W. Traeden, M. Aureli and K. K. Leang, *Smart Materials and Structures*, 2015, **24**, 125021.
8. P. Martins, D. Correia, V. Correia and S. Lanceros-Mendez, *Physical Chemistry Chemical Physics*, 2020, **22**, 15163-15182.
9. Y. Bar-Cohen and I. A. Anderson, *Mechanics of Soft Materials*, 2019, **1**, 5.
10. Q. Shi, H. Liu, D. Tang, Y. Li, X. Li and F. Xu, *NPG Asia Materials*, 2019, **11**, 1-21.
11. J. Szkopek and G. Redlarski, *Applied Sciences*, 2019, **9**, 4090.
12. J. Cai, A. Vanhorn, C. Mullikin, J. Stabach, Z. Alderman and W. Zhou, 2015.
13. B. Mosadegh, P. Polygerinos, C. Keplinger, S. Wennstedt, R. F. Shepherd, U. Gupta, J. Shim, K. Bertoldi, C. J. Walsh and G. M. Whitesides, *Advanced functional materials*, 2014, **24**, 2163-2170.
14. Y. Bar-Cohen, 2005.
15. M. Shahinpoor, *Ionic Polymer Metal Composites (IPMCs): Smart Multi-Functional Materials and Artificial Muscles, Volume 2*, Royal Society of Chemistry, 2015.
16. N. Kamamichi, T. Maeba, M. Yamakita and T. Mukai, 2008.
17. B. Luo, H. Chen, Z. Zhu, B. Xie, C. Bian and Y. Wang, *Materials & Design*, 2018, **155**, 125-133.
18. A. K. Bhowmick and H. Stephens, *Handbook of elastomers*, CRC Press, 2000.
19. C. Hepburn, *Polyurethane elastomers*, Springer Science & Business Media, 2012.
20. J. Onorato, V. Pakhnyuk and C. K. Luscombe, *Polymer Journal*, 2017, **49**, 41-60.
21. S. Ashley, *Scientific American*, 2003, **289**, 52-59.
22. M. Tyagi, G. M. Spinks and E. W. Jager, *Soft Robotics*, 2020.
23. C. Keplinger, J.-Y. Sun, C. C. Foo, P. Rothemund, G. M. Whitesides and Z. Suo, *Science*, 2013, **341**, 984-987.
24. K. Asaka and H. Okuzaki, *Soft actuators: materials, modeling, applications, and future perspectives*, Springer Nature, 2019.
25. E.-F. M. Henke, S. Schlatter and I. A. Anderson, *Soft robotics*, 2017, **4**, 353-366.
26. G. Alici, *MRS Advances*, 2018, **3**, 1557-1568.
27. Y. Bar-Cohen, T. Xue, M. Shahinpoor, J. Simpson and J. Smith, 1998.
28. R. Baughman, *Synthetic metals*, 1996, **78**, 339-353.
29. Y. Bar-Cohen and Q. Zhang, *MRS bulletin*, 2008, **33**, 173-181.
30. K. Asaka, K. Mukai, T. Sugino and K. Kiyohara, *Polymer international*, 2013, **62**, 1263-1270.
31. Y. Bar-Cohen, *SPIE Newsroom*, 2009, **11**.
32. A. Richter and G. Paschew, *Advanced Materials*, 2009, **21**, 979-983.
33. A. Richter, S. Klatt, G. Paschew and C. Klenke, *Lab on a Chip*, 2009, **9**, 613-618.
34. A. Richter, G. Paschew, S. Klatt, J. Lienig, K.-F. Arndt and H.-J. P. Adler, *Sensors*, 2008, **8**, 561-581.
35. O. Kim, S. J. Kim and M. J. Park, *Chemical Communications*, 2018, **54**, 4895-4904.
36. J. Canny, J. Risner and V. Subramanian, in *Algorithmic Foundations of Robotics V*, Springer, 2004, pp. 203-219.
37. K. Kiyohara, T. Sugino and K. Asaka, *Smart materials and structures*, 2011, **20**, 124009.
38. K. J. Kim and M. Shahinpoor, *Smart materials and structures*, 2003, **12**, 65.
39. W. Kaal and S. Herold, *IEEE/ASME Transactions on Mechatronics*, 2010, **16**, 24-32.
40. J. D. Carrico, K. J. Kim and K. K. Leang, 2017.
41. J. Liu, Y. Wang, D. Zhao, C. Zhang, H. Chen and D. Li, 2014.
42. O. Ivanova, A. Elliott, T. Campbell and C. Williams, *Additive Manufacturing*, 2014, **1**, 24-31.
43. A. Zolfagharian, A. Z. Kouzani, S. Y. Khoo, A. A. A. Moghadam, I. Gibson and A. Kaynak, *Sensors and Actuators A: Physical*, 2016, **250**, 258-272.
44. F. G. Helfferich, *Ion exchange*, Courier Corporation, 1995.

45. S. Koneshan, J. C. Rasaiah, R. Lynden-Bell and S. Lee, *The Journal of Physical Chemistry B*, 1998, **102**, 4193-4204.
46. A. Anantaraman and C. Gardner, *Journal of Electroanalytical Chemistry*, 1996, **414**, 115-120.
47. M. Shahinpoor, Y. Bar-Cohen, J. Simpson and J. Smith, *Smart materials and structures*, 1998, **7**, R15.
48. C. Jo, H. E. Naguib and R. H. Kwon, *Smart Materials and Structures*, 2011, **20**, 045006.
49. R. Kanno, S. Tadokoro, T. Takamori, M. Hattori and K. Oguro, 1996.
50. H. Nulwala, A. Mirjafari and X. Zhou, *European Polymer Journal*, 2018, **108**, 390-398.
51. S. Saito, Y. Katoh, H. Kokubo, M. Watanabe and S. Maruo, *Journal of Micromechanics and Microengineering*, 2009, **19**, 035005.
52. R. Luo, H. Li and K. Y. Lam, *Analytical and Bioanalytical Chemistry*, 2007, **389**, 863-873.
53. K. Suzumori, H. Nabae, K. Asaka and T. Horiuchi, 2020.
54. J. D. Carrico, T. Hermans, K. J. Kim and K. K. Leang, *Scientific reports*, 2019, **9**, 1-17.
55. J. Wang, C. Xu, M. Taya and Y. Kuga, *Smart Materials and Structures*, 2007, **16**, S214.
56. J. H. Park, M. J. Han, D. S. Song and J. Y. Jho, *ACS applied materials & interfaces*, 2014, **6**, 22847-22854.
57. J. M. Rossiter, B. L. Stoimenov and T. Mukai, 2007.
58. Y. Nakabo, T. Mukai and K. Asaka, 2005.
59. M. Park, J. Kim, H. Song, S. Kim and M. Jeon, *Sensors*, 2018, **18**, 3126.
60. M. Shahinpoor and K. J. Kim, *Smart materials and structures*, 2001, **10**, 819.
61. M. Shahinpoor and K. J. Kim, *Sensors and Actuators A: Physical*, 2002, **96**, 125-132.
62. K. Oguro, *J. Micromachine Society*, 1992, **5**, 27-30.
63. T. Fukushima, K. Asaka, A. Kosaka and T. Aida, *Angewandte Chemie International Edition*, 2005, **44**, 2410-2413.
64. J. Kim, M. Park, S. Kim and M. Jeon, *Polymers*, 2020, **12**, 396.
65. R. H. Baughman, C. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. De Rossi and A. G. Rinzler, *Science*, 1999, **284**, 1340-1344.
66. G. Spinks, G. Wallace, R. Baughman and L. Dai, *Electroactive polymer (EAP) actuators as artificial muscles–reality, potential and challenges*, 2004, 261-295.
67. D. Y. Lee, I.-S. Park, M.-H. Lee, K. J. Kim and S. Heo, *Sensors and Actuators A: Physical*, 2007, **133**, 117-127.
68. Z. Zeng, H. Jin, L. Zhang, H. Zhang, Z. Chen, F. Gao and Z. Zhang, *Carbon*, 2015, **84**, 327-334.
69. T. Ampo and T. Oya, *Molecules*, 2021, **26**, 1463.
70. J. D. Madden, P. G. Madden and I. W. Hunter, 2002.
71. B. Bhandari, G.-Y. Lee and S.-H. Ahn, *International journal of precision engineering and manufacturing*, 2012, **13**, 141-163.
72. X. Cao, M. Zhang, Z. Zhang, Y. Xu, Y. Xiao and T. Li, *Acta Mechanica Solida Sinica*, 2019, **32**, 566-579.
73. H. Wang and C. Li, 2009.
74. J. Rossiter, P. Walters and B. Stoimenov, 2009.
75. J. D. Bernal and R. H. Fowler, *The Journal of Chemical Physics*, 1933, **1**, 515-548.
76. A. M. Affoune, A. Yamada and M. Umeda, *Journal of power sources*, 2005, **148**, 9-17.
77. K. O. Börnsen, M. D. Mohr and H. M. Widmer, *Rapid communications in mass spectrometry*, 1995, **9**, 1031-1034.
78. T. Okada, G. Xie, O. Gorseth, S. Kjelstrup, N. Nakamura and T. Arimura, *Electrochimica Acta*, 1998, **43**, 3741-3747.
79. I. Stenina, P. Sistat, A. Rebrov, G. Pourcelly and A. Yaroslavtsev, *Desalination*, 2004, **170**, 49-57.
80. P. De Gennes, K. Okumura, M. Shahinpoor and K. J. Kim, *EPL (Europhysics Letters)*, 2000, **50**, 513.
81. H. Tang, S. Peikang, F. Wang and M. Pan, *Journal of Power Sources*, 2007, **170**, 85-92.
82. M. Vinothkannan, A. R. Kim, S. Ramakrishnan, Y.-T. Yu and D. J. Yoo, *Composites Part B: Engineering*, 2021, 108828.
83. D. Pletcher and T. A. Davis, *A first course in ion permeable membranes*, The electrochemical consultancy, 1997.
84. X. Du, J. Yu, B. Yi, M. Han and K. Bi, *Physical Chemistry Chemical Physics*, 2001, **3**, 3175-3179.
85. W. Pu, X. He, L. Wang, C. Jiang and C. Wan, *Journal of membrane science*, 2006, **272**, 11-14.

86. M. Saito, N. Arimura, K. Hayamizu and T. Okada, *The Journal of Physical Chemistry B*, 2004, **108**, 16064-16070.
87. S. Nemat-Nasser and J. Y. Li, *Journal of Applied Physics*, 2000, **87**, 3321-3331.
88. Y. Liu, M. Ghaffari, R. Zhao, J.-H. Lin, M. Lin and Q. Zhang, *Macromolecules*, 2012, **45**, 5128-5133.
89. S. Imaizumi, Y. Kato, H. Kokubo and M. Watanabe, *The Journal of Physical Chemistry B*, 2012, **116**, 5080-5089.
90. R. Gao, D. Wang, J. R. Heflin and T. E. Long, *Journal of Materials Chemistry*, 2012, **22**, 13473-13476.
91. M. D. Green, D. Wang, S. T. Hemp, J.-H. Choi, K. I. Winey, J. R. Heflin and T. E. Long, *Polymer*, 2012, **53**, 3677-3686.
92. T. Wu, D. Wang, M. Zhang, J. R. Heflin, R. B. Moore and T. E. Long, *ACS applied materials & interfaces*, 2012, **4**, 6552-6559.
93. O. Kim, S. Y. Kim, B. Park, W. Hwang and M. J. Park, *Macromolecules*, 2014, **47**, 4357-4368.
94. O. Kim, T. J. Shin and M. J. Park, *Nature communications*, 2013, **4**, 1-9.
95. N. Festin, A. Maziz, C. Plesse, D. Teyssié, C. Chevrot and F. Vidal, *Smart Materials and Structures*, 2013, **22**, 104005.
96. C. Plesse, A. Khaldi, Q. Wang, E. Cattan, D. Teyssié, C. Chevrot and F. Vidal, *Smart materials and structures*, 2011, **20**, 124002.
97. F. Vidal, C. Plesse, G. Palaprat, J. Juger, C. Gauthier, J.-M. Pelletier, K. Masenelli-Varlot, C. Chevrot and D. Teyssié, *European polymer journal*, 2013, **49**, 2670-2679.
98. R. Bischoff and S. Cray, *Progress in Polymer Science*, 1999, **24**, 185-219.
99. Y. Kang, H. J. Kim, E. Kim, B. Oh and J. H. Cho, *Journal of power sources*, 2001, **92**, 255-259.
100. Y. Matoba, Y. Ikeda and S. Kohjiya, *Solid state ionics*, 2002, **147**, 403-409.
101. Z. Zhang and S. Fang, *Electrochimica acta*, 2000, **45**, 2131-2138.
102. P. A. Kilmartin and J. Travas-Sejdic, *Nanostructured Conductive Polymers*, 2010, 599-630.
103. J. Kim, S. Deshpande, S. Yun and Q. Li, *Polymer journal*, 2006, **38**, 659-668.
104. M. Cho, H. Seo, J. Nam, H. Choi, J. Koo, K. Song and Y. Lee, *Sensors and Actuators B: Chemical*, 2006, **119**, 621-624.
105. M. Cho, J. Nam, Y. Lee, H. Choi and J. Koo, *Molecular Crystals and Liquid Crystals*, 2006, **444**, 241-246.
106. H. Yan, K. Tomizawa, H. Ohno and N. Toshima, *Macromolecular Materials and Engineering*, 2003, **288**, 578-584.
107. K. Oguro, H. Takenaka and Y. Kawami, *Journal*, 1993.
108. M. Silva, A. Rodrigues Vaz, S. Moshkalev and J. W. Swart, *ECS Transactions*, 2007, **9**.
109. D. Guo, L. Wang, X. Wang, Y. Xiao, C. Wang, L. Chen and Y. Ding, *Sensors and Actuators B: Chemical*, 2020, **305**, 127488.
110. S.-S. Kim, J.-H. Jeon, C.-D. Kee and I.-K. Oh, *Smart materials and structures*, 2013, **22**, 085026.
111. T. Otero, H. Grande and J. Rodriguez, *Journal of Electroanalytical Chemistry*, 1995, **394**, 211-216.
112. P. M. Ajayan and O. Z. Zhou, *Carbon nanotubes*, 2001, 391-425.
113. Q. Song, K.-z. Li, H.-l. Li, H.-j. Li and C. Ren, *Carbon*, 2012, **50**, 3949-3952.
114. J. J. Vilatela and D. Eder, *ChemSusChem*, 2012, **5**, 456-478.
115. A. Katchalsky and M. Zwick, *Journal of Polymer Science*, 1955, **16**, 221-234.
116. P. Calvert, *MRS bulletin*, 2008, **33**, 207-212.
117. K. Sadeghipour, R. Salomon and S. Neogi, *Smart Materials and Structures*, 1992, **1**, 172.
118. M. Shahinpoor, 2000.
119. A. Kusoglu and A. Z. Weber, *Chemical reviews*, 2017, **117**, 987-1104.
120. P. A. Anquetil, H.-h. Yu, J. D. Madden, P. G. Madden, T. M. Swager and I. W. Hunter, 2002.
121. T. Otero, J. Rodriguez, E. Angulo and C. Santamaria, *Synthetic metals*, 1993, **57**, 3713-3717.
122. J. Ding, L. Liu, G. M. Spinks, D. Zhou, G. G. Wallace and J. Gillespie, *Synthetic Metals*, 2003, **138**, 391-398.
123. N. T. Nguyen, Y. Dobashi, C. Soyer, C. Plesse, G. T. Nguyen, F. Vidal, E. Cattan, S. Grondel and J. D. Madden, *Smart Materials and Structures*, 2018, **27**, 115032.
124. K. Surana, P. K. Singh, B. Bhattacharya, C. Verma and R. Mehra, *Ceramics International*, 2015, **41**, 5093-5099.

125. W. C. Chong, Y. T. Chung, Y. H. Teow, M. M. Zain, E. Mahmoudi and A. W. Mohammad, *Journal of Cleaner Production*, 2018, **202**, 591-600.
126. P. Yadav, N. Ismail, M. Essalhi, M. Tysklind, D. Athanassiadis and N. Tavajohi, *Journal of Membrane Science*, 2021, **622**, 118987.
127. E. Fontananova, J. C. Jansen, A. Cristiano, E. Curcio and E. Drioli, *Desalination*, 2006, **192**, 190-197.
128. Q.-H. Liao, Y. Wu, Q.-L. Yang, M.-L. Zhao and L. Li, *Journal of Shanghai University of Engineering Science*, 2012, **26**, 36-39.
129. H. Okuzaki, S. Takagi, F. Hishiki and R. Tanigawa, *Sensors and Actuators B: Chemical*, 2014, **194**, 59-63.
130. T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii and T. Aida, *Science*, 2003, **300**, 2072-2074.
131. S.-G. Lee, H.-C. Park, S. D. Pandita and Y.-T. Yoo, *International Journal of Control, Automation, and Systems*, 2006, **4**, 748-755.
132. H. Yuk, B. Lu, S. Lin, K. Qu, J. Xu, J. Luo and X. Zhao, *Nature communications*, 2020, **11**, 1-8.
133. J. C. Dias, D. M. Correia, C. M. Costa, C. Ribeiro, A. Maceiras, J. L. Vilas, G. Botelho, V. de Zea Bermudez and S. Lanceros-Mendez, *Electrochimica Acta*, 2019, **296**, 598-607.
134. H. Zhao, W. E. Price and G. G. Wallace, *Journal of Electroanalytical Chemistry*, 1992, **334**, 111-120.
135. P. Kappler and V. Gauthe, *Journal*, 2006.
136. F. Al-Rimawi and U. Pyell, *Journal of Chromatography A*, 2007, **1160**, 326-335.
137. J. Qiao, T. Hamaya and T. Okada, *Polymer*, 2005, **46**, 10809-10816.
138. S. Scognamillo, V. Alzari, D. Nuvoli, J. Illescas, S. Marceddu and A. Mariani, *Journal of Polymer Science Part A: Polymer Chemistry*, 2011, **49**, 1228-1234.
139. B. Garrett, *Global Policy*, 2014, **5**, 70-75.
140. Y. Mao, Z. Ding, C. Yuan, S. Ai, M. Isakov, J. Wu, T. Wang, M. L. Dunn and H. J. Qi, *Scientific reports*, 2016, **6**, 1-13.
141. Y. Yang, Y. Chen, Y. Wei and Y. Li, *The International Journal of Advanced Manufacturing Technology*, 2016, **84**, 2079-2095.
142. S. S. Nakshatharan, J. G. Martinez, A. Punning, A. Aabloo and E. W. Jager, *Sensors and Actuators B: Chemical*, 2020, **305**, 127355.
143. I. Põldsalu, U. Johanson, T. Tamm, A. Punning, F. Greco, A.-L. Peikolainen, R. Kiefer and A. Aabloo, *Synthetic metals*, 2018, **246**, 122-127.
144. E. Luis, H. M. Pan, S. L. Sing, R. Bajpai, J. Song and W. Y. Yeong, *Polymers*, 2020, **12**, 1031.
145. L. Ge, L. Dong, D. Wang, Q. Ge and G. Gu, *Sensors and Actuators A: Physical*, 2018, **273**, 285-292.
146. T. Dikova, D. Dzhendov, D. Ivanov and K. Bliznakova, *Arch. Mater. Sci. Eng*, 2018, **2**, 65-75.
147. T. Finnes, *The Journal of Undergraduate Research*, 2015, **13**, 3.
148. C. Groth, N. D. Kravitz, P. E. Jones, J. W. Graham and W. R. Redmond, *J Clin Orthod*, 2014, **48**, 475-485.
149. X. L. Ma, 2013.
150. D. K. Patel, A. H. Sakhaei, M. Layani, B. Zhang, Q. Ge and S. Magdassi, *Advanced Materials*, 2017, **29**, 1606000.
151. H. Quan, T. Zhang, H. Xu, S. Luo, J. Nie and X. Zhu, *Bioactive materials*, 2020, **5**, 110-115.
152. B. Steyrer, B. Busetti, G. Harakály, R. Liska and J. Stampfl, *Additive Manufacturing*, 2018, **21**, 209-214.
153. Z. X. Khoo, J. E. M. Teoh, Y. Liu, C. K. Chua, S. Yang, J. An, K. F. Leong and W. Y. Yeong, *Virtual and Physical Prototyping*, 2015, **10**, 103-122.
154. X. Kuang, D. J. Roach, J. Wu, C. M. Hamel, Z. Ding, T. Wang, M. L. Dunn and H. J. Qi, *Advanced Functional Materials*, 2019, **29**, 1805290.
155. T. Wallin, J. Pikul and R. Shepherd, *Nature Reviews Materials*, 2018, **3**, 84-100.
156. K. Jung, J. Xu, P. B. Zetterlund and C. Boyer, *ACS Macro Letters*, 2015, **4**, 1139-1143.
157. M. Aureli, V. Kopman and M. Porfiri, *IEEE/ASME transactions on mechatronics*, 2009, **15**, 603-614.
158. J. J. Hubbard, M. Fleming, V. Palmre, D. Pugal, K. J. Kim and K. K. Leang, *IEEE Journal of Oceanic Engineering*, 2013, **39**, 540-551.
159. J. W. Zhou, H.-Y. Chan, T. K. To, K. W. Lai and W. J. Li, *IEEE/ASME Transactions on mechatronics*, 2004, **9**, 334-342.
160. S. Lee and K. J. Kim, *Smart materials and structures*, 2006, **15**, 1103.

161. T. T. Nguyen, N. S. Goo, V. K. Nguyen, Y. Yoo and S. Park, *Sensors and Actuators A: Physical*, 2008, **141**, 640-648.
162. G. Shuxiang and A. Kinji, *Acta Mechanica Sinica*, 2004, **20**, 146-151.
163. A. T. Abdulsadda and X. Tan, *International Journal of Smart and Nano Materials*, 2012, **3**, 226-242.
164. B.-K. Fang, C.-C. K. Lin and M.-S. Ju, *Sensors and Actuators A: Physical*, 2010, **158**, 1-9.
165. R. B. Moore, K. M. Cable and T. L. Croley, *Journal of Membrane Science*, 1992, **75**, 7-14.
166. G. Yin, Q. He, X. Zhou, Y. Wu, H. Li and M. Yu, *International Journal of Smart and Nano Materials*, 2021, 1-14.
167. J. C. Ma and D. A. Dougherty, *Chemical reviews*, 1997, **97**, 1303-1324.
168. D. Correia, L. Fernandes, N. Pereira, J. Barbosa, J. Serra, R. Pinto, C. Costa and S. Lanceros-Méndez, *Applied Materials Today*, 2021, **22**, 100928.
169. X. Liu, Y. Shang, J. Zhang and C. Zhang, *ACS Applied Materials & Interfaces*, 2021, **13**, 14334-14341.
170. F. Hernández-Fernández, A. P. de los Rios, F. Tomás-Alonso, J. Palacios and G. Víllora, *Journal of Membrane Science*, 2009, **341**, 172-177.
171. A. R. Schultz, P. M. Lambert, N. A. Chartrain, D. M. Ruohoniemi, Z. Zhang, C. Jangu, M. Zhang, C. B. Williams and T. E. Long, *ACS Macro Letters*, 2014, **3**, 1205-1209.
172. Z. Chen, T. I. Um, J. Zhu and H. Bart-Smith, 2011.
173. M. J. Kushmerick, R. A. Meyer and T. R. Brown, *American Journal of Physiology-Cell Physiology*, 1992, **263**, C598-C606.
174. Q. He, Z. Liu, G. Yin, Y. Yue, M. Yu, H. Li, K. Ji, X. Xu, Z. Dai and M. Chen, *Smart Materials and Structures*, 2020, **29**, 045013.
175. L. Lu, J. Liu, Y. Hu, Y. Zhang, H. Randriamahazaka and W. Chen, *Advanced Materials*, 2012, **24**, 4317-4321.
176. K. Xiang, T. Chen and Y. Wang, *Materials Letters*, 2021, **286**, 129267.