

Research Trends of Soft Actuators based on Electroactive Polymers and Conducting Polymers

K Kaneto

Department of Biomedical Engineering, Faculty of Engineering, Osaka Institute of Technology, 5-16-1, Ohmiya, Asahi-ku, Osaka 535-8585 Japan

E-mail: keiichi.kaneto@oit.ac.jp

Abstract. Artificial muscles (or soft actuators) based on electroactive polymers (EAPs) are attractive power sources to drive human-like robots in place of electrical motor, because they are quiet, powerful, light weight and compact. Among EAPs for soft actuators, conducting polymers are superior in strain, stress, deformation form and driving voltage compared with the other EAPs. In this paper, the research trends of EAPs and conducting polymers are reviewed by retrieval of the papers and patents. The research activity of EAP actuators showed the maximum around 2010 and somehow declining now days. The reasons for the reducing activity are found to be partly due to problems of conducting polymer actuators for the practical application. The unique characteristics of conducting polymer actuators are mentioned in terms of the basic mechanisms of actuation, creeping, training effect and shape retention under high tensile loads. The issues and limitation of conducting polymer soft actuators are discussed.

1. Introduction

Since the industrial revolution in 18th century, the consumption of natural resources like metals and fossil fuels has been increasing extensively. As the result, the global environment is suffering from the greenhouse effects and depletion of resources. To solve the problems industrial technologies have to change their directions from the mass production and consumption to saving resources and reuse of rare materials. The developments of low energy fabrication techniques and high efficient devices are also urgent issues. Recently, however, clever human beings found that the technology should follow the way of life. Then, the research field turns to direct to life and bio science and technology.

Among research fields of life and bio sciences, the energy sources are intentionally directed to renewable energies, like solar cell, fuel cell, and etc. by the governmental project. Especially, electronic devices using organic materials, that is, organic electronics are being studied intensively. This is because of the low fabrication cost, which results in energy saving, as well as light weight and flexible devices. Most of organic electronics devices are analogy of inorganic solid state devices in the functionality such as transistors (field effect transistor: FET), solar cell and light emitting diode (LED). These organic devices are inferior to the conventional semiconductor devices in element density, response time and efficiency, because of the low carrier mobility, poor crystallinity and purity. However, the novel feature of organic device technology is the fabrication technique, namely, printable devices, such as organic LED color displays, and wearable personal data assistance (PDA).

In organic materials, low molecular weight compounds and functional polymers have been studied for the electronic devices. The low molecular weight compounds like pentacene[1] demonstrated high carrier mobility in FET, because of easy purification and crystallization. On the other hand, the polymers for electronic devices are mostly conducting polymers. The conducting polymers like



poly(3-hexylthiophene)[2] are semiconductor and also exhibit large carrier mobility in FET, due to the high crystallinity in region-regular structure. The conducting polymers are also one of electroactive polymers (EAPs). The high conductivity at the oxidized state, inherent flexibility and toughness against mechanical stress are suitable for artificial muscle or soft actuator. The artificial muscle sounds a complicated transducer of chemical energy into the mechanical power. However, the artificial muscles mentioned in this paper are in fact soft actuators, and can't be similar to the complicated natural muscle. Hereafter, we call soft actuator instead of artificial muscle, though the artificial muscle is more attractive.

2. Trend of research activity of electroactive polymers for soft actuator

Presently, ionic polymers (ion exchange membrane) and metal composite (IPMC), conducting polymers, dielectric elastomers, gels (hydrogel and dielectric polymer gels) and carbon nano-tubes (CNTs) are studied as the materials of EAP soft actuators[3]. The trend of research activity on EAP actuators is depicted in figure 1 (a) papers searched by SCOPUS with the keywords of artificial muscle or soft actuator and (b) patents applied in Japan by the keyword of artificial muscle. The term of artificial muscles covers the most of soft actuators. There may be other results by adopting different research items, namely, in title, keyword and abstract. However, the present result statistically suggests the trend of research activity on the EAP actuators. It is found that the study of artificial muscle started around 1990 and showed the maximum activity in 2010, then declining. Taking the fact that patents are disclosed 2 years after the application into consideration, the research activity of soft actuators is apparently decreasing after 2008. The reason can be seen from the decrease of research activity in conducting polymer actuators as clear in figures 1 (a) and (b).

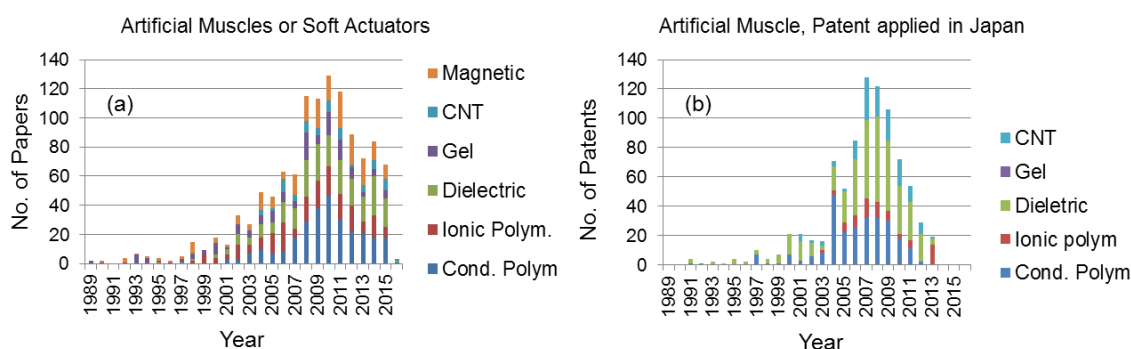


Figure 1. Trends of research activity of soft actuators, (a) the number of papers searched by SCOPUS and (b) the number of patents applied in Japan.

3. Conducting polymers as EAP soft actuators

Conducting polymers have been widely known, since 2000's Nobel Prize of chemistry was awarded to Profs. H. Shirakawa, A. G. MacDiarmid and A.J. Heeger for their invention and study of polyacetylene. Conducting polymers are semiconductor (or insulator) as they are, however, the conductivity increases markedly upon oxidation. The conductivity of oxidized state is as high as metals or more than 10 S/cm. The oxidation is carried out by exposure of conducting polymers to oxidizing agents like bromine and iodine gases or by electrochemical oxidation. During oxidation conducting polymers are swollen by insertion of bulky ion, because of weak inter-chain bonding and fibril structure of the polymer network. On the other hand, the oxidation does not easily occur in solid crystal or inorganic semiconductors, since ions or oxidizing agents hardly penetrate into bulk region. The conductivity, which turns back to those of semiconductors or insulators upon reduction, can be controlled by the applied potential in the electrochemical cell. In the electrochemical reaction, the high conductivity is key factors for the quick response and uniform oxidation in the materials. Consequently, conducting polymers are soft and

flexible, mechanically tough and high conductivity, which are suitable to electrically controllable soft actuator. The actuation induced by electrochemical reaction is named as electrochemomechanical deformation (ECMD).

Inventors of soft actuator at the early stage of research using conducting polymers are searched with SCOPUS by the conditions of (artificial muscle)*(conducting polymer). The dimensional change of conducting polymer, polypyrrole, upon electrochemical redox reaction was first reported by Otero et al in 1992[4]. They fabricated bilayer flexible films with polypyrrole and inert films, and demonstrated bending motion due to the expansion and contraction of polypyrrole film by electrochemical redox reaction. They initiated and led the research field on conducting polymer actuators until now. Using polyaniline film in 1993, Pei et al[5] reported a bilayer laminate strip actuator, which demonstrated bending motion. Bending micro actuator was reported by Smela et al[6] using conducting polymers in 1993. The *in-situ* measurement of deformation of bilayer polyaniline film and cyclic voltammetry was reported by Takashima et al[7] in 1995 using laser displacement meter. They also succeeded to measure directly the rate of anisotropic elongation of polyaniline film upon electrochemical redox reaction, and discussed the mechanism of actuation[8]. Spinks and Wallace et al[9] discussed detailed mechanism of electrochemical deformation in polypyrrole films in 1995. Baughman[10] reported the conducting polymer actuators as the transducer of electrical energy to mechanical energy as well as energy conversion efficiency.

4. Trend of research activity of conducting polymer soft actuators

Figure 2 shows the number of articles searched by SCOPUS with the condition of actuator (title of paper) and conducting polymer (keyword), and the number of patents by SRPARTNER of US/EU countries with the condition of (artificial muscle + actuator)*(conducting polymer) by the claim. Papers on actuators based on conducting polymers appeared from 1992 and showed the maximum at 2010, then slightly declined in the number. On the other hand, the number of patents applied appeared in 1990 and showed the maximum in 2008 and gradually decreased. It is interesting to note that patents were applied a little earlier than papers published. This indicates that the right of patent is superior to writing papers. Anyways, the research activity for soft actuators of conducting polymers as well as other electroactive polymers seems to be declining now days.

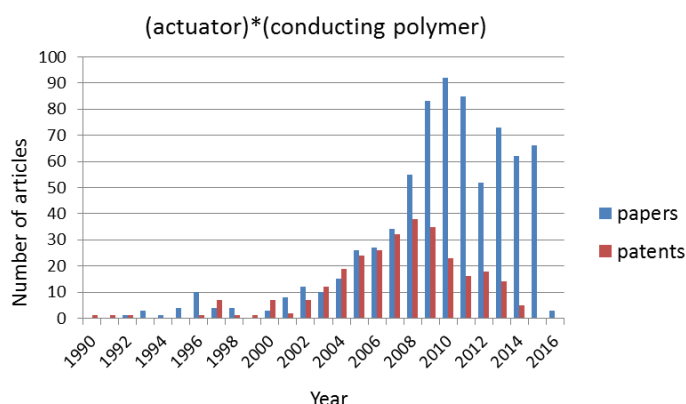


Figure 2. Number of papers and patents on conducting polymer actuators.

From the study of conducting polymer actuators during the last two decades, the attractive points are (1) low operating voltage, (2) large strain, (3) large contraction force (stress), (4) quick response and (5) easy preparation (synthesize) in the optimized circumstance, in comparison with other EAPs. However, we have faced several issues to be overcome before the commercialization of conducting polymer

actuators. We will discuss the issue and trend of activity on conducting polymer actuators.

Figure 3 depicts the number of papers of actuators using various conducting polymers, namely, polypyrrole (PPy), polyaniline (PANi), polythiophene, poly(3,4-ethylenedioxythiophene) (PEDOT) and carbon nanotube (CNT). The number of papers is searched by the condition of (actuators)*(PPy) (or the name of conducting polymers) in SCOPUS. The number of paper related to PPy is 313, which is nearly half of the total number of conducting polymer actuators. The next one is PANi of 116 and PEDOT of 57. That of CNT is 52 and polythiophene is 11. The others are negligible. It is noted that the study of PPy is declining and determines the trend of research activity. The research activities for PANi, PEDOT and CNT are minor, however, nearly constant in the recent decade, as seen in figure 3.

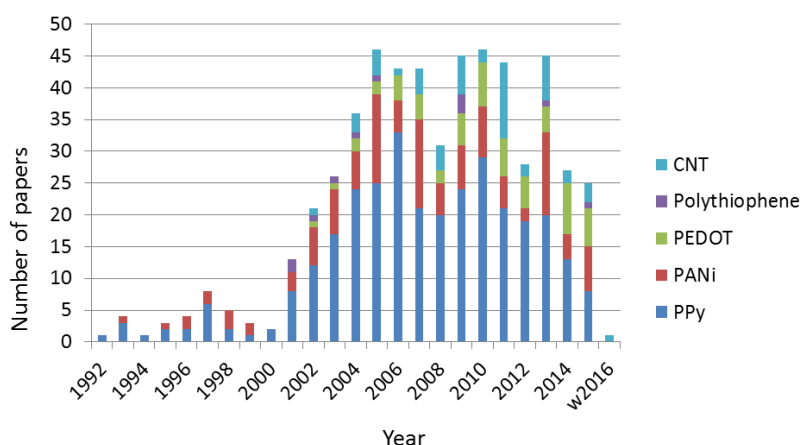


Figure 3. Number of papers of various conducting polymers studied for actuators.

5. Various conducting polymers for soft actuators

Chemical structures of PPy, PANi and PEDOT are shown in figure 4 (a), (b) and (c), respectively. These polymers are aromatic structure in the unit molecule, hence, generally they are stable polymers compared with linear polymer like polyacetylene. These are mostly studied for soft actuators.

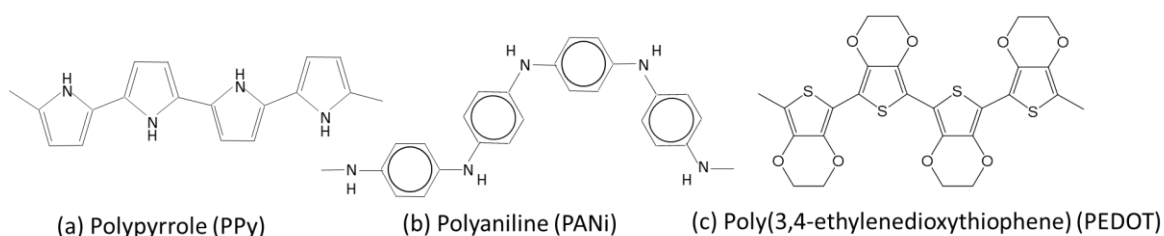


Figure 4. Chemical structures of PPy, PANi and PEDOT

5.1. Polypyrrole

As is noted that the PPy is the most studied conducting polymer for actuators, the reason is that PPy is easily electrodeposited on appropriate metal electrode, and is obtained as high conductive and tough films. Namely, PPy can be prepared in aqueous or organic electrolytes in either form of high density compact film or porous gel like film. Furthermore, the PPy film exhibits large electrochemical strain[11] of 39% and force[12] of 49 MPa at the optimized condition in actuation, and long cycle life[13] in addition. It is noted, however, that preparation of PPy by chemical polymerization in the form of tough and flexible film has not been known, so far. Also PPy obtained by chemical methods

are usually insoluble either in aqueous or organic solutions.

5.2. Polyaniline

The major reason for PANi being studied next to the PPy is that PANi is prepared chemically in bulk by the oxidative polymerization in aqueous acid solution of aniline. The reduced state of emeraldine base form is soluble in N-Methyl-2-Pyrrolidone (NMP) and Dimethyl Sulfoxide (DMSO), that is, easy fabrication of the solution into films, fiber or desired shapes. The PANi is electrochemically active in acid at $\text{pH} < 3$. The acidic electrolyte is inferior for practical actuators, since leakage of acidic solution is harmful. It has been studied intensively to increase pH for safety operation by using high concentration of supporting electrolyte. It has been found that the highest pH region for stable operation[14,15] is pH4. Another demerit of PANi is the strain of 7% at most, which is smaller compared with that of polypyrrole.

5.3. PEDOT/PSS

PEDOT/PSS; (PSS; poly(styrene sulfonate)), is the most intensively studied conducting polymer for variety of application, such as transparent electrode, capacitor and conductor, because of the high stability, conductivity and easy handling. For the actuator[16,17], the electrochemical strain is limited to 2-3 % and the toughness is not good as PPy and PANi. PEDOT/PSS films mostly show cathodic expansion[17,18], indicating anion immobilized in the film and cation movement. However, PEDOT is still interested in studying as actuators, because of PEDOT being high stability in electrochemical reaction. Okuzaki et al[19] demonstrated PEDOT/PSS film actuators, in which water content is controlled by joule heating of the film, namely, at high temperature water goes out and the film shrinks.

5.4. Carbon Nano Tube (Bucky film)

The CNT is also interesting material for actuators[20] besides high conductivity and high mechanical strength. The CNT actuators, which are fabricated by triple layered Bucky films, namely, the porous film soaked with electrolyte was sandwiched by Bucky films. The CNT actuators demonstrate the bending motion similar to IPMC actuator[21]. The actuator showing bending motion is simply interesting for the demonstration of moving. However, the usage of bending motion is rather difficult for the practical application, because the bending force is suppressed by the flexibility of film.

6. Basics of electrochemomechanical actuation in conducting polymers

The mechanism of ECMD in conducting polymers is shown in figure 5. Usually, conducting polymers are obtained by either chemical or electrochemical oxidative polymerization of monomers; hence, the as-grown form is oxidized as shown in figure 5 (a). The oxidized state is swollen by the total volume of inserted anions A^- , and stiffened due to the ionic crosslink. The ionic crosslink is formed by the ionic bonding between polarons and anions, resulting in fastening inter-polymer chain bonding. The oxidized state is reduced by the application of negative voltages in electrochemical cell to figure 5 (c) or (e) by either way of figure 5 (b) or (d), depending on the size of anion used for the polymerization. When small anion like *p*-phenol sulfonic acid (PPS)[22] is employed, the anion can be ejected during reduction and the conducting polymer shrunk as shown by figure 5 (c) through (b). Upon oxidation, the conducting polymers expand, following the reversed way from figure 5 (c) to (a) via (b). In this case, move-in ions are anion, then, named as the anion drive.

On the other hand, if large anion like dodecylbenzene sulfonic acid (DBS)[22] is employed in the synthesis, the large anion is immobilized inside of polymer, and the conducting polymer is reduced by inserting cation to neutralize anions as shown in figure 5 (e) via (d). Namely, the conducting polymer is swollen furthermore. In this case move-in ions are cation, then, the actuation is named as the cation drive. With this idea, a linear actuator is fabricated by laminating with anion and cation drive conducting polymer films on an inert stretchable film. When the actuator is operated by applying voltage between two polymers, the actuator will show the linear motion.

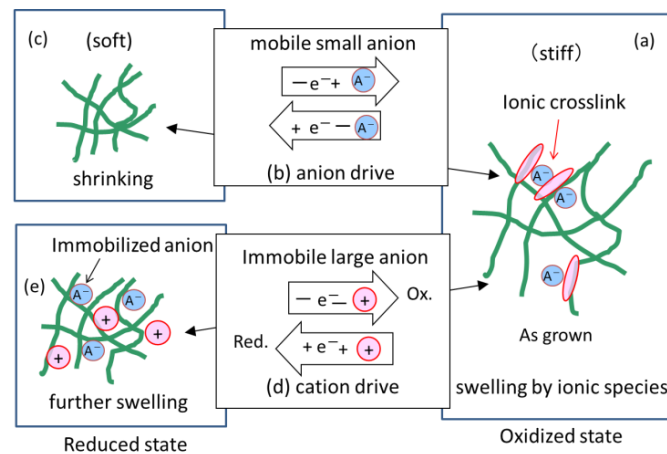


Figure 5. Mechanism of electrochemomechanical actuation in conduction polymers.

The oxidized state is stiffer compared with that of reduced state by about 2-3 times. For example, as shown in figure 6, the Young's modulus (Y) of PPy/DBS at oxidized state is 0.3 GPa and that of reduced state is 0.11 GPa[3]. The curves are obtained by applying tensile stress to a film, and measure the change of film length. The stress (σ) is plotted against strain (ε) as shown in figure 6, namely, stress-strain curve. The Young's modulus (Y) is obtained from the gradient of the curve, $\sigma = \varepsilon Y$, at the linear portion. The high stiffness (large Y) is originated from the delocalization of π -electrons, i.e., polaronic states and the ionic crosslink. On the other hand, at the reduced state the polaronic state and ionic crosslink disappear, then the PPy comes soft. In this way, it is interesting to note that the rheology of conducting polymers can be controlled by electrochemical oxidation and reduction.

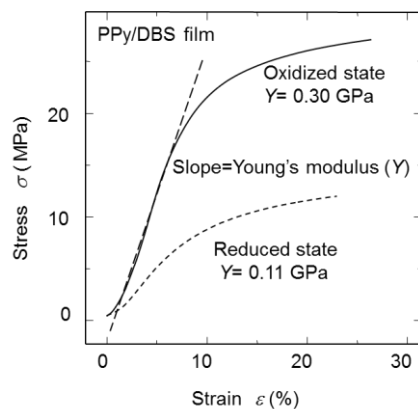


Figure 6. Static stress-strain curves of PPy/DBS films at oxidized and reduced states.

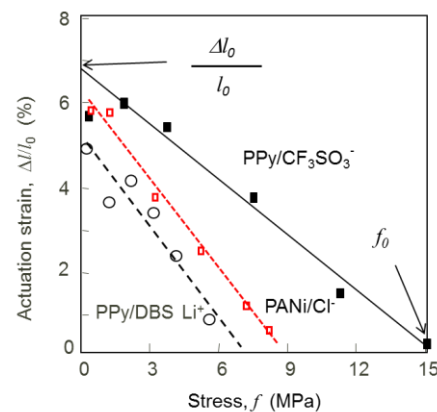


Figure 7. Actuation Strain-Stress curves in of PPy and PANi films.

$$\frac{\Delta l}{l_0} = \frac{\Delta l_0}{l_0} - \frac{f}{Y} \quad (1)$$

By the electrochemical reaction, the conducting polymer films changes in the dimension, and the length of films is measured and defined by the change of length (Δl) (or stroke). The actuation strain is given by dividing Δl by the original length (l_0) of the film, i.e., $\Delta l/l_0$ in %. The ECMD strain ($\Delta l/l_0$) depends on the size of ions and degree of oxidation[3]. The $\Delta l/l_0$ also depends on the tensile loads, namely, $\Delta l/l_0$ decreases with increasing the tensile loads (stress; f) as shown in figure 7 by the typical strain-stress curves. The actuation stress (namely, contraction force) strictly depends on the Young's modulus (or stiffness of films), as shown by empirical equation (1), where Δl_0 is the maximum stroke at non tensile load. The f_0 is the maximum contraction force, which is obtained by letting $\Delta l/l_0 = 0$ in equation (1) and shown in figure 7. Consequently, Y is obtained from the actuation strain-stress curve by $Y = f_0/(\Delta l_0/l_0)$. It is interesting to note that from the curve of PPy/DBS in figure 7 the Y is estimated to be 0.14 GPa ($f_0 = 7\text{MPa}$, $\Delta l_0/l_0 = 0.05$), which approximately coincides with the average Young's modulus of 0.11 and 0.3 GPa as shown in figure 6.

The result indicates that the empirical equation (1) is useful to discuss the ECMD and how to improve the actuator performance, when the materials are given. The Δl_0 and Y seem to be conflicting parameters, namely, the stiff material is hard and shows small deformation. The issues to improve the actuator performance are to prepare materials with large Δl_0 and Y .

7. Unique characteristic of conducting polymer actuators based on creeping

Creeping is a phenomenon that is observed as the irreversible and uncontrollable elongation, when the tensile load stress goes over the elastic or Hook's law region. In soft actuators the creeping is serious problem for the precise positioning[23-25]. The creeping is thought to be resulted from (1) uniaxial alignment of polymer chains, (2) slipping of polymer chains and (3) partial breaking of polymer chains before the breakdown of film. Figure 8 shows an observation of creeping in PANi film under tensile load stress. The short period waves with the stroke of ca. 0.5 mm were due to ECMD, and the shifting of elongation resulted from creeping, as seen stepwise increase of elongation at 1 and 3 MPa. Creeping is significantly enhanced[24] during actuation under tensile stress as shown in figure 8. However, it is noted that the creeping was recovered by removing the tensile loads and repeat of electrochemical cycle. It was also observed that the shape of elongated film is retained by the quitting of electrochemical cycle, indicating the shape retention effect. Furthermore, the stroke of ECMD was slightly increased by electrochemical cycles after the removal of tensile loads. This phenomenon could be named as the training effect.

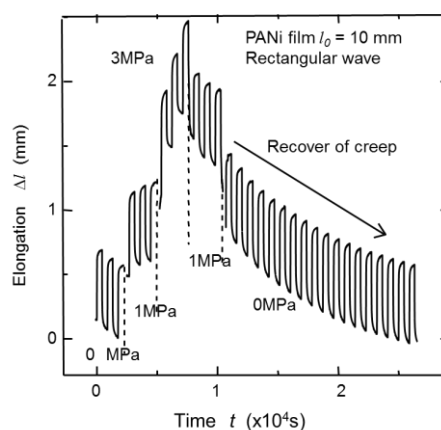


Figure 8. Creeping in PANi actuator under tensile loads of 1 and 3 MPa, and the recovery.

The shape retention and recovery of creeping are unique and interesting phenomena in conducting polymer actuators. These effects result from the conformation change and uniaxial stretching of polymer chains during creeping[23,24]. The mechanism of shape retention is considered to be due to

that the tensile stress stretches polymer chains, which is fixed by ionic crosslink. The fixing of aligned conformation with ionic crosslink is recovered to original shape by thermal relaxation of the polymer chain and by the number of electrochemical cycles. The training effect is supposed to originate from the disentanglement of polymer chains and enhancement of electrochemical activity.

8. Epilogue and conclusion

Electronics is a device technology, which controls the movement of electrons in solid materials like semiconductors, and utilizes the resulting optical and electrical functionality for electronic devices. For example, transistors, photodiodes, solar cells, electroluminescence (EL) diodes and etc. are the typical electronics devices. The electronics has been developed since the discovery of transistors by J. Bardeen, W. B. Shockley and W. H. Brattain in 1947. They received Nobel Prize in 1956, 10 years after the discovery.

Iontronics is a new technology, which controls either electrons or ions in solid and/or fluid materials, and utilizes the optical and electrical functionality. For instance, batteries, electrochemical displays, dye sensitized solar cell, electrochemomechanical actuators and etc. are typical iontronic devices. Of course these have been known as electrochemical devices, however, have not been called as iontronics. The organic iontronics is aiming novel devices such as biosensors, enzyme sensors and artificial muscles, in which ions play the key role of the functions. These devices are unique and cannot be realized by the technology of electronics solely.

The high conductivity and flexibility of conducting polymers are important factors for iontronics, because the electrochemical activity depends on the conductivity and the porosity, that is, weak bonding between atoms or molecules. Insulators or rigid metals may not be used in the iontronics. It should be remembered that the conducting polymers are also excellent materials for electronics, like flexible transistors, solar cells and EL diodes.

Artificial muscle or soft actuator is a future device of the human dream for a long time, to fabricate human friendly robots. Soft actuators have been studied for more than 25 years using EAPs including conducting polymers. However, none of them has been commercialized yet. We hope that the research activity on soft actuators come to be aggressive again to realized human friendly robots and etc.

References

- [1] Horowitz G, Peng X.-Z, Fichou D and Garnier F 1992 Role of the semiconductor/insulator interface in the characteristics of p-conjugated-origomer-based thin-film transistors *Synthetic Metals* **51** 419
- [2] Kaneto K, Lim W Y, Takashima W, Endo T and Rikukawa M 2000 Alkyl Chain Length Dependence of Field-Effect Mobilities in Regioregular Poly(3-Alkylthiophene) Films *Jpn. J. Appl. Phys.* **39** L872
- [3] Asaka K and Okuzaki H 2014 *Soft Actuators -Materials, Modeling, Application, and Future Perspectives-* (Springer)
- [4] Otero T F, Angulo E, Rodríguez J and Santamaría C 1992 Electrochemomechanical properties from bilayer; polypyrrole/non-conducting and flexible material –artificial muscle *Journal of Electroanalytical Chemistry* **341** 369
- [5] Pei Q, Inganäs O and Lundström I 1993 Bending bilayer strips built from polyaniline for artificial muscle *Smart Materials and Structure*, **2** 1
- [6] Smela E, Inganäs O and Lundström I 1993 Conducting polymers as artificial muscles: challenges and possibilities *Journal of Micromechanics and Microengineering* **3** 203
- [7] Takashima W, Kaneto M, Kaneto K and MacDiarmid A G 1995 The electrochemical actuator using electrochemically-deposited poly-aniline film *Synthetic Metals* **71** 2265
- [8] Takashima W, Fukui M, Kaneko M and Kaneto K 1995 Electrochemomechanical Deformation of Polyaniline Films *Jpn. J. Appl. Phys.* **34** 3786
- [9] Gandhi M R, Murray P, Spinks G M and Wallace G G 1995 Mechanism of Electromechanical

actuation in polypyrrole *Synthetic Metals* **73** 247

[10] Baughman R, 1996 Conducting polymer artificial muscles *Synthetic Metals* **78** 339

[11] Hara S, Zama T, Takashima W and Kaneto K 2005 Free-standing gel-like polypyrrole actuators doped with bis(perfluoroalkylsulfonyl)imide exhibiting extremely large strain *Smart Mater. Struct.* **14** 1501

[12] Zama T, Hara S, Takashima W and Kaneto K 2005 Comparison of Conducting Polymer Actuators Based on Polypyrrole Dope with BF_4^- , PF_6^- , CF_3SO_3^- , and ClO_4^- *Bulletin of the Chemical Society of Japan* **78** 50

[13] Madden J, Rinderknecht D, Anquetil P A and Hunter I W 2007 *Sensors and Actuators A: Physical* **133** 210

[14] Takashima W, Nakashima M, Pandey S S and Kaneto K 2004 Enhanced electrochemical activity of polyaniline films towards high pH region: condition of Donnan effect *Electrochimica Acta* **49** 4239

[15] Takashima W, Nakashima M, Hashimoto H, Tominaga K and Kaneto K 2009 Suppression of pH effect on the electrochemical deformation in polyaniline film *Thin Solid Films* **518** 674

[16] Vendeteeg N, Madden P G, Madden J D, Anquetil P A and Hunter I W 2003 Synthesis and characterization of EDOT-based conducting polymer actuators *Proceeding of SPIE* **5054** 349

[17] Kiefer R, Kilmartin P A, Bowmaker G A, Cooney R P and Travas-Sejdic J 2007 Mixed-ion linear actuation of PPy and PEDOT in propylene carbonate-triflate electrolytes *Proceedings of SPIE* **6524** 65240U.

[18] Kaneto K, Takayanagi K, Tominaga K and Takashima W 2012 How to improve electrochemomechanical strain in conducting polymers *Proceeding of SPIE* **8340** 917879

[18] Okuzaki H, Suzuki H and Ito T 2009 Electrically driven PEDOT/PSS actuators *Synthetic Metals* **159** 2233

[20] Baughman R H, Cui C, Zakhidov A A, Iqbal Z, Barisci J N, Spinks G M, Wallace G G, Mazzoldi A, De Rossi D, Rinzler A G, Jaschinski O, Roth S and Kertesz M 1999 Carbon nanotube actuators *Science* **284** 1340

[21] Fukushima T, Asaka K, Kosaka A and Aida T 2005 Fully plastic actuator through layer-by-layer casting with ionic-liquid bucky gel *Angew. Chem. Int. Ed.* **44** 2410

[22] Takashima W, Pandey S S and Kaneto K 2003 Cyclic voltammetric and electrochemical characteristics of freestanding polypyrrole films in dilute media *Thin Solid Films* **438-439** 339

[23] Kaneto K, Hashimoto H, Tominaga K and Takashima W 2011 Shape retention in polyaniline artificial muscles *Jpn. J. Appl. Phys.* **50** 02160

[24] Tominaga K, Hashimoto H, Takashima W and Kaneto K 2011 Training and shape retention in conducting polymer artificial muscles *Smart. Mater. Struct.* **20**124005

[25] Madden J D, Rinderknecht D, Anquetil P A and Hunter I W 2007 Creep and cycle life in polypyrrole actuators *Sensors and Actuators A* **133** 210