Synthesis and Development of Gold Polypyrrole Actuator for Underwater Application

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\textbf{Abstract.} Electro-active polymer (EAP) such as Polypyrrole has gained much attention in the category of functional materials for fabrication of both active actuator and sensor. Particularly, PPy actuator has shown potential in fluid medium application because of high strain, large bending displacement and work density. This paper focuses on developing a low cost active actuator promising in delivering high performance in underwater environment. The proposed Au-pyrrole actuator is synthesized by adopting the layer-by-layer electrochemical polymerization technique and is fabricated as strip actuator from aqueous solution of Pyrrole and NaDBS in room temperature. In the follow-up, topographical analysis has been carried out using SEM and FESEM instruments showing surface morphology and surface integrity of chemical components of the structure. Several experiments have been conducted under DC input voltage evaluating performance effectiveness such as underwater bending displacement and tip force etc. This is observed that the actuator exhibits quite similar stress profile as of natural muscle, endowed with high modulus makes them effective in working nearly 10,000 cycles underwater environment. In addition, the bending displacement up to 5.4 mm with a low input voltage 1.3 V makes the actuator suitable for underwater micro-robotics applications.

1. Introduction

Polypyrrole (PPy) is an ionic electroactive polymer (i-EAP) has gained much attention due to its light weight, large dimensional changes in low driving power and natural muscle like working makes them attractive as biomimetic actuator for wide range of applications in robotics, biomedical, defence and aerospace etc. The ability to generate high strain and stress with minimal operating voltage and natural muscle like working are EAP’s core competencies. Besides, flexibility and light weight makes it suitable for replacing the large and heavy high power driven conventional actuators for wide range of applications in robotics, aerospace, defense, marine and medical fields [1–4]. However, the EAP actuators gained attention for developing biomimetic underwater micro robotics to explore the large unknown underwater environment including wide range of underwater applications like manipulation, scanning and surveillances. Over the last two decades, many leading EAPs have been developed viz. the shape memory alloys (SMA) [5–6], ionic polymer metal composites (IPMC) [7–10], dielectric elastomers (DE) [11] Piezoelectric (PZT) actuator [3] and conducting polymers (CP) [12–15] towards underwater application. The mechanical parameters and performances of many actuators for underwater operations have been studied. The shape memory alloys (SMAs) based fins can work effectively in underwater but the total efficiency remains inferior due to complex body structures [6]. Though the SMAs can provide high stress and work density, the operational voltage is high and reaction speed is less [5]. SMA wire based fin can generate high swimming speed up to 112 mm/s but the turning radius is large because of large skeleton based body which can be suitable for medium to large scale fish [6]. IPMC based biomimetic robots were developed by many research groups with impressive bending displacement and frequency up to the speed of 6 mm/V [7]. The wireless tadpole...
robot with passive fins and swimming fish like biomimetic robots are also developed by using IPMC actuator [8]. However, the hydration effect causes low stiffness and shortens life span and eventually hinders its real time application. In contrast, though the reaction speed is high, the dielectric elastomer provides low stress and strain at high voltage, hence not suitable for underwater actuator application [11]. The PZTs can provide high stress similar to SMA and efficiency like IPMC but the strain is very low and may restricts its real world application [3]. Further, PZTs are suitable for passive structures only because of its low deformation and bending displacement. Recently, PPy has been used to develop actuator for underwater robots for micro to nano scale range applications. The PPy actuator can operate both in air [13, 14] and water medium [16-19] by using solid polymer electrolyte that enhances the stiffness of actuator [17, 18]. PPy actuator can exhibit high strain (32%) with low operational voltage (1-3V) [19], high stress, large bending displacement, high work density and moderate reaction time as compared to other EAP based actuator [16]. Further the mechanical performances of the actuator can be improved by proper selection of fabricating material and process parameters. Though the various PPy actuators proposed and developed for underwater operations, low life cycle, fatigue failure, high cost, slow response and low bending displacement restrict its real time underwater application in micro robotics.

This paper focuses on evaluation of mechanical properties and performances of gold based PPy actuator for underwater based application such as micro robots based propulsion and undulation motion. To begin with, gold-polypyrrole based actuator was synthesized following the layer-by-layer electrochemical polymerization from aqueous solution of Pyrrole (Py) and Sodium dodecyl-benzene-sulphonate (NaDBS) at room temperature. Subsequently, numerous experiments have been conducted that covers investigation on the bending displacement, tip force and life cycle estimation including evaluation of their correlation with surface morphology, conductivity and stiffness. Finally the actuator properties and performances compared with the earlier developed underwater actuator for validation.

2. General Experimental Techniques
This section discusses the details of materials required for fabrication, and the step-by-step fabrication procedures for the Au-PPy actuator.

2.1 Material Required:
Monomer: Pyrrole (Py) (98% pure): Doping salt: Sodium Dodecyl-benzene-sulfonate (NaDBS) reagent grade, Solvent: MilliQ water, SPE: commercially available PVDF membrane 110 µm thickness). All the materials are purchased from Sigma-Aldrich. For Coating: Gold (Au) (99% purity) purchased from Tanishq, India. Pyrrole (Py) was vacuum distilled and stored in cool and dark place (Nitrogen environment) prior to use; other chemicals were used as received. All the experiments were carried out in IIT Guwahati.

2.2 Synthesis and Fabrication
The preliminary process of fabrication is to make the PVDF film conductive owing to the coating of Gold (Au) on film surface. A Vacuum coater unit (Vacuum Technologies Pvt. Ltd, Bangalore) is used for Au coating on PVDF surface. The coating thickness is maintained nearly 5000Å while ongoing coating diminishes the voltage drop across the actuator during operation. The step-by-step flowchart for synthesis and fabrication is shown in figure 1.

The synthesis process carried on the Au-PVDF membrane suspended vertically in a three electrode electrochemical cell (Gamry Inc) that acts as the working electrode on which Polypyrrole gets deposited while Glassy carbon is used as counter electrode and Ag/AgCl is used as reference electrode. The electrodes were hold firmly at equidistance ensuring no lateral movement during synthesis. The other end of the electrodes connected to the Potentiostat/Galvanostat with inbuilt data acquisition system. The electrochemical solution prepared by adding aqueous solution of 0.2M of Pyrrole (0.78 ml in 60 ml of MilliQ water) into the aqueous solution of 0.2M of NaDBS (4.2gm in 60 ml of MilliQ water) slowly. Initially the solutions get stirred for 5-10 min and then a constant current of intensity 0.15 mA/cm² is applied in room temperature i.e 22°C-30°C and monitored carefully
during the synthesis process. After 30 min PPy deposited on Au-PVDF membrane, subsequently retrieved from the solution, washed thoroughly with water and finally dried at 45°C.

The initial layer deposition ends up by measuring and studying the deposition thickness and studying the surface morphology by FESEM (Carl Zeiss NTS GmbH). Subsequently in the next step, and again put in freshly prepared electrochemical solution is used for deposition of another layer with same synthesis parameters. The same process is repeated for number of individual layer depositions unlike continuous deposition for long time [20]. Particularly, for this work 6 individual layers are being deposited up to the duration of 3 h. During this process, this is possible to tune the process parameters and can enhance the structural properties discuss in detail in section 4. After the complete deposition, the PPy deposited Au-PVDF is taken out from the solution, washed several times with distilled water to remove the bulk polymerization of PPy. Then dried at room temperature for nearly 48h and stored in dry place.

2.3 Topographical Characterization

The surface morphology of Au-PPy actuator and the deposition thickness from cross sectional view are studied by using Field Emission Scanning Electron Microscope (FESEM) (Model: Carl Zeiss NTS GmbH), shown in figure 2(a) and (b) respectively.

Fig.2 (a) Micro structure of Au-PPy surface  
Fig. 2(b) Microstructure of PPy actuator Cross – section
Following the fabrication, conductivity of the actuator is measured as 46 S/cm by using multimeter. For accurate estimation, we recorded the conductivity of various points across the surface and take the mean of all values and comparing the individual value with the mean value.

The actuation voltage of the actuator estimated and studied by using Cyclic Voltametery (CV) technique as shown in figure 3. For this the actuator placed horizontally as a cantilever in an aqueous solution of NaCl where the fixed end of the actuator connected to the potentiostat (Gamry Inc) with two electrode mode with sweeping voltage of -1V to +1V with 50mV/sec scan rate.

![Figure 3. CV curve for Au-PPy Actuator](image1)

![Figure 4. Schematic Diagram of Bending Experimental setup](image2)

### 2.4 Mechanical Performance Evaluation

The mechanical performances like tip displacement and force are estimated from the bending experiment of cantilever like actuator in an open face water tank having dimension 60x50x30 cm³ with zero flow velocity. The bending displacement of the actuator in fluid medium is recorded by video camera (Sony DSC-RX10M II Cyber Shot) and ruler places inside the water tank. A pointed needle placed behind the actuator tip to block the deflection of actuator tip which is connected with a physical balance to measure the tip force of the actuator while bending. The schematic diagram of bending experimental setup and force measurement setup is shown in figure 5.

![Figure 5 Schematic diagram of force measurement setup](image3)

![Figure 6. Laboratory setup for Bending of PPy actuator in underwater environment](image4)
2.5 Effectiveness of Au-PPy actuator

The effectiveness of actuator is studied by estimating the elastic modulus, work life cycle and cost. The modulus is estimated from the stress-strain behavior of PPy actuator in wet condition obtained from tensile test by using Micro Tensile Tester (Maker: Deben UK Ltd., Model: Microtest 5kN). Prior to test, the PPy film cut as ASTM standard and stored in water for 30 minutes. The test performed with a speed of 0.5mm/min.

The PPy actuator of size 35x8x0.15 (mm$^3$) operated underwater by applying 1.3 V DC to assess the operational life. The actuator is allowed to operate for a time period of 60s, and then allowing the PPy to deflect in opposite direction by reversing the polarity. The same experimental procedure is repeated until the PPy stops to exhibit bending deformation.

Finally the cost of the present actuator is estimated and compared with the existing actuator to study the effectiveness and feasibility of the actuator use for real time application

3. Results and Discussion

3.1 Topographical Analysis

The microstructure of PPy film surface in figure 2 (a) clearly shows that the PPy-DBS surface is compact, globular and uniform. The size of the globules is approximately 0.3µm and uniformly present in the surface. The bulk polymerization and defects in polymer chain is minimized due to layer by layer polymerization which may lowers the rate of failure of the actuator. These globules are formed by an aggregation of small particles on porous Au-PVDF membrane. From the microstructure it can be believed that the PPy film synthesized in room temperature (23°C - 25°C) with higher Py concentration is as smooth as compared to film synthesized in low temperature range (23°C - 25°C and low monomer concentration [17]. The uniform thickness of PPy layer can be clearly visible from cross sectional view of actuator as shown in figure 2 (b). The total thickness of trilayer actuator is approximately 150µm and both of the PPy layer is approximately 18.60µm while the deposition thickness of PPy layer is 21µm on both sides. It is due to the penetration of PPy into the porous Au-PVDF membrane by approximately 2.5-3µm and this can increase the rate of actuation as well as conductivity.

The conductivity of the PPy actuator is fabricated here is 46S/cm, nearly same or high as compared to the PPy actuator fabricated by using Ionic Liquids in Propylene Carbonate (PC) or Acetonitrile (ACN) like organic solvent [17]. Tough the NaDBS doped actuator shows low conductivity due to large size of DBS anion, the higher concentration, room temperature, vacuum coating and layer by layer deposition technique enhances the conductivity significantly. Because of high concentration and moderate temperature the inter-ionic distances is lowers which increases the inter chain jumping rate. The uniform deposition can also enhance the conductivity and uniform across the surface. The higher conductivity results the better actuation with high response time. The conductivity is one of the important properties which enhances the performances of the actuator to a great extent.

The oxidation and reduction peaks roughly estimated as -0.41V and -0.09V. The peak values are shifted according to the voltage range used but the oxidation peak stabilize at 0.60V even increasing in voltage. The range of redox peak is nearly 0.5V, hence the minimum voltage required for actuation of PPy-DBS actuator is 0.5V. But the oxidation curve extends up to 0.69V while the reduction curve terminates at -0.62V, therefore it can be determined that the minimum operational voltage should not be less than 1.3V for fully oxidation and reduction of actuator. The CV curve for the PPy actuator is shown below in figure. 3.

3.2 Bending Displacement and Force

The bending displacement with various input voltage over a time period of 60 seconds is shown in figure 7 and the real time bending of actuator during experiment is shown in figure 6.
Here, the actuator works in a fluid environment; the underwater bending displacement of the cantilever-like actuator tip is recorded for different amplitudes of step input voltage starting from 0.5 V for a time period of 60 sec as shown in figure 7. It has been shown that at higher voltages, the bending displacement fluctuates or gradually decreases, and it is believed that the decrease in displacement is due to material loss due to very fast actuation. Here, we can see that at 1.3 V the actuator exhibits displacement up to 5.4 mm and can remain constant for a long time. For further experiments, the input voltage for the actuator is taken as 1.3 V.

While bending, the actuator tip exhibits some force which was recorded from the digital weigh machine over a time period of 60 seconds for a voltage range of 0.5-2.1 V as shown in figure 8. The force is increasing with voltage amplitude; alternatively, it can be said that the force increases with increasing bending displacement. At higher voltages, the displacement becomes unstable and gradually decreases, and the force follows the same pattern as shown in figure 8. Though the maximum force obtained at 1.9 V is 4.8 mN, which is highly unstable; the force measured at 1.3 V is 4.1 mN which remains stable for a long time as shown in figure 9.

3.3 Modulus and Operational Life
The modulus is one of the important parameters for bending actuators, especially underwater bending actuators. It directly influences the bending displacement as well as force, which are the primary performances of actuators. The modulus is directly related to strain, which is one of the key properties of PPy actuators. Figure 10 shows the stress-strain curves obtained for PPy actuator in wet condition and the average Young’s modulus is found to be 310 MPa. Here, the average value has been taken as the
modulus is not constant i.e. modulus is higher in oxidation and lower in reduction state. The difference between the higher and lower modulus is less and it can be operated for a long time. Higher modulus needs higher potential which may lead to failure. The modulus is present actuator is suitable for underwater micro-robotics applications.

The operational life is the major drawback of PPy actuator. Because of low life, commercialization and real time application of PPy actuator still a challenge. The present actuator shows a significant improvement in operational life. The bending displacement and force is steady upto 10,000 cycles as shown in fig.12, hence can use for developing tadpole like biomimetic robots.

The effectiveness of the present actuator further explained in figure 11. The displacement of the present actuator is compared with some existing actuators. Including this, the cost of the present actuator is nearly 30% less of these existing actuator.

![Figure 11. Bending displacement of present actuator with recently developed actuator](image1)

![Figure 12. Variation of Force and Displacement Actuator with recently developed actuator of Au-PPy actuator throughout its operational life under DC input voltage](image2)

4. Conclusion

This paper presents the synthesis of low cost fabrication of active Polypyrrole (PPy) actuator by using layer-by-layer electrochemical polymerization process. Parameter estimation such as actuation voltage, bending displacement, tip force, modulus and operational life has been carried out that determines the effectiveness of the actuator in underwater application. Surface morphology and conductivity of PPy actuator has been studied understanding their role in improving the performance has been discussed.

The specific conclusions of the proposed works are summarized below.

- A low cost, high performance delivering Au-Polypyrrole actuator has been fabricated from aqueous solution of Pyrrole and NaDBS at room temperature.
- The actuator can generate the bending displacement up to 5.4 mm and yields force output up to 4.2 mN with a low input voltage 1.3 V.
- Even synthesizing with the solution of NaDBS at room temperature, the developed low cost actuator exhibits significantly high conductivity of 46 S/cm results in enhancement of the rate of actuation.
In addition, the bending stiffness of 310 MPa and working life of over 10000 cycles makes the actuator effective for long duration underwater applications like biomimetic micro-robotics, underwater micro robotics manipulations etc.

The actuator exhibits superior performance index in reverse polarity near 10000 cycles and thus can be easily extended for micro switching and bending propulsion application as well.

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