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Bio-inspired fish robot based on chemical sensors

Andrea Ravalli [a], Claudio Rossi [b], Giovanna Marrazza [a,*]

[a] Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy
[b] Centre for Automation and Robotics, UPM-CICS, University of Madrid, Jose Gutiérrez Abascal 2, 28006, Madrid, Spain

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ABSTRACT

In this study, we designed bio-inspired fish robot capable of swimming according to the directives sent in form of chemical messengers. The concentration of hydrogen ions in the environment was detected by electro-chemical multi-sensors platform. The acquired signal was then transformed into electronic signal to be used in robot control electronics. The pH sensors were realized by polyaniline (PANI) film electrochemically deposited on the graphite screen-printed electrode surface. The electrochemical characteristics of the modified sensors were studied using electrochemical and microscopic techniques. Experiments on PANI-modified sensors in order to obtain the best sensitivity as chemical sensing used in fish robot were carried out. Finally, preliminary experiments were performed using pH sensors to control fish robot's tail movement. The realized robotic platform is considered as a proof-of-concept for the development of multi-sensors fish robot that can be used for water monitoring and warning tool in fish farms.

1. Introduction

The production of fish, crustaceans and shellfish by aquaculture has become the fastest growing animal food sector in the world. Today, aquaculture supplies an estimated around fifty percentage of all fish that is consumed by humans globally [1]. Recently, the aquaculture industry is growing faster than land-based animal agriculture and the fish farms will become even more prevalent as our natural fisheries [2–4]. However, there are still a number of issues that have to be dealt with in the aquaculture sector in order to maintain or even increase the growth rate dictated by the market demand [5]. In order to keep the health of any aquaculture system at an optimal level and to avoid physiological stress and disease of fish certain water quality and adequate nutrition must be monitored and controlled. Poor water quality means low concentration of dissolved oxygen, undesirable temperature or pH, increased levels of carbon dioxide, ammonia and hydrogen sulfide and inappropriate concentration of salinity and hardness which all lead to fish stress [6–9]. Therefore, a good management of the farm is the best solution to prevent fish disease, which manly involves good water quality [10–12].

While land-based autonomous robots have already made a significant breakthrough in markets related service robotics, including the agro-alimentary sector, automation, robotics and advanced information technology tools are still underdeveloped in the fishery sector [13].

To address this problem, we are designing an autonomous underwater vehicle with on-board (bio)sensors to provide the water quality monitoring *in-situ* sensing of fish farming cages. Because pH directly affects other water quality variables and thus fish health, we investigated the application of a robot mimicking a swimming fish in order to minimize fish disturbance and stress integrated with a multi-sensors platform sensible to hydrogen ions in the environment.

We realized a polyaniline-modified sensors that are considered to be useful candidate as electrochemical sensing [14–16] and biosensing [17–20]. Polyaniline (PANI) film exhibits excellent chemical and physical properties couples with low cost. It can exist in four main forms (pernigraniline, emeraldine base, emeraldine salt and leucoemeraldine) in equilibrium each other by the changing of oxidation state or protonation. The reversible protonation of PANI amino groups confers to the electrode the ability to change its potentiometric responses depending on the variation of hydrogen ions concentration. Several studies reported the use of PANI modified sensors for pH determination using both optical and/or electrochemical transduction mechanism [21–24].

In this work, we report the study of a bio-inspired artificial fish unit capable of changing its swimming patterns according to the directives sent in form of chemical messengers from PANI-modified sensors. Open-circuit potential (OCP) measurements of the sen-

* Corresponding author.
E-mail address: giovanna.marrazza@unifi.it (G. Marrazza).

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sors at various hydrogen ions concentrations were performed by an electrochemical transducer. The acquired signals were then transformed into electronic signal to be used in control of proportional movement of the fish robot's tail.

Here, we introduce the proof-of-concept for the development of multi-sensors fish robot as future core technology in aquaculture farm management.

2. Materials and methods

2.1. Chemicals

Aniline, perchloric acid, hydrochloric acid, acetic acid, sodium acetate, sodium hydroxide, disodium hydrogen phosphate, sodium dihydrogen phosphate dihydrate, sodium citrate, citric acid, diethanolamine, potassium ferrocyanide and potassium ferricyanide were purchased from Merck (Milan, Italy).

Potassium chloride, sodium chloride and were obtained from Sigma-Aldrich (Milan, Italy).

All solutions were prepared using MilliQ (obtained from Milli-Q Water Purification System, Millipore, UK) and HPLC grade water (Merck. Milan, Italy) added with 0.1 M KCl. All chemicals were used as received without any further purification.

The solutions used in this work were:

0.1 M citrate buffer 0.1 M KCl, pH 3.0;

2.2.1 M acetate buffer 0.1 M KCl, pH 5.0;

0.1 M phosphate buffer, 0.1 M KCl, pH 7.0;

0.1 M diethanolamine buffer, 0.1 M KCl, pH 10.0;

pH solutions at pH 1.0 and pH 13.0 were prepared adjusting the pH with diluted hydrochloric acid and sodium hydroxide solutions.

2.4. Apparatus

Electrochemical measurements were carried out in a digital potentiostat/galvanostat AUTOLAB PGSTAT 30(2)/FRA2 controlled with the General Purpose Electrochemical System (GPES) and Frequency Response Analyzer (FRA2) 4.9 software (Eco Chemie, Utrecht, The Netherlands).

The pH sensor was assembled using screen-printed cells, comprising graphite-working electrode (2.5 mm in diameter), counter graphite electrode and silver/silver chloride (Ag/AgCl) pseudo-reference electrode. Screen-printed cells were produced in house on a DEK 248 screen-printing machine (DEK, Weymouth, UK). The printing was performed on a polyester film (Autostat CT5) from Autotype (Milan, Italy) using polymeric inks (Electrodag PF-410 (silver)) and (Electrodag 423 SS (graphite)), which were purchased from Acheson (Milan, Italy). Vinylfast 36–100 was used as the insulting ink and was obtained from Argon (Lodi, Italy).

Peristaltic pump was purchased from Gilson Inc., USA. Wall-jet electrochemical micro-flow cell polyacrylate was homemade. It is composed by methacrylate with dimensions of $30 \times 10 \times 20$ mm (width x depth x height). Low lead internal volume is lower than 500 μL.

Environmental Scanning Electron Microscope (ESEM) was equipped with high vacuum secondary electrode detector, a low vacuum large field detector a back-scattered electron detector (Oregon, USA) with the following experimental parameters: Magnification: 600×, Acceleration Voltage: 26.5 kV, Pressure: 1 Torr.

2.5. Electro-polymerization of aniline onto graphite screen-printed electrodes

Electro-polymerization of aniline onto screen-printed electrodes was carried out by cyclic voltammetry in 50 μL of degassed 0.025 M aniline solution in 0.05 M $HClO_4$ using the planar screen-printed cell as a drop-on cell. The potential was then cycled from −0.4 V to +0.8 V (*vs.* Ag/AgCl pseudo-reference electrode) for 10 times using a scan rate of 0.05 V/s. Successively, polyaniline-modified graphite screen-printed electrodes (PANI/GSPEs) were washed 3 times with Milli-Q water.

2.6. Electrochemical PANI-modified sensor surface characterization

Cyclic voltammetry (CV) measurements for surface characterization were carried out in a range of potentials between −0.8 and +0.8 V (*vs.* Ag/AgCl pseudo-reference electrode) in presence of 0.01 M $[Fe(CN)_6]^{3-/4-}$ equimolecular mixture in KCl 0.1 M at scan rate of 0.1 V/s.

Electrochemical Impedance Spectroscopy (EIS) surface characterization was performed with 0.01 M $[Fe(CN)_6]^{3-/4-}$ equimolecular mixture in 0.1 M KCl using the following experimental conditions: amplitude 0.01 V, frequency range 100 kHz – 10 mHz, DC potential +0.13 V. Experimental spectra, presented in the form complex plane diagrams (i.e. Nyquist plot), were fitted with proper equivalent circuits using the facilities of the FRA2 4.9.004 (Eco-Chemie) software. Charge transfer resistance (R_{ct}) values were taken as analytical signals.

2.7. Open-circuit potential measurements

The PANI-modified sensor was connected to the electrochemical transducer for open-circuit potential (OCP) measurements. Various pH solutions were flowed into the electrochemical flow-cell until the complete coverage of the screen-printed sensors. The flow was then stopped and open circuit potential measurements were carried out.

Measurements were also performed in flow system using a flow rate of 1 mL/min.

The PANI-modified sensors were used for many times until the average their reproducibility remained below 10% RSD.

2.8. Robotic apparatus and data acquisition

Our prototype adopts shape memory alloys (SMAs) actuators that bend a continuous flexible structure (the backbone of the robot fish), made of polycarbonate of 1 mm thickness. An additional structure of ribs was employed to support the latex-based skin. The overall length of the fish is 30 cm (not including the tail).

Six antagonistic actuators based on SMAs are employed to bend three segments of the backbone whose length is 1/3 of the body length (i.e. 8.5 cm, not counting the tail and the head). This type of structural arrangement is bio-inspired by fish red muscles, which used during steady swimming for bending of a flexible but nearly incompressible structure such as the fishbone. For further details in the robotics mechatronics, we refer the reader to [25]. The robot was controlled by and Arduino Nano(tm) microcontroller and the SMAs are powered by in-house developed pulse width modulation-to-direct current (PWM-to-DC) power circuitry.

For the purpose of data acquisition and control during the experiments, National Instrument Compact Rio real-time acquisition and control system (Austin, USA) has been used. Analog signals were acquired using a NI 9215 AI Module (16-Bits A/D, 100 kS/s/ch, 4-Ch). Digital control signals were generated via both a NI 9381 DIO C Series Module, and sent to the robot via an Arduino Uno(TM) microcontroller (Fig. 1).