

## Self-maintained colorimetric acid/base sensor using polypyrrole actuator

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### Abstract

A novel approach to autonomous chemical sensor regeneration is explored in this paper. It involves the movement of a sensor surface into measurement or regeneration zones using low powered conducting polymer actuators. The system demonstrated the feasibility of repeatedly cycling through a measurement–regeneration regime, which in principle allows remotely deployed chemical sensors to perform simple self-diagnostics. The sensor-actuator device is shown to repeatedly switch through 120 measurement–regeneration cycles. Detection of pH-dependent colour changes is demonstrated using LED-based colorimetry and remotely deployed video cameras.

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### 1. Introduction

The drift in analyte response and the deterioration of the sensitive interface are problems intrinsic to most chemical sensors. These issues are exacerbated in remote autonomous monitoring systems. A chemical sensor generally consists of a chemically selective interface in/on a non-specific transducer. The interface is expected to selectively interact with the chemical species of interest and induce a change in either optical and/or electronic properties [1]. Due to the variation between individual sensors and the material deterioration of the chemically selective interface over time, a calibration process is required to convert the output signal to a measurable quantity.

Recently, autonomous chemical sensors with minimal or no human input have become important due to national security and

environmental issues [2]. The decreased cost, size and power consumption makes large-scale deployments of such sensors feasible.

However, on board calibration and/or sensor surface regeneration remains a challenge. van der Schoot et al. [3] introduced an integrated self-calibrating sensor system to measure the concentration of acids and bases in situ by an absolute coulometric titration method, in which the local pH change induced by the electrolysis of water on a gold electrode was used for self-calibrating purpose. Following the above study, oxygen and hydrogen bubbles generated electrochemically from two electrodes were employed to do a two-point calibration (100% and 0% oxygen) for an integrated oxygen sensor in microfluidic devices [4]. For general applications, several self-calibration methodologies have been reported and were based on flow injection analysis manifolds to enable automatic calibration and sample preconditioning [5–7]. Among these, DeGrandpre et al. [7] described a self-maintained sensor configuration by renewing the analyte-sensitive solution for absorbance and fluorescence-based chemical sensors. One of the examples

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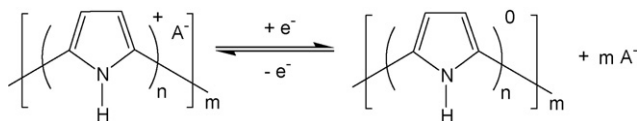


Fig. 1. Schematic diagram showing the electrochemical doping and dedoping process of PPy,  $A^-$  is the dopant anion incorporated into the PPy during synthesis,  $n$  is the number of pyrrole units for each  $A^-$  incorporated and  $m$  is the numbers of PPy repeat units that determine the molecular weight of polymer.

raised in that study was for the autonomous mooring-based measurements of  $pCO_2$  (partial pressure of  $CO_2$ ) in sea water. Recently Hahn [8] reported an auto-maintained chloride-ion chemical sensor at low-cost for remote river water monitoring. It employed a two-point calibration methodology, in which two stepper motors and valves were utilised for the injection of a calibration reference liquid, distilled water aliquot and water sample to the sensor cavity for sensor calibration, cleaning and sample water monitoring, respectively. All on board calibration studies to date depend on the mobility of the analyte or calibrate containing solution. Use of the mobility of sensitive chemical interfaces such as the moveable, bendable or rotary interchangeable electrode/sensitive surface does not appear in the literature, presumably due to the lack of innovative and cost effective actuation materials.

One class of emerging actuation materials are the inherently conducting polymers (ICPs). Their novel actuation mechanism is based on the reversible ion doping/dedoping process with the application of electrical stimulation in electrolyte solution [9] (Fig. 1). A polypyrrole (PPy) trilayer actuator coupled to an oxygen sensor (galvanic cell) has been used to control the atmosphere within an enclosed space with potential for applications in smart packaging [10]. In this case the galvanic cell which is the oxygen sensor is used to trigger the power required to move the polymer actuator. Generally ICP-based actuators like PPy trilayer actuator have the advantages of compact and durable structure, low operating voltage ( $<1.0$  V) and can be miniaturized to smaller dimensions, especially suitable for portable diagnostic devices requiring less complicated automation [11,12].

Here we introduce a new approach that addresses some of the requirements of autonomous chemical sensors. It involves the use of ICP actuators to move and position the sensor so as to locate it in the measurement, regeneration or calibration environment as required. A colorimetric pH sensor attached to the bending actuator was used to demonstrate the principle.

## 2. Experimental

### 2.1. Reagents and materials

Polyvinylidene fluoride membrane (PVDF, Millipore) with  $\sim 110$   $\mu m$  thickness and average pore size  $\sim 0.45$   $\mu m$  was used as received without additional treatment. Pyrrole (Merck) was distilled and stored under nitrogen at  $\sim -20$   $^\circ C$  before use. Propylene carbonate (PC) (Aldrich), tetrabutylammonium hexafluorophosphate (TBA.PF<sub>6</sub>) (Aldrich), acetic acid (Aldrich) and aqueous ammonia solution (30%) (BDH Laboratory Sup-

plies) were used without further purification. A bromocresol green (BCG) dye formulation was generated in-house according to a previously described procedure [13].

### 2.2. Preparation of colorimetric pH sensor

The colorimetric pH sensor was produced by dip coating a layer of BCG dye formulation onto a polyethylene film. It was then left in open air at room temperature overnight to complete the drying process. Sensors with a rectangular head of 5.0 mm  $\times$  12.0 mm were cut out with great care exerted so as not to damage the coated surface. The amount of dye formulation per area was controlled by the number of dippings. The average BCG dye coated on polyethylene film was estimated at  $\sim 0.14$  mg/cm<sup>2</sup>.

### 2.3. Preparation of PPy actuator

The PPy actuator was constructed as a compact trilayer membrane in which the porous PVDF membrane was utilised as the backing material in the middle layer. The PVDF membrane was initially sputter coated with a layer of Au (70 nm) on each side and used as the anode for the electrochemical synthesis of polypyrrole. The Au-coated membrane was placed in an electrochemical cell containing 0.06 M pyrrole monomer, 0.06 M TBA.PF<sub>6</sub> and 0.5% (w/w) water in PC. The entire cell setup was placed in a freezer at  $-20$   $^\circ C$  and the polymerisation of pyrrole was carried out galvanostatically on both sides of the membrane at a current density of 0.10 mA/cm<sup>2</sup> over 12 h. The resulting PPy films have an average thickness of  $\sim 30$   $\mu m$  on each side, and are relatively even over the entire surface except at the edge. It is strongly anchored into the pores of PVDF membrane during synthesis and does not delaminate upon mechanical stress. After trimming off the edges, the as-prepared film was cut to rectangular strips of dimensions 1.0 cm  $\times$  5.0 cm and thoroughly rinsed with PC to remove any residue of pyrrole. After pad-drying with tissue, PPy trilayer strips were stored in 0.25 M TBA.PF<sub>6</sub>/PC electrolyte until used to construct the sensor system.

Normally, a thinner film ( $\sim 10$   $\mu m$ ) would be sufficient for carrying out the electrochemical bending actuation, as this actuator has to carry an optical sensor at the end of the strip, a thick PPy film was used to increase its mechanical stability and to ensure that the actuator could exert enough force to carry the load to and from the destined locations. The size of the sensor strip was determined by the size of the colour sensor attached onto the tip of the strip such that mechanical stability and the strain to load ratio was maintained.

### 2.4. System configuration and operation

The bending sensor system comprised of two components (Fig. 2): (1) a dye-coated film that changes colour in response to an analyte, (2) a PPy actuator to perform mechanical work for controlled placement of sensor to the measurement and regeneration site. The two components were joined together by a lightweight plastic clamp.

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