

A galvanic cell driven controlled release system based on conducting polymers

Caiyun Wang, Philip G. Whitten, Chee O. Too, Gordon G. Wallace*

ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia

Received 31 May 2007; received in revised form 6 September 2007; accepted 6 September 2007
Available online 19 September 2007

Abstract

A self-powered controlled release system is achieved via galvanic coupling of a conducting polymer and a zinc anode. Release of an anionic dye molecule, phenol red (PR), as the polymer is reduced is quantified. Triggered release using the galvanic cell is demonstrated in a freeze–thaw experiment when melting of the electrolyte completes the galvanic cell and enables oxidation/reduction to occur.

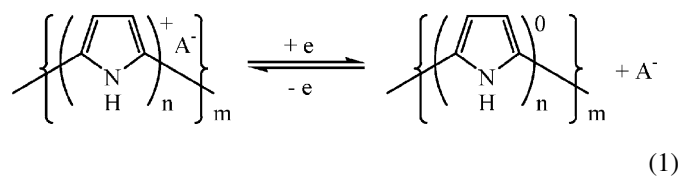
© 2007 Elsevier B.V. All rights reserved.

Keywords: Controlled release; Phenol red; Conducting polymer; Electrochemical quartz crystal microbalance; Galvanic cell

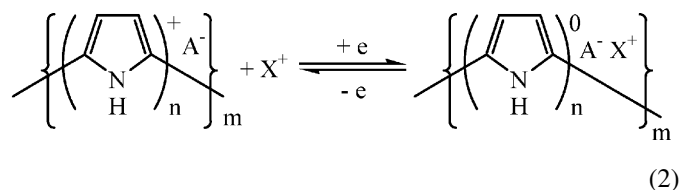
1. Introduction

Polymer structures capable of triggering release in response to discrete thermal transitions [1,2], pH [3,4] or electrical stimuli [5–7] have been demonstrated previously. Those based on the use of electrical stimulation have the advantage that the release profile can be tuned by the nature of the stimulation conditions (the current/potential magnitude and frequency) employed. They have the disadvantage of requiring a power supply of some description for operation.

Conducting polymers represent a class of materials capable of responding to electrical stimulation to induce controlled release. This ability can be traced to the inherent redox capabilities of these polymer structures according to:



and/or



Anions (A^- , Eq. (1)) are expelled into the solution during the reduction process [8,9]. However, when immobile counter-anions are employed in the conjugated conducting polymers, the redox mechanism involves the entry of cations (X^+ , Eq. (2)) during reduction and expulsion during oxidation [10,11]. Obviously these processes can be used to provide release on demand systems for either cations or anions [12,13].

For example, it has been reported that anthraquinone disulphonic acid (AQSA) can be electrochemically released from a polypyrrole matrix [14], with the rate of release determined by the potential applied. The electrically stimulated release of sulfosalicylic acid (SSA) from polypyrrole has also been reported [15]. In other work, Pyo and Reynolds [16] incorporated adenosine 5'-triphosphate (ATP) as the counter-anion into polypyrrole (PPy) and demonstrated electrochemical release of the molecule.

In this work, phenol red (Fig. 1) sodium salt dye was chosen as the molecular dopant. Phenol red was incorporated as a counter-anion into the polypyrrole matrix during electrochemical growth. When this polymer was stimulated at negative

* Corresponding author. Tel.: +61 2 4221 3127; fax: +61 2 4221 3114.
E-mail address: gwallace@uow.edu.au (G.G. Wallace).

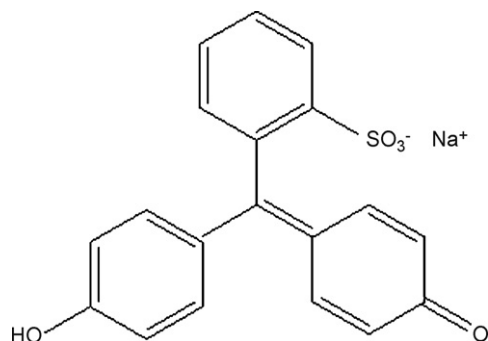


Fig. 1. Structure of phenol red sodium salt.

potential, the dopant, phenol red, was expelled and migrated into the solution, and the solution exhibited a red colour which can be easily observed by eye. This, like most conducting polymer-controlled release systems, required an external power supply to apply the required electrochemical stimulus. Therefore, a further novel development of this work was the adoption of a galvanic cell system whereby the dye was released when the PPy–phenol red electrode was connected to a zinc counter electrode in an electrolyte. This system required no external power source to trigger and control the dye release. Here we describe a self-powered controlled release system, particularly for autonomous applications, based on coupling a conducting polymer cathode to a zinc anode. It is envisaged that such systems would find applications in situations where the couple is immediately connected. For example, a self-powered controlled release system or where the cell is coupled by a change in environmental conditions (e.g. a thawing electrolyte) to act as a triggered monitoring system.

2. Materials and methods

2.1. Polymer electrosynthesis and characterization

Phenol red (PR) dye was incorporated into polypyrrole as a dopant in this experiment. This polymer was electrosynthesised galvanostatically at a current density of 0.5 mA cm^{-2} on stainless steel mesh or gold-coated quartz crystal from Milli-Q water containing 0.1 M pyrrole and 5 mM phenol red sodium salt. Phenol red sodium salt (Aldrich) was used as received and pyrrole (Merck) was freshly distilled. The solution was purged with nitrogen before use. The charge consumed during the electrosynthesis of polypyrrole was 1.0 C cm^{-2} . Stainless steel mesh was used as counter electrode, and the reference electrode was Ag/AgCl (3 M NaCl). After deposition the polymer-coated electrode was rinsed thoroughly with deionised H_2O , then soaked in acetonitrile for 10 min to extract H_2O from the polymer matrix. The as-polymerized polymer-coated electrode was dried in air for 48 h before use.

All the electrochemical properties were investigated using a standard one compartment three-electrode cell with a stainless steel mesh counter electrode, and Ag/AgCl (3 M NaCl) reference electrode. Cyclic voltammetry (CV) was carried out using an EG&G PAR 363 Potentiostat/Galvanostat, a

MacLab 400, and EChem v 1.3.2 software (AD Instruments).

PPy–PR samples, as electrosynthesised and after dye release, were sent to the Microanalytical Unit of the Australian National University for elemental analysis.

2.2. EQCM

The resonance frequency of the polypyrrole-coated quartz crystal was measured in situ during both electrochemical synthesis of, and the electrochemical characterization of the polypyrrole with a Stanford Research System (QCM 200) Quartz Crystal Microbalance. The gold-coated quartz crystals were obtained from Stanford Research Systems, and have an unloaded resonant frequency of approximately 5 MHz . The electrochemical surface area of the crystal (1.37 cm^2) is much larger than the oscillation surface area (0.4 cm^2) meaning that edge effects do not affect the frequency measurement. The crystal loaded with polypyrrole was rinsed with Milli-Q water and dried slowly in air to avoid any crack formation in the film.

Mass change, Δm , was calculated directly from the change in resonant frequency, Δf , of the gold-coated quartz crystal using the Sauerbrey equation [17]:

$$\frac{\Delta m}{A} = \frac{-\Delta f \sqrt{\rho \mu}}{2f_0^2} = \frac{-\Delta f}{C_f} \quad (3)$$

where f_0 is the resonant frequency of the crystal, A the oscillation area of the crystal, ρ the density of quartz and μ is the shear modulus of quartz. C_f is known as the crystal sensitivity factor and is constant for crystals with the same resonant frequency. For crystals with a resonant frequency of 5 MHz (as used here) C_f is equal to $56.6 \text{ Hz } \mu\text{g}^{-1} \text{ cm}^2$.

The Sauerbrey equation was derived for thin rigid films in a gas environment. Variation from the Sauerbrey equation for the samples reported here is not significant, as indicated by the observation that the change in mass was proportional to the charge passed for the growth of the polypyrrole film.

The polypyrrole-coated quartz crystal was immersed in the testing electrolyte (0.1 M sodium dodecyl sulfate (SDS)) for 30 min before electrochemical characterization of the film was initiated. This procedure allowed the electrolyte to swell the polypyrrole, and hence minimize the mass change during electrochemical cycling due to the swelling of the previously dried polypyrrole film.

2.3. UV–vis spectrum

The release of dye into the solution from the polymer film was monitored and characterised using UV–vis spectroscopy. Vigorous stirring was applied continuously during the dye releasing process to maintain the homogeneity of the solution. The UV–vis spectra of the solution containing phenol red dye in 0.1 M NaCl or 0.1 M SDS were recorded between 300 and 1100 nm using a Shimadzu UV 1601 spectrophotometer.

Download English Version:

<https://daneshyari.com/en/article/746652>

Download Persian Version:

<https://daneshyari.com/article/746652>

[Daneshyari.com](https://daneshyari.com)