



The cooperative actuation of polypyrrole electrochemical machines senses the chemical conditions as muscles sense their fatigue state

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ABSTRACT

Polypyrrole films are constituted by multistep electrochemical molecular machines, counterions and water, and have been considered here as a material model of the intracellular matrix in muscular cells. Their reversible oxidation/reduction in different concentrations of NaCl aqueous solution was studied by consecutive square current waves. The evolution of both, the material potential and the consumed electrical energy during every reaction, changes as a function of the electrolyte concentration. The reactions involving molecular motors as reactants respond to (and sense) any chemical energetic perturbations of the reaction ambient (variations of electrolyte concentration here), by adapting the evolution of the material potential and that of the consumed reaction energy to fit the new energetic conditions. A theoretical description of the attained empirical results is presented getting the sensing equations and the concomitant sensitivities. The results could indicate how the neuronal signal informing the brain about the fatigue state of a muscle is generated from the muscular chemical potential or the consumed reaction energy at any time. The actin-myosin-ATP reaction should originate, simultaneously, actuating and sensing biological functions.

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1. Introduction

Animal and human muscles are biological motors constituted by molecular chemical machines: actin-myosin motors driven by chemical reactions (ATP hydrolysis). They transduce chemical energy (ATP hydrolysis) into mechanical energy (muscle contraction) and heat. Muscles sense, simultaneously, any perturbation of the mechanical, thermal or chemical working energetic conditions. The brain is aware at any time of those working conditions. The origin of the sensing signals remains as a pending issue. Probably by influence of nowadays solid-state physical technologies (actuators and sensors are independent devices), most of the efforts trying to clarify the dual activity have been focused for decades on the localization of the different sensors working in muscles [1,2]. Alternatively, some researchers suspect that the actin-myosin-ATP chemical reaction originates, simultaneously, the muscular actuation and the sensing signals sent to the brain to communicate the working conditions [3–6]. Actin-myosin cytoskeletons also are being proposed as mechanical sensors in some plants [7].

The control of actin-myosin actuating gels and their actuation driven by the ATP reaction has experienced great advances during the last years, [8–10]. At the moment the control of this system is not enough to allow a systematic investigation in the laboratory of the reaction sensing properties. In addition, nobody knows which reaction magnitude should be proportional to the experimental variables, that means should be the experimental sensing magnitude. In parallel new material families have been developed from the seventies of the past century whose films (supported on metals or self-supported) can be used as electrodes in liquid electrolytes: conducting polymers, graphenes, carbon nanotubes, among others. Used as a self-supported film electrode or as a film coating a metal electrode the voltammetric charge is a lineal function of the film mass: any polymer chain or carbonaceous structure from the film participates in the film reaction [11,12]. The reaction is a three-dimensional electrochemical reaction. Focusing on conducting polymers, their reversible electrochemical reactions (i.e. reaction (1), Section 4) in liquid electrolytes drive reversible conformational movements (σ bonds between monomeric units change to π conjugated linear polaronic units involving 3–5 monomeric units) of their constitutive polymeric chains: every chain becomes an electrochemically-driven molecular machine [13]. Under faradaic control the cooperative actuation of those molecular motors (the

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polypyrrole chains) taking part of a polymer film generates by oxidation (or destroys by reduction) inside the film the free volume required to lodge or expel counterions needed for charge balance and solvent needed for osmotic balance (reaction (1), Section 4). The film expands during oxidation, or contracts during reduction, becoming a dense reactive gel constituted by reaction-driven molecular motors, ions and water: this is the simplest system replicating both, the dense gel from the sarcomere and its basic components originating the muscular contraction [14,15]. Our group has been using those dense gels to explore the reaction chemical kinetics when the molecular motors are the reactants [16,17] and to develop macroscopic artificial muscles [18,19] and bifunctional sensing-actuators replicating haptic muscles [20–22]. Bifunctional or multifunctional means here that one chemical or electrochemical reaction drives the change of the material composition (polymer/counterion content) and the simultaneous change of the value of any composition-dependent property: material volume, material potential, stored charge, stored ions, liberated ions, material colour, transversal ionic conductivity, among others [13]. At the moment some bi-functional devices mimicking biological organs, as sensing and tactile muscles [21,23–28], electrochromic supercapacitors [29–31] and electrochromic actuators [32,33] and one three-functional device (muscles-battery-sensor) [34] have been developed.

Apparently chemists, physicists, engineers and robot designers find some difficulties to understand and use this ability of the polymeric reaction to sense the working chemical and physical conditions. The different families of the electroactive materials above mentioned have been used as electrodes to develop classical electrochemical sensors of an analyte solved in the electrolyte or adsorbed on the electrode. An alternative way was proposed for those material by investigation of the electrochemical reaction of the material constituted by molecular machines (conducting polymer [18,24,27,35], carbon nanotube [36], graphene [37]) as a self-sensor of the reaction working conditions. This manuscript takes part of a series concerning the ability (empirical and theoretical) of the polypyrrole reactions to self-sense the chemical, thermal, electrical or mechanical reaction conditions using different electrochemical methodologies: cyclic voltammetry [38–40], square current waves and square potential waves [41]. In this way our primary aim here is to explore the influence of the electrolyte concentration (available chemical energy) on the polypyrrole oxidation/reduction reactions in NaCl aqueous solutions driven by square current waves. The secondary goal is to check the ability of those reactions driving molecular machines to sense the electrolyte concentration identifying the sensing magnitudes that give us quantitative information of that concentration. Finally, we will discuss if the actin-ATP-myosin chemical motors in natural muscles can produce similar sensing signals and if the nature of our sensing signal is suitable to be understood by a nervous terminal, collected by a neuron and sent through the nervous system to inform the brain about the working chemical conditions.

2. Material and methods

2.1. Chemicals

Potassium nitrate, KNO_3 , (Merck) and sodium chloride, NaCl, (Panreac), being A.R quality were used as received. Pyrrol (Fluka) was purified by distillation under vacuum and stored at -10°C before use. Ultra-pure water, obtained from a Milli-Q equipment of $18.2\text{ M}\Omega\text{ cm}$ (at 25°C), was used for the preparation of all solutions.

2.2. Electrochemical equipment

The working electrode was a platinum sheet with a total surface area of 1 cm^2 , the counter electrode was a stainless steel sheet with a total surface area of 10 cm^2 , and the reference electrode was of Ag/AgCl (3 M KCl) from CRISON. A single compartment electrochemical glass cell, together with an AUTOLAB/PGSTAT100 potentiostat-galvanostat, connected to a PC and controlled by NOVA 1.11 electrochemical software was used throughout the experiments. The films obtained were weighted in a Sartorius SC-2 Micro precision balance. All the experiments were carried out at room temperature.

3. Results

3.1. PPy electrosynthesis: reproducibility

The polypyrrole films were electrogenerated by flow of a constant current density of 2 mA cm^{-2} for 70 s on a clean Pt electrode through a fresh 0.1 M pyrrole and 0.1 M KNO_3 aqueous solution every time. The used methodology, the reproducibility of the attained film masses ($\omega = 25.3 \pm 0.15\ \mu\text{g}$) and that of their voltammetric control in 0.1 M NaCl aqueous solution, by consecutive potential sweeps between -0.35 V and 0.25 V (potential window) at a scan rate of 90 mV s^{-1} was described in previous papers [38–42]. As described in the literature the use of nitrate ions improves both the reproducibility of the film synthesis and the physical properties of the films [43–45]. The four most divergent chronopotentiometric responses obtained during the synthesis of different films are shown in Fig. 1 from the supplementary material. Fig. 2a and b from the supplementary material present the stationary voltammetric and coulombometric, respectively, responses (voltammetric control after two consecutive potential cycles) from the different synthesized films (arrows indicate the direction followed by the potential sweep). Those stationary voltammetric responses guarantee the removal of any structural material memory as well as the replacement of the NO_3^- ions used during the synthesis by the new Cl^- ions [38,46,47]. The voltammetric potential window to check the electroactivity of the material was selected in order to minimize the presence of irreversible electrolyte discharges (oxygen and chlorine, or hydrogen evolution) on the Pt electrode, which can promote the film degradation. This degradation is indicated by a

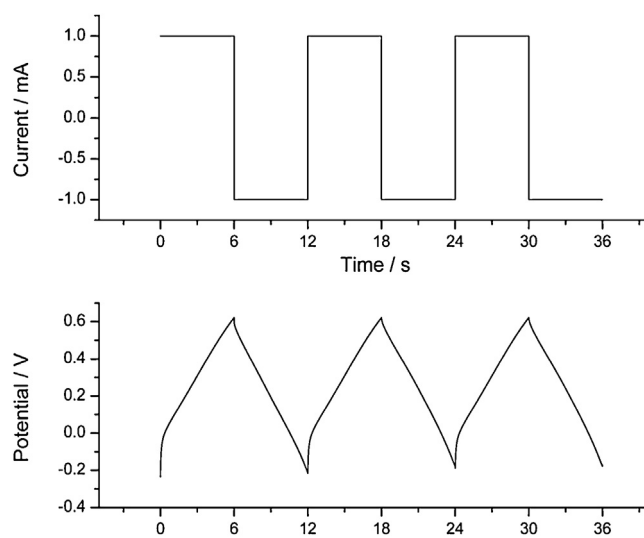


Fig. 1. (a) Consecutive square current waves by flow of current of 1 mA and -1 mA , each applied during 6 s . (b) Consecutive chronopotentiometric responses to those square current waves from a pPy/Pt electrode in a 0.1 M NaCl aqueous solution.

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