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Reprint of: Oxidation kinetics of polypyrrole films: Solvent influence[☆]

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During electrochemical reactions films of conducting polymers exchange counterions, for charge balance, and solvent, for osmotic balance, with the electrolyte. A physical process drives the solvent exchange: the solvent cannot be considered as a reactant. Here we explore the solvent influence on the reaction rate. The oxidation empirical kinetics of polypyrrole film was attained from the chronoamperometric responses to potential steps in solutions of different solvents and the same electrolyte. Seven different organic solvents were studied: two protic (water and methanol) and four aprotic (acetonitrile, acetone, *N,N*-dimethylformamide dimethylsulfoxide and benzonitrile) solvents. The attained reaction coefficients in a solvent decrease exponentially for deeper reduced initial states and, under similar initial reduced conditions, change among the different solvents for one order of magnitude. A good correlation is attained between empirical and theoretical results when the kinetic coefficient is related to the dipolar moment and dielectric constant of each solvent. The solvent, even if it cannot be considered as a reactant, has a strong influence on the reaction rate of electrochemical reactions involving dense reactive gels of conducting polymers.

1. Introduction

Electrodes of conducting polymers constitute the central part of different electrochemical devices [1] such as batteries [2,3] smart windows [4–6], smart membranes [7–10], artificial muscles [11–18], nervous interface [15,19], drug delivery systems [15,20–23], etc. The actuation of those devices involve the reversible oxidation/reduction of the constitutive materials in presence of an electrolyte [15,24–26]. From that point of view those devices mimic biological organs which actuation is also supported by reactions taking place in their functional cells.

The reversible electrochemical reaction of a polypyrrole film in presence of small anions can be summarized as:

$$(pPy^{*}) + n{\cdot}A^{-} + m(S) \leftrightarrow [(pPy^{n+})(A^{-})_n(S)_m]_{gel} + n{\cdot}e^{-}_{metal} \qquad (1)$$

where pPy^{*} means the active centers of the polypyrrole chains taking part of the film, understood as those places of the polymeric chains able to store a positive charge by oxidation, A^{-} the anion present in the electrolyte, S is the solvent molecule, the subscript *gel* indicates that the material becomes an expanded gel and the subscript *metal* indicates that the extracted electrons are transported through the metallic support.

As indicated by Eq. (1), the polypyrrole film is immersed in the electrolyte constituted by a solvent and the solved salt (i.e. $LiClO_4$). The oxidized polymer film contains a great density of positive and negative charges: [pPy^{n+} and n anions, A^{-}]. The system is not stable forcing the entrance of solvent molecules for osmotic balance [27,28]. Osmosis is a physical process following here the electrochemical reaction. The polymer film becomes a dense reactive gel (reactive polymeric chains, anions and solvent). Thus, even if the solvent cannot be considered as a reactant it plays an important role on the electrochemical reactions and on the concomitant electrochemical responses from conducting polymers [29–40] and could play a key role in the reaction kinetics.

Here we present the results attained from the kinetic studies of the “same” polypyrrole film in presence of electrolytes having the same solved salt and different solvents. The oxidation empirical kinetics will be attained from the chronoamperometric responses when the polypyrrole films are submitted to potential steps. We have selected two protic solvents (water and methanol) and five aprotic solvents: two protophylic solvents as *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMS) and three protophobic solvents as acetonitrile, benzonitrile and acetone.

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2. Experimental

Pyrrole (Fluka) was purified by distillation under vacuum using a diaphragm vacuum pump MZ 2C SCHOTT and stored under nitrogen atmosphere at − 10 °C. Anhydrous lithium perchlorate salt (Fluka) was used as received. Ultrapure water from Millipore Milli-Q equipment was used. Methanol (Fluka), acetone (Sigma-Aldrich), *N,N*-dimethylformamide (Aldrich), dimethylsulfoxide (Fluka), benzonitrile (Sigma Aldrich) and acetonitrile (Sigma Aldrich) were used after drying using a molecular sieve UOP Type 3A (Fluka).

All the electrochemical experiments were performed with a potentiostat-galvanostat EG & G 273 PAR controlled by a computer using the ECHEM electrochemical software. A platinum electrode having 1 cm^2 area (0.5 cm^2 by side) was used as working electrode. A steel plate having 4 cm^2 of surface area was used as counter electrode. The steel electrode was polished and cleaned in a sonic bath of the studied solvent for 15 min before every electrogeneration. The reference electrode was a Crison Ag/AgCl (3 M KCl) electrode. Before every electrochemical experiment the solution was deaerated by bubbling nitrogen for 10 min. All the experiments were performed at 22 °C (room temperature).

Polypyrrole films were electrogenerated on the platinum electrode from 0.1 M pyrrole and 0.1 M $LiClO_4$ acetonitrile solutions with 1% of water content under potentiostatic polarization at 0.90 V vs. Ag/AgCl by consumption of a constant charge of 400 mC every time. The water content hinders any parallel chemical polymerization initiated by protonation of the monomer around the electrode: the electrogenerated polymer is more electroactive (stores more charge per unit of weight) than those films electrogenerated in pure acetonitrile [41–44]. Each electrogenerated film is rinsed, dried and weighed using a Sartorius SC2 balance with a precision of 10^{-6} g. The electropolymerization is a very reproducible process as corroborated by the weight of the attained films: 190 ± 10 μg.

2.1. Chronoamperometric control and reproducibility

The coated electrode was then transferred into a 0.1 M $LiClO_4$ acetonitrile solutions and there submitted to consecutive square potential waves from − 1.30 V, kept for 30 s to 0.2 V also kept for 30 s. Fig. 1 show the attained responses to 14 consecutive square potential waves. Reproducible chronoamperometric responses are attained after the second square potential wave. This anodic response (chronoamperometric and chronocoulometric) will be taken as a reference to check the state of any film during kinetic studies. When the charge involved in the film oxidation deviates over 5% from that of the chronoamperometric control attained after electrosynthesis a new film will be used to go on the kinetic study.

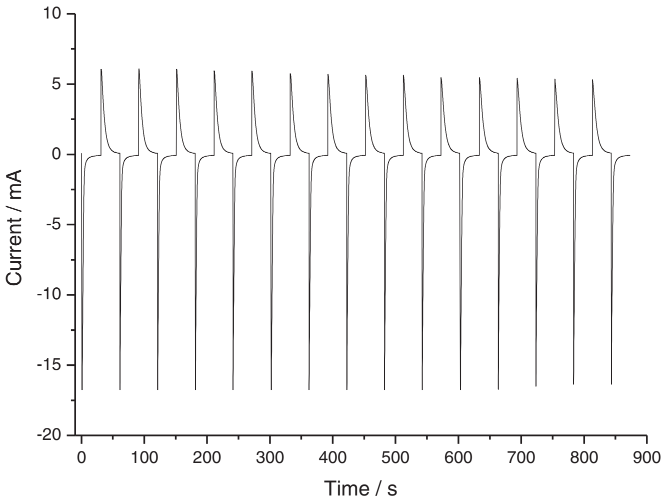

Fig. 1. Consecutive chronoamperometric responses obtained from a polypyrrole film submitted to consecutive square potential waves from 1.3 V, kept for 30 s to 0.2 V also kept for 30 s in 0.1 $LiClO_4$ acetonitrile solution at room temperature.

2.2. Oxidation kinetic methodology

After the chronoamperometric control the coated electrode is transfer into the solution of the solvent to be studied. There it was submitted to the chronoamperometric analysis, following a four steps procedure [45–52]:

1. The film is submitted to an oxidation potential (0.20 V kept during 30 s) in order to erase any previous structural memory.
2. The film is then reduced by polarization at a cathodic potential during 30 s. This will be the initial reduced state used to follow the film oxidation.
3. Oxidation of the film by a potential step to an anodic potential recording the chronoamperometric response to obtain the reaction rate.
4. Cathodic potential step to the original potential of reduction in order to start a new experiment.

2.3. Theoretical background

The empirical kinetics of the polypyrrole oxidation, Eq. (1), is:

$$r = -\frac{d[pPy^*]}{dt} = k\cdot[A^-]^\alpha\cdot[pPy^*]^\beta \tag{2}$$

where k ($L\cdot mol^{-1}\cdot s^{-1}$) is the rate coefficient of the oxidation reaction; r ($mol\cdot s^{-1}\cdot L^{-1}$) is the oxidation reaction rate, being proportional to the current; α is the reaction order related to the counterion concentration in solution, β is the reaction order related to the concentration of active centers in the polymer film.

The reaction rate, r, is related to the current flowing through the electrode, i (A):

$$r = \frac{\rho}{m\cdot F}\frac{dq}{dt} = \frac{\rho}{m\cdot F}i \tag{3}$$

where F is the Faraday's constant (96,485, $C\cdot mol^{-1}$), m is the mass of the polymer film and ρ is the polymer density (1540 $g\cdot L^{-1}$) [13].

[pPy^*], the concentration of active centers can be calculated from the oxidation charge (every active center losses one electron during oxidation) as follows:

$$[pPy^*] = \frac{Q_{ox}\cdot\rho}{m\cdot F} \tag{4}$$

where Q_{ox} is the charge required to oxidize the film (C).

By taking logarithms from Eq. (2):

$$\log(r) = \log(k) + \alpha\cdot\log[A^-] + \beta\cdot\log[pPy^*] \tag{5}$$

Eq. (5) indicates that the reaction order α can be obtained by submitting the polypyrrole film to potential steps in a given electrolyte from the same initial reduced state (attained by reduction at the same cathodic potential for the same reduction time) to the same anodic potential (same concentration of [pPy^*] attained by consumption of the same charge during the film oxidation) in a different concentration of electrolyte [A^-] every time and under constant temperature (T). The response to the potential step will be a chronoamperogram.

Under those experimental conditions Eq. (5) becomes:

$$\log(r) = \log(k') + \alpha\cdot\log[A^-] \tag{6}$$

where:

$$\log(k') = \log(k) + \beta\log[pPy^*]$$
$$k = \frac{k'}{[pPy^*]^\beta} \tag{7}$$

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