



Electrochemically induced free solvent transfer in thin poly(3,4-ethylenedioxythiophene) films

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ABSTRACT

In dynamic intrinsically conducting films, counterions transfer and conformational movements stimulated by the electrochemical reactions affect the free water molecules transfer. Poly(3,4-ethylenedioxythiophene) or PEDOT is included in this category. Here, *p*-doping of PEDOT immersed in LiClO₄ aqueous solution was explored by *ac*-electrogravimetry. Electrochemical impedance spectroscopy combined with mass impedance spectroscopy proves useful for species identification and kinetics. For PEDOT, new equations have been developed to analyze the *ac*-electrogravimetry response. Quantitatively, faster free water transfer and slower coupled ClO₄⁻/free water transfer were separated. Free water transfer plays a key role as a “fingerprint” of conformational movements. This might respond to fundamental questions about the mechanism of PEDOT as well as their implication in technological devices based on this polymer.

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1. Introduction

Since discovery of Poly (ethylenedioxythiophene) or PEDOT, scientific community undertakes several work to prove that this material is historically one of the most successful conducting polymers [1,2]. The reversible doping state, excellent stability, regular structure without cross-linking, low band-gap, and electrochemical properties of PEDOT [3] allow this conducting polymer to be used in promising practical applications like sensors [4], anti-static coatings [5], light-emitting devices [6], solar cells [7], supercapacitors [8], actuators [9] and even as a biological tissue interfacing agent [10].

Morphology and electrochemical properties of conducting polymers like PEDOT depend strongly on the experimental conditions of polymerization [11,12]. In PEDOT films, the role of incorporated free solvent molecules (not structural) during the electrochemical reaction of synthesized polymers is as important as the transfer of ions for charge balance [13]. Free solvent stored by films lubricates the intermolecular movement acting as a plasticizer. On the contrary, film dehydration leads to stiffness of material [14,15] or increase of conductivity [16].

Mainly, the reversible transfer of anions and solvent between solution and polymer takes place during electrochemical reactions of PEDOT [17,18]. Free-volume inside the film fixes the number of free non-charged molecules, which can be inserted by the films [19]. Simplistically, rigid film oxidation involves anion insertion for charge balancing (*p*-doping) in this kind of polymers. At the same time, anions exclude free solvent molecules. During film reduction, free solvent occupies rapidly the free space left by anions (undoping). This fact is the so-called anion exclusion effect. In a more realistic view, redox reactions in conducting polymers often involve macromolecular rearrangements of polymer by creation and destruction of double bonds and by the accommodation of the anions. These conformational movements affect the free volume inside the film, which is occupied by free solvent molecules. Thus, doping state of the film and molecular reconfigurations during the electrochemical reactions control the free-volume [20–23].

Hillman et al. and Bund et al. have specifically explored the ion and solvent transfer in PEDOT films by cyclic electrogravimetric methods [17,18,22,23]. However, the temporal sequence in the transfer of the species and the corresponding mechanisms are not fully explored [24,25]. These processes are kinetically inseparable on the timescales accessed by slow transient electrochemical techniques. Electrochemical impedance analysis proves useful to separate temporally different ions/charge transfer, however, this technique is blind for non-charged species transfer [26].

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Combining electrochemical and mass impedance spectroscopy, *ac*-electrogravimetry, allows an objective separation between ions/charge and solvent transfer [27–29].

The aim of this work is to go beyond of the previous electrogravimetric investigations exploiting the *ac*-electrogravimetry. This technique may separate the dynamic processes (anion transfer and free water transfer) that occur during the redox reactions of thin PEDOT films. Moreover, the study of free solvent transfer can extend the level of detail of the electrochemically induced conformational changes in PEDOT films.

Recently, a refined analytical procedure was proposed to study the anion p-doping of intrinsically conducting polymers (ICPs) by *ac*-electrogravimetry [30]. Here, the theory section is limited to present basic mathematical developments. The anion exclusion effect is constantly assumed in the analytical equations used to interpret the results. Thus, if the coupled anion/free water electrogravimetric response is removed from the experimental data, the remaining electrogravimetric response is because of the free water transfer stimulated by the conformational changes of the films. The kinetics transfer of this free solvent acts as a “fingerprint”.

In addition to the *ac*-electrogravimetry study, cyclic voltammetry (CV) coupled with the Electrochemical Quartz Crystal Microbalance (EQCM) were exploited to estimate the solvent transfer during PEDOT film electrogeneration in acetonitrile/LiClO₄ solution and during the redox reaction of PEDOT film in aqueous LiClO₄ solution.

Conformational changes have a key role in applications as actuators and few studies have directly addressed the kinetics of conformational changes in electroactive polymers [31,32]. Therefore, the results presented here may have marked importance for several technological applications involving PEDOT as functional coatings in contact with a liquid phase.

2. *Ac*-electrogravimetry theory

In aqueous solution, during the redox reaction of a p-type conducting polymer (P), monovalent anion, A[−], transfer, which compensates the excess or defect of charge inside the film, can govern the opposite transfer of water molecules (exclusion effect in Fig. 1). Assuming a rigid polymer, the number of water molecules, *n*, replaced by the anion insertion depends on anion volume, V_{A[−]}, therefore, V_{A[−]} = *n*V_{H₂O}.

As it was demonstrated earlier [33,34], species kinetics in thin films depend on their resistance to cross the polymer|solution interface:

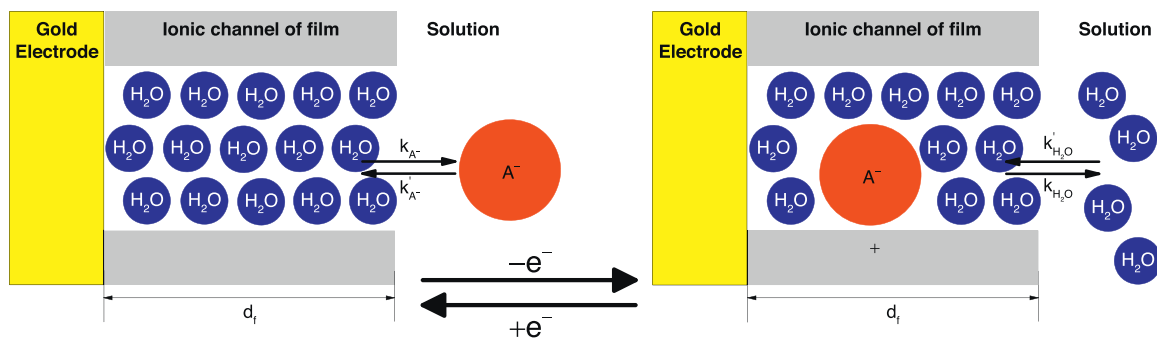
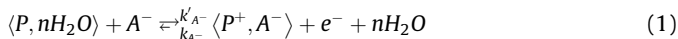


Fig. 1. Electrode|film|solution cross-section of a rigid polymer showing the exclusion effect caused between anions (A^-) and free water molecules (H_2O). k'_{A^-} and k'_{H_2O} are the kinetic constants of anion and free water insertion to polymer, respectively. k_{A^-} and k_{H_2O} are the kinetic constants of anion and free water expulsion from polymer, respectively. d_f is the polymer film thickness and the circles represent the molecule volume.

where P, nH_2O is the hydrated polymer and P^+, A^- is the doped polymer matrix. The k_{A^-} parameter is the kinetic constant of anion expulsion from polymer and k'_{A^-} is the kinetic constant of anion insertion to polymer from solution.

Changes of anion concentration, ΔC_{A^-} , during the small sine wave potential perturbation, ΔE , can be defined as a function of perturbation frequency, f , [35]:

$$\frac{\Delta C_{A^-}}{\Delta E}(\omega) = \frac{-G_{A^-}}{j\omega d_f + K_{A^-}} \quad (2)$$

where d_f is the thickness of the polymer film, ω is the angular frequency ($2\pi f$), $j = \sqrt{-1}$,

$$K_{A^-} = k_{A^-} + k'_{A^-} C_{A^-}^{sol} \quad (3)$$

and

$$G_{A^-} = -b_{A^-} k_{A^-} (C_{A^-} - C_{A^-}^{min}) + b'_{A^-} k'_{A^-} (C_{A^-}^{max} - C_{A^-}) C_{A^-}^{sol} \quad (4)$$

where, $C_{A^-}^{max}$ is the maximum concentration of the sites for A^- insertion, $C_{A^-}^{min}$ is the minimum concentration of the occupied sites and $C_{A^-}^{sol}$ is A^- concentration in solution. k_{A^-} is $k_{A^-00} \exp(b_{A^-} (E - E^0))$ and $k'_{A^-} = k_{A^-00} \exp(b'_{A^-} (E - E^0))$ where E^0 is the formal potential and k_{A^-00} is a preexponential factor of the kinetic rate constants independent of applied potential E .

The parameters, b_{A^-} and b'_{A^-} are the Tafel coefficients:

$$b_{A^-} - b'_{A^-} = B_{A^-} = \frac{n_e F}{RT} \quad (5)$$

where R is the gas constant and T is the absolute temperature. From these coefficients, one can estimate the number of electrons (n_e) involved in the faradaic process and the symmetry of direct and reverse transition on the formal redox potential [36,37].

Often, electrochemical reactions of film induce conformational changes (swelling, shrinking, compaction, or relaxation). Therefore, a constant thickness of films cannot be considered since it may change depending on the polarization potential [38–41].

Eq. (2) is slightly modified in terms of surface concentration as [28,29]:

$$d_f \frac{\Delta C_{A^-}}{\Delta E}(\omega) = \frac{\Delta \Gamma_{A^-}}{\Delta E}(\omega) = \frac{-G_{A^-}}{j\omega + K'_{A^-}} \quad (6)$$

where K' is K/d_f .

Based on this model, theoretical electrochemical impedance, $\Delta E/\Delta I(\omega)$ is expressed as:

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