



# Ion transfer dynamics of poly(3,4-ethylenedioxythiophene) films in deep eutectic solvents



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## ABSTRACT

Mechanistic studies are reported for redox switching (doping/undoping) of Au-supported poly(3,4-ethylenedioxythiophene) (PEDOT) films exposed to LiClO<sub>4</sub>/CH<sub>3</sub>CN (a conventional electrolyte based on a molecular solvent) and to Ethaline and Propaline (two choline chloride-based deep eutectic solvent (DES) media). A combination of electrochemical, acoustic (quartz crystal microbalance, QCM) and optical (probe beam deflection, PBD) methods was used to monitor the exchange of mobile species between the film and the bathing electrolyte. Qualitatively, film responses to a potentiodynamic control function showed that the redox switching mechanisms are quite different in all three media. When exposed to acetonitrile, *anion* transfer is dominant, with some accompanying solvent transfer but negligible cation transfer; application of the convolution protocol allowed these transfers to be quantified. Analogous observations in the DES media could be interpreted qualitatively in terms of dominant *cation* transfer, but the convolution protocol could not be used to quantify the contributions of individual species; in these viscous media, this is a consequence of the long transit times from the film/solution interface to the optical detection zone. Chronoamperometric experiments, in which the measurement time was an order of magnitude (or more) longer permitted the diffusional processes driven by the polymer/DES interfacial population changes to reach the optical detection zone.

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## 1. Introduction

Quite generally, rapid switching – manifested in terms of (dis)charge rate, optical response time or sensor response time, according to the application – is central to the performance of devices using electroactive conducting polymer films as the active material. Since the rate of electron transport is relatively rapid, changes in charge state are invariably limited by the rate(s) of ion transfer(s) required to maintain electroneutrality (“doping” in the parlance of the field). Commonly, one chooses to use an electrolyte of high ionic strength in order to maximise the availability of dopant ions, but for conventional electrolytes based on molecular solvents (even as polar as water or acetonitrile) the ionic concentration is seldom much more than 1 M. Encouraged by other practical reasons – including wide potential window, low volatility, low toxicity, environmental acceptability and cost – we have been investigating the use of room temperature ionic liquids as electrolytic media. An additional attraction of these media, which we seek to exploit

here, is that the ion concentration is extremely high: there is no “solvent” in the conventional sense of the term and the fluid is entirely ionic. Not only does this hold the promise of practically limitless availability of ions from the liquid phase, but also even modest partition of electrolyte (equivalent amounts of anions and cations) into the film will provide high conductivity to accelerate switching of films from the undoped (neutral) state. The purpose of the present study is to explore these very attractive technological possibilities and the interesting fundamental questions presented by the absence of molecular solvent, which is generally associated with such phenomena as osmosis and plasticisation-driven viscoelasticity.

The electronic and optical properties of conducting polymers make them attractive materials for diverse (electro)chemical applications, as reviewed elsewhere [1,2]. The structural feature upon which these applications rely is a conjugated  $\pi$ -electron system able to act as a source/sink for electronic charge, such that oxidation (p-doping) or reduction (n-doping) results in partially filled bands containing highly mobile charge carriers. Pyrrole, thiophene and aniline and a number of their substituted derivatives can be polymerised to produce materials that fulfil these criteria. When polymerisation is carried out electrochemically, the resultant

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polymers are deposited on the electrode surface as thin films that can subsequently (in monomer-free solution) be reversibly doped and undoped at a rate and to an extent that can be controlled by the applied potential [1,2].

In this study we focus on poly(3,4-ethylenedioxythiophene) (PEDOT), a polythiophene derivative whose substitution pattern results in facile polymerisation, enhanced chemical/environmental stability, excellent longevity under redox cycling, convenient redox energetics and a p-doped state with conductivity up to  $500 \text{ S cm}^{-1}$  [1,2]. These attributes have led to the use of PEDOT in charge storage devices [3], micro-electrochemical [4] and organic thin film [5] transistors, antistatic coatings [6], photovoltaic energy conversion [7], electrochromic and optical display devices [8,9], corrosion protection coatings [10], drug delivery [11], biosensors [12], electrocatalysis [13], memory devices [14], fluid handling devices [15] and mechanical actuators [16].

Performance optimisation in the above applications has motivated a number of mechanistic studies of the (un)doping of PEDOT [17–24] and other conducting polymers [25–28]. Nevertheless, the details of the underlying redox-driven ion and solvent exchange processes – in terms of both the overall film population changes of these mobile species and the rates at which they occur – are not fully understood. One reason for this is that the rates of the competing ion transfers, e.g. anion entry vs cation ejection during p-doping, depend significantly on a number of factors: on the *ions* themselves (*via size and geometry*); on the *solvent* (which may be coordinated to the ions and/or swell the polymer); and on the *polymer* morphology (which will depend on the film deposition conditions and subsequently film redox history) [29,30]. Significantly, the polymer is not a static medium, but has a rich dynamics commonly manifested *via viscoelastic phenomena* [31,32]. All these factors complicate not only the analysis of individual studies but also comparison with nominally identical studies by different researchers.

PEDOT is one of the most intensely studied of all the substituted heterocyclic conducting polymer systems. This is partly because of its chemical and electrochemical stability, by virtue of complete substitution of the thiophene ring system, and partly because of its unusual optical and electrochromic properties [33]. In addition, PEDOT is easily blended with polyanionic materials, such as polystyrenesulfonate, in order to produce solution processable materials. Much of this research has been focussed on potential applications of PEDOT films in functional materials; this diverse range of applications has been reviewed elsewhere [34]. More recently the studies of PEDOT and substituted variants have focussed on particular applications and challenges. These include, for example roll-to-roll manufacturing of printed sheet plastic electronics [35], photocatalysis [36], integrated textile heating elements as well as heat sensors [37,38], solar cell energy harvesting films [39] and ink-jet printable photovoltaics [40]. In all of these applications the key challenges associated with optimising performance focus on electron transfer, counterion transfer and polymer chain dynamics. In applications where the polymer film is in contact with a liquid/electrolyte phase, e.g. energy storage or sensing, it is also important to understand and quantify the influence of coupled solvent transfer. This is clearly a moot point when comparing molecular solvent systems and ionic liquids.

The majority of mechanistic studies of conducting polymer redox chemistry and of its implementation in practical devices have involved the use of electrolytes dissolved in molecular solvents, notably water and acetonitrile. More recently, the use of room temperature ionic liquids [41,42] has been explored in this context. In many instances, the motivation for using these media has been elimination of volatile, toxic or combustible solvent (for safety reasons) or the opportunity to exploit a wide potential range [43]. While these are attractive features, our motivation has centred on the goal of increasing the ion transfer rate. Since the fluid

is composed entirely of ions, the availability of dopant is raised to levels that are not possible in conventional electrolyte media.

An extension of the ionic liquid concept is the formation of a deep eutectic solvent (DES) [44,45], formed by mixing a suitable combination of a solid quaternary ammonium salt (QAS) and a hydrogen bond donor (HBD). In general, the HBD forms a complex with either the cation or anion of the QAS. In the present study, the QAS is choline chloride ( $\text{Ch}^+ \text{Cl}^-$ ) and the HBD is either ethylene glycol (EG) or propylene glycol (PG), in each case in a 1:2 molar ratio of QAS:HBD. In these formulations (formally denoted Ethaline 200 and Propaline 200, respectively, to indicate stoichiometry, but hereafter referred to simply as Ethaline and Propaline), the HBD complexes the anion, to give a fluid that is mixture of  $\text{Ch}^+$  cations and  $[(\text{EG})_2\text{Cl}]^-$  or  $[(\text{PG})_2\text{Cl}]^-$  anions.

A recent report [46], based on electrochemical and acoustic wave (EQCM) data, showed that the ion transfer processes accompanying PEDOT redox switching in Ethaline 200 and Propaline 200 are different to each other and to those in a conventional acetonitrile-based electrolyte. Overall, we seek an understanding of ion dynamics accompanying PEDOT (un)doping in DES media. Specifically, we wish to determine the individual contributions of anion and cation to maintenance of electroneutrality as functions of timescale and polymer charge state (doping level). Second, we wish to identify the rate limiting process; this is important both for fundamental and practical reasons. Third, simple considerations show that some mechanistic possibilities, e.g. cation ejection upon film oxidation, require the presence of a “reservoir” of net neutral electrolyte (“salt” in the parlance of the ion exchange literature [47,48]). We therefore wish to establish the population of the film-based reservoir able to support this process.

In a recent EQCM study [46] we showed that during the potentiodynamic oxidation (p-doping) of neutral (undoped) PEDOT exposed to  $\text{LiClO}_4/\text{CH}_3\text{CN}$ , to Ethaline and to Propaline, respectively, the film mass increased, decreased, and varied non-monotonically (decreased then increased). This indicated anion entry in acetonitrile (the anticipated result in a conventional electrolyte), cation ejection from a DES swollen film in Ethaline, and a mixed mechanism in Propaline. Qualitatively, these observations were compelling, but each medium presents its challenges to the EQCM. In the case of a conventional electrolyte, there are three mobile species (anion, cation and solvent) so, strictly, measurement of mass (*via frequency*) and charge is an under-determined situation and one is obliged to make the approximation of permselectivity at modest electrolyte concentrations [47,48]. In DES media this chemical problem does not exist, since there is no “solvent”, but the high fluid viscosity makes the acoustic measurement physically much more difficult, since the resonance is highly damped and less precisely defined, even in the absence of film viscoelastic phenomena [46].

Previously, we demonstrated the power of the combined EQCM/probe beam deflection (PBD) technique [49,50] in situations where complex mobile species transfers occur at electroactive film/electrolyte interfaces. The PBD technique (sometimes referred to as the “mirage effect”) is a contactless optical method in which deflection of a light beam (generally from a small laser) passing close and parallel to the electrode surface is used as a measure of interfacial concentration gradients [51]. In the present context, these concentration gradients are generated by redox-driven exchange of species between an electroactive film and the electrolyte to which it is exposed. From a mathematical perspective, the problem is now uniquely defined: three measurands (charge ( $Q$ ), mass change ( $\Delta m$ ) and optical deflection ( $\theta$ )) permit unambiguous determination of the three mobile species population changes. More subtly, the acoustic and optical techniques are complementary in two respects. First, one (QCM) probes the “dry” side of the interface and the other (PBD) probes the “wet” side of the

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