



Electroactive polymers made by loading redox ions inside crosslinked polymeric hydrogels. Effects of hydrophobic interactions and solvent dynamics



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ABSTRACT

Electroactive polymers are made by loading redox complexes inside different polymeric crosslinked hydrogels. A redox cation (tris(phenanthroline)iron(II) (TPFeII) is sorbed in anionic, neutral and cationic hydrogels while redox anions (ferricyanide) is taken up inside an anionic hydrogel. Moreover, a redox anion (nitrite) and a cation (TPFeII) are simultaneously absorbed in an anionic hydrogel. Homopolymeric hydrogels of 2-acrylamidopropanesulfonic acid (PAMPS), acrylic acid (PAA) or (3-acrylamidopropyl) trimethylammonium chloride (PAPMTAC), crosslinked with bisacrylamide, are synthesized by radical polymerization. The same method is used to produce a 1:1 copolymeric hydrogel of acrylic acid and 2-acrylamidopropanesulfonic acid (PAA-co-AMPS). The physicochemical properties of the hydrogels are evaluated by measuring the swelling kinetics, in the same conditions of the electrochemical measurements. The cyclic voltammetric response of all electroactive polymers show quasireversible electron transfer (E_{qrev} mechanism) while the hydrogel loaded with TPFeII and nitrite show a catalyzed oxidation (E_{qrevC} mechanism). The electrochemical parameters (diffusion coefficient and charge transfer constant) of TPFeII loaded inside PAMPS, PAA and PAA-co-AMPS are measured using chronoamperometry and digital simulation of the cyclic voltammetry. The Stokes-Einstein equation is used to calculate the effective viscosity of the hydrogel matrixes using the diffusion coefficients of a redox complex (TPFeII) determined inside the hydrogels and the same parameters determined in aqueous solution. The calculated viscosity correlates, with a negative slope, with the swelling rate constant of the hydrogel matrix. The heterogeneous charge transfer of the redox complex inside ionomers (PAMPS and PAA-co-PAMPS) is nearly as fast as in solution, while the charge transfer inside the neutral PAA is ca. 100 times smaller. The measured charge transfer constants correlate with the calculated viscosity, revealing the effect of solvent dynamics on the charge transfer, according to Marcus theory for strongly adiabatic electron transfer. In that way, it is shown that the electrochemical measurements are able to monitor the local solvation properties of the hydrogel matrix. These results suggest novel ways to produce electroactive polymers by loading redox active substances inside hydrogels, even when the hydrogel matrix is neutral or bear the same charge than the redox probe. The redox complexes are present as dilute solutions and the hydrogel dimensions fulfill the semi-infinite diffusion boundary conditions. Therefore, the data analysis can be performed using the theoretical framework for electrochemical measurements in liquid solvents.

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1. Introduction

Electroactive polymers are materials of great interest both for basic understanding [1], and technological applications [2]. Lyons, [3] define three main kinds of electroactive polymers, which are:

conducting polymers, redox polymers and loaded ionomers. All contain entities that can exchange electrons with a conductive substrate giving rise to an electrochemical response. In redox polymers the electrons are transported by electron hopping between neighboring redox centers [4]. In loaded ionomers the electrons are transported across the materials by physical diffusion/migration of the loaded redox species [5,6], while a contribution of electron hopping between neighboring redox centers to charge transport is possible if the internal concentration

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is high enough [7]. Conducting polymers could act as three dimensional electrodes since they have intrinsic electronic conductivity [8]. However, if the conductive matrix is not electrically connected, electron hopping between conducting domains could occur.

In all electroactive polymers mass transport of mobile counterions/coions inside the polymer need to be coupled with electron transport to maintain electroneutrality. Therefore, some concentration of mobile ions is required to be present inside the polymer. While there are neutral redox polymers (e.g. polivinylferrocene), the material insert ions during oxidation and a process of loading with electrolyte solution (“break in”) is observed [9]. In the case of conducting polymers, they are usually produced in the salt state, where an stoichiometric amount of counterions is present. However, when the polymers are electrochemically reduced, the amount of counterions decreases and the film become neutral. This is likely to be one of the reasons that the oxidation depends on the level of reduction, the so called “memory effect” [10,11]. In the case of loaded ionomers, the ionic conductivity is high due to the presence of large concentrations of mobile counterions of the fixed charges in the ionomer. Since in this paper we propose to study not only loaded ionomers but loaded neutral hydrogels, the situation can be different and should be taken into account [12].

The electrochemistry response of electroactive polymers depart from a simple model of a single electron transfer at the electrode/polymer interface coupled to some form of charge transport across the polymer sample [1,2]. In the case of redox moieties covalently linked to the polymer, the mobility and microenvironment can affect the concentration/potential relationship [13]. While it is usually assumed that the linked redox species (e.g. ferrocene) has the same physicochemical properties than the same species in solution, this is usually not the case [14].

Moreover, since usually the concentration of redox sites is usually large (>0.1 M), even in the case of loaded ionomers with well-known redox species, infinite dilution conditions cannot be assumed and therefore activity effects could be present. The usual way to measure electrochemistry of electroactive polymers is depositing a film of the material, containing redox moieties, on a solid electrode (e.g. glassy carbon) [15].

In the case of loaded ionomers, the redox species is then sorbed from aqueous solution inside the deposited film [16].

The polymer film has to be wetted by the solvent but the whole polymer film needs to be insoluble in the solution. This is achieved by using polyelectrolytes with hydrophobic domains which crosslink the film during deposition by solvent evaporation (e.g. Nafion[®]) or by chemical reaction of the polymer chains (e.g. polyvinylpyridine) with a crosslinker (e.g. 1,4-dichlorobutane). Another method involves layer-by-layer self-assembly of opposite charge polyelectrolytes [17]. In the case of conducting polymers, the monomer is oxidized on the electrode forming a slightly soluble polymer which adsorbs on the electrode, while following layer are retained by non-covalent interaction between polymer chains [18]. Those methods are difficult to control and the deposition conditions strongly influence the solid state properties [19].

Moreover, the characterization of solid state properties of the polymers like swelling, porosity, elasticity, is quite difficult due to the small dimensions of the polymer films [20]. Therefore, it is usually assumed that the properties are the same that bulk materials which is usually not the case due to different formation procedures. Additionally, deposited films could show large difference between the layers closer to the substrate (electrode) and those in the bulk of the film [21]. The use of polymer films deposited on electrodes makes the electrochemistry easy because the hydrogel is contacted in the innermost layer with the electrode and the outside layer is exposed to the solution [22]. However, in

thin films the semi-infinite boundary condition, usually assumed in liquid solutions, is not necessarily fulfilled. The thickness of the diffusion layer inside the film depends on the mass transport parameters, the time frame of the measurement (e.g. scan rate in cyclic voltammetry) and the thickness of the film. Three regimes can exist: i) a semi-infinite layer with diffusion; ii) a thin layer with complete electrolysis and (iii) a finite diffusion layer. While the (i) and (ii) are amenable for data analysis, (iii) has a complex dependence on the thickness and morphology [23]. Indeed, Leddy and coworkers have recently proposed a diagnostic criteria for cyclic voltammetry which allows to know in which regime is the experimental measurement [24]. In any case, the determination of diffusion coefficient requires measuring at short times (high scan rates in cyclic voltammetry) where other effects (capacitive and heterogeneous charge transfer) are usually important [25]. Since thin layer conditions can be achieved, at long times (chronocoulometry) or small scan rates (cyclic voltammetry) the number of moles of active species can be calculated from the measured charge. However, to calculate the concentration, the thickness needs to be known. This value is usually done ex-situ and likely does not represent the in-situ thickness [5].

In the present work we describe a new system, related to loaded ionomers with redox species, where well known redox species are adsorbed, at low concentrations, inside neutral or charged bulk hydrogels. The hydrogel samples are thick enough to assure semi-infinite conditions.

Hydrogels made of crosslinked polymer matrixes are interesting materials for different technological applications: drug release, chemical actuators, sensors, etc. [26,27]. Polyacrylamides, [28] and related materials (e.g. poly(acrylic acid) have been extensively studied [29]. The materials can be easily synthesized by radical polymerization in water or similar solvents [30]. An additional advantage is the widespread availability of monomers combined with the feasibility of copolymerization allowing to create crosslinked polymers bearing different functional groups. In that way, different chemical structures can be easily built [31]. Moreover, hydrogels responsive to chemical or electrochemical oxidation have been devised [32]. However, the electrochemical properties of such materials have been scarcely studied.

In ionomers (e.g. Nafion[®]) loaded with redox species (e.g. Fe(bpy)₃²⁺) the redox couple could physically diffuse as in a dilute solution. However, when the concentration of redox species is large enough, neighboring species of different redox state could exchange electrons; such a process could contribute to mass transport or even dominate it. The formalism to model the phenomena was developed by Dahms [33], and Ruff [34], for concentrated solutions of redox species in liquids. In the case of polymers, besides the bulk concentration, the possibility of phase separation due between hydrophobic and hydrophilic domains in the hydrogel has to be considered. Indeed, in Nafion[®] the proton diffusion through the membrane does not occur as a bulk diffusion process but as a percolation controlled process between hydrophilic domains containing $-SO_3^-H^+$ groups, which are surrounded by hydrophobic domains containing fluorinated chains [35]. Such considerations have been taken into account by Leddy and coworkers for the understanding of the electrochemistry of redox couples (e.g. Ru(bpy)₃²⁺) in electrodes modified with Nafion[®] films [36].

Unlike films deposited on electrodes, macroscopic hydrogels can be easily characterized in terms of chemical structure [37], swelling capacity [38], porosity [39], mechanical properties [40], and inner concentration [41]. Previously, we found that metallic complexes (e.g. Ru(bpy)₃²⁺) are strongly retained inside the polymeric hydrogels, even neutral ones [41]. Therefore, electroactive hydrogels could be produced not only by loading redox ions on ionomers bearing groups with the opposite charge but also

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