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Interpenetrated triple polymeric layer as electrochemomechanical actuator: Solvent influence and diffusion coefficient of counterions

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ABSTRACT

Full polymeric trilayers formed by two lateral polypyrrole-dodecylbenzoesulfate (PPyDBS) films interpenetrating a polyvinylidene fluoride (PVdF) central membrane were electrochemically characterized. Square wave voltammetric and square wave amperometric responses in 0.5 M $LiClO_4$ solutions using different solvents was undertaken with parallel video-recording of the reversible angular displacements. According to the bending movements in aqueous and ethylene glycol (EG) solutions the PPyDBS films shrunk upon oxidation and swelled during reduction: the electrochemical reactions drive the exchange of cations in both solvents. In propylene carbonate (PC) and acetonitrile (AN) solutions the PPyDBS films swelled and shrunk by oxidation and reduction, respectively, driven by the exchange of anions. Propylene carbonate and acetonitrile hinder the dissociation of the LiDBS ionic couples inside the PPyDBS film forcing the exchange of anions to compensate polarons on polypyrrole. The diffusion coefficient of the exchanged ions and the angular rates follow the sequence: aqueous > PC > AN > EG solutions. Whatever the solvent, actuators are Faradaic devices: the described angle is a linear function of the consumed charge.

1. Introduction

Conducting polymers are supporting the development of two different technological domains constituted by solid-state (constant composition) devices or reactive and biomimetic devices where the polymer/counterion/solvent relative composition changes during actuation [1,2].

Solid state and transparent semiconducting films can support the reconstruction of electronics, microelectronics and optoelectronics giving full polymeric and transparent devices. A solid theoretical background developed during the past century is supporting Engineers and Device Designers for a fast technological development of well-known devices such as capacitors, LEDs or transistors [3]. These are solid-state physical devices: their actuation does not include any chemical or electrochemical reactions.

In addition conducting polymers offer the possibility to develop new biomimetic devices as actuators [4,5], smart windows [6,7], sensors [8], biomedical devices [9], and composites [10], flexible electrodes [11] or super capacitors [12], among others. They are reaction-driven devices: electrochemical reactions include the device constitutive polymer as one of the reactants, driving the exchange of ions and solvent with the electrolyte. The reaction of the constitutive material drives the device actuation, as happens with biological organs [2,13]. During actuation the composition (polymer/counterion/solvent) of the conducting polymer shifts by exchange (entrance or expulsion) of ions for charge balance and solvent for osmotic balance with the electrolyte. Oxidation and reduction reactions drive the reversible actuation of each device and the actuation rate [14]. Both composition (reactive macromolecules, ions and solvent) and reaction-driven actuation of these devices mimic natural organs from living beings: they are electro-chemo-biomimetic devices. Thus, materials, reactions and

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devices can be considered as basic models for a better description of life chemistry [15,16], which constitutes one of the present scientific borders. This is the context for this paper.

Unlike well-known physical devices, the development of reliable industrial biomimetic devices, as polymeric actuators (also named artificial muscles), lacks of a solid theoretical chemical background identifying, describing and quantifying how the intermolecular forces change inside the conducting polymer during reactions. The task to decipher those shifting interactions is complex but very stimulating because any attained chemical model should support the development and improvement of robust and reliable biomimetic devices, tools and robots, like sensing-muscles or artificial proprioceptive systems [17]. In parallel it should provide basic models for the quantitative description of life chemistry and life functions, and predict malfunctions.

Different models such as polaron/bipolaron transitions [18], the reversible σ-dimerization [19] models, the conducting/insulator transition model [20] and the electrochemically stimulated conformational relaxation (ESCR) model [15,21,22] have been proposed to explain the electrochemical responses from conducting polymers and other electroactive organic or carbon based materials. The ESCR model includes reaction-driven conformational and structural changes [23]. It describes solvent [24,25], electrolyte [26] or overoxidation [27] influence and the simultaneous dual actuating-sensing nature of any reaction-driven biomimetic device [22], and provides a good approach to decipher the polymer-polymer and polymer-solvent interaction variations during reactions.

Bending artificial muscles (bilayer or triple layer) transduce very small reaction-driven volume variations (due to the exchange of ions and solvent) in films of conducting polymers into large (>20°) angular displacements [17]. For films of conducting polymers generated in the presence of small anions the reaction driving their actuation is usually simplified as follows:

$$\left(\mathrm{Pol}^0\right)_s + n(\mathrm{A}^-)_{sol} + m(\mathrm{S}) \rightleftarrows \left[(\mathrm{Pol}^{n+})_s(\mathrm{A}^-)_n(\mathrm{S})_m\right]_{gel} + n(\mathrm{e}^-) \qquad (1)$$

where the different subindices mean s, solid; sol, in solution; Pol^0 represents the active sites along each polymeric chains where a positive charge will be stored after oxidation; A^- are the anions entering from the solution for charge balance (counterion) and S are the solvent molecules exchanged for osmotic balance forming a dense gel (indicated by sub index gel). The polymer swells and shrinks during oxidation and reduction, respectively, originating the concomitant reversible bending of bilayer and triple layer actuators.

For those conducting polymers generated in the presence of large anions, as with films of polypyrrole-dodecylbenzoesulfate (PPyDBS), the macroanion (MA^-), in this case the DBS^-, remains trapped during electrochemical (oxidation/reduction) reactions in presence of electrolytes. The trapped anions force the exchange of cations (C^+) and solvent (S) for charge and osmotic balance [28–30]:

$$\left[\left(\mathrm{Pol}^0\right)(\mathrm{MA}^-)_n(\mathrm{C}^+)_n(\mathrm{S})_m\right]_{gel} \rightleftarrows \left[(\mathrm{Pol}^{n+})(\mathrm{MA}^-)_n\right] + n(\mathrm{C}^+) + m(\mathrm{S}) + n(\mathrm{e}^-) \qquad (2)$$

The polymer shrinks and swells during oxidation and reduction, respectively: cation-driven actuators give during the same reaction (i.e. oxidation) opposite displacements to those observed from anion-driven actuators (i.e clockwise vs. anticlockwise bending). As a consequence those polymeric actuators are useful tools to clarify the reaction-driven ionic exchanges (anions or cations) [31].

The presence of mixed (anion and cation) ionic exchanges during redox cycles should originate unpredictable actuation [32]. Recently [33], a consecutive exchange of cations and anions was deduced from the movement of PPy–HpPS/tape (para-phenolsulfonic acid, intermediate anion size) bilayers when cycled in NaCl electrolytes. Free-standing PPyDBS films studied in sodium chloride aqueous solutions revealed the increase of the chloride content in deep oxidized films, indicating the existence of free oxidized PPy chains, not balanced by DBS^- macro ions, which force the entrance of Cl^- for charge compensation [34]. Changes from cation- to anion-driven actuation in $\mathrm{TBACF_3SO_3}$ propylene carbonate solutions have been observed in PPyDBS-PVdF linear films [35]. Studies of the anion mobility in PPyDBS films revealed some DBS^- exchange in $\mathrm{NaClO_4}$ ethanol solutions [36] that can be evoked by osmotic pressure [29]. Both, PPyDBS and $\mathrm{PPyClO_4}$ films exchange anions in $\mathrm{NaClO_4}$ propylene carbonate solutions during redox reaction [37]. In parallel to ionic exchanges huge amount of solvent is exchanged as determined by EQCM measurements [29] or using bending bilayer actuators [38–40]. Higher specific charges are stored in the same CP film from solvents having higher dipolar moments and lower polarizability [41]. All those results point to a great influence of the solvent on the intermolecular forces (polymer-polymer, polymer-anion, polymer-cation, polymer-solvent, and anion-cation) and their variation inside the conducting polymer during reversible oxidation/reduction. PPyDBS/PVdF/PPyDBS interpenetrated trilayer actuators allow the study in different organic solvents where the PVdF layer is non soluble. The interpenetrated nature of the polypyrrole layers below the PVdF surface avoids peeling effects during actuation [42]. Recent studies [24] have revealed that in presence of the same solved salt $\mathrm{LiClO_4}$ in different solvents (water, ethylene glycole, acetonitrile or propylene carbonate) the solvent influences the reaction-driven actuation (anion, reaction 1, or cation, reaction 2, driven actuation).

Here triple layer full polymeric artificial muscles (PPyDBS/PVdF/PPyDBS), will be used as macroscopic tools for the clarification of those reaction-driven intermolecular forces inside PPyDBS films and its consequences on large bending movements in different solvents. Square wave voltammetric or square wave amperometric experiments at different frequencies will control the oxidation/reduction driven actuation. The diffusion coefficient in relation to actuation rate will be discussed and corroborated by SEM analysis of the oxidized and reduced films.

2. Materials and Methods

2.1. Materials

N,N-dimethylacetamide (DMAc, ≥99.5%) was obtained from Fluka and used as received. Commercial Durapore (Millipore) polyvinylidene fluoride (PVdF) membranes (thickness 110 μm, hydrophilic, porosity 70%, pore size 0.1 μm) were used for PVdF-based samples. Sodium dodecylbenzenesulfonate (NaDBS, 99%), ammonium peroxydisulfate (APS, 98%), ethylene glycol (EG, 99.8%), acetonitrile (AN, 99.8%), propylene carbonate (PC, 99%) and lithium perchlorate ($\mathrm{LiClO_4}$, 95%) were obtained from Sigma-Aldrich and used as supplied. Pyrrole (Py, ≥98%) from Sigma-Aldrich was distilled prior to use and stored in the dark under nitrogen atmosphere at low temperature.

2.2. Preparation of PPy(chem.)-PVdF-PPy(chem.) and electropolymerization of PPyDBS

In order to make the PVdF membrane conducting enough to allow electrochemical polymerization, an initial chemical polymerization of PPy material oxidized with APS was carried out using a method developed recently that avoids delamination and increases actuator life-time [42]. PVdF (3 × 3 cm) membranes having a thickness of 110 μm (measured using an electronic