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A unified bottom up multiscale strategy to model gas sensors based on conductive polymers

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ABSTRACT

A multiscale bottom up procedure, based on an atomistic description, able to model the sensing mechanism of devices based on intrinsic conductive polymers (ICP) is described. The proposed procedure has been successfully applied to describe the response of devices based on polyaniline (PANI), the most widely used material for this application. In particular, using a recently developed Monte Carlo technique, atomistic PANI structures at different doping levels have been modeled. Thermodynamic and conductivity properties obtained from atomistic simulations have been bridged to a macroscopic modeling scheme, describing diffusion and reaction processes and, finally, the time dependent sensor response in good agreement with experiments. A similar scheme has been then adopted in order to understand at molecular level the effect of humidity in the sensor response. The proposed approach is general and can be extended to different or more complex systems giving a useful connection between the microscopic structure of the sensing material and the sensor behavior.

1. Introduction

The electrical conductivity of intrinsically conducting polymers (ICP) is affected by exposure to various gases and it makes them useful for gas sensing application [1–4]. Sensors based on ICP are able to operate at room temperature, furthermore, ICP can be synthesized through easy chemical or electrochemical processes and modified conveniently by copolymerization or structural derivations [1–5]. On the other hand, micro- and nano-patterning of these sensing materials and formation of ultrathin sensing films facilitate enhanced vapor diffusion and response speed when compared to conventional polymeric films.

Doping and undoping processes play key roles in the sensing mechanism of ICP based sensors [5,6]. ICP can be doped by redox or protonation reactions. In the case of redox reaction some electrons are added or removed from ICP chains and charge carriers are formed. Differently, in the case of protonation reactions, the number of electrons does not change, but due to addition or removal of protons, the energy levels of ICP chains are rearranged. This doping type is observed in polyaniline (PANI) (see Fig. 1b). During the doping process conductivity of ICP can increase by up to 10 order of magnitudes. The conductivity may be also changed by modifying dopant type and material preparation method, however the effect of these structure modification is less strong and the resulting conductivity change of doped PANI is usually less than 2 orders of magnitudes [7,8]. Polyaniline in its forms (see Fig. 1) emeraldine base (PANI EB) or salt (PANI ES) are most widely used ICPs because of its ease of synthesis, high chemical and environmental stability and tunable properties [6,9–14].

Modeling the response of sensor to analyte gases at atomic level is particularly relevant to improve the development of devices [15]. Despite large interest in the potential applications of conducting polymer as gas sensors, a detailed molecular picture of the sensing mechanism of PANI (and more in general ICP) based devices is still under debate [5,6,16]. For example though importance of humidity in the PANI sensing mechanism [5], molecular understanding of response of PANI to humidity is not well established and several different mechanisms have been proposed: polymer swelling, increase in the interchain electron transfer and enhancement of dopant ions mobility [17,18]. Last but not least, there is no commonly accepted model for the charge transport in ICP [19].

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The steady state response is basically controlled by interaction of gas molecules with sensing material, while the time-dependent response depends also on transport of gas molecules inside sensing material. Several macroscopic phenomenological approaches have been used to model the time dependent response of sensors based on ICP. In particular, chemisorption and diffusion reaction models are usually used for modeling the time dependent response of conducting polymers. Chemisorption model [20] assumes that the sensing properties are completely defined by dynamics of surface adsorption and is proposed for very thin films. Diffusion reaction model [16] assumes that the guest molecules go quickly to the surface, but the limiting step for sensing is the diffusion of gaseous species into the polymer bulk. Although these approaches are very useful to understand the effects of macroscopic variables (film thickness, transport properties, material conductivity) they have several limitations. In particular, the large number of parameters needed to fit the model results to experimental sensor response makes a molecular interpretation of the behavior very difficult. For this reason, from this kind of modeling, clear indications about possible chemical or morphological alterations aimed to modify or improve the performances in a given direction are difficult to obtain. Furthermore, these approaches need several strong and sometimes oversimplifying assumptions on important aspects such as the behavior of electrical conductivity during the sensing experiments [16,20].

On the other hand, for a microscopic modeling, atomistic simulations are very useful for a detailed understanding of several phenomena and, in particular, for structure properties relationship of polymeric materials these studies have been performed since a long time [21,22]. However, these simulations usually limited on nanosecond and nanometer scales are not applicable to study processes involved in the sensor response occurring on macroscopic time (>s) and length scales (>μm). Therefore, in order to bridge this gap, computational schemes aimed to connect the microscopic and macroscopic descriptions in a bottom to up fashion would be very useful.

In this paper we propose a combination of molecular and finite element simulations to model PANI based gas sensor behavior starting from atomic structure and its modifications during the doping process. In particular, to model the microscopic scale, we propose a scheme based on combination of a recently developed Grand Canonical Monte Carlo technique (UEMC) [23] and the calculation of electrical conductivity from atomistic PANI structures at different doping levels. These results are casted in a diffusion reaction scheme giving a connection between microscopic structures and the response of ICP sensors to analyte gases.

The paper is organized as follows. The method for modeling the electrical conductivity of atomistic ICP structures is proposed in Section 2 and strategy for sensor response modeling is described in Section 3. In particular in Section 3.1 atomistic models of PANI and their electrical behavior are discussed. Finite element method (FEM) simulations of the sensor behaviors are presented in Section 3.2 (response to acidic gases) and analytical expressions for the sensor response to nonacidic gases are proposed in Section 3.3.

2. Methods and models

The electrical conductivity of ICP may be studied by atomistic simulation [24,25]. Once the atomistic structure is obtained, the conjugated segments (hopping sites) are defined, the parameters of Marcus equation [26] for charge hopping rate are estimated by different models and the time evolution of charge is modeled. Though the determination of conjugated segment is often empirical, the simulation of charge transport by these models is too time consuming to study the effect of doping level on ICP conductivity. Here we propose a more simple model, based on existing charge transport models. The existing models are: (1D) variable range hopping (VRH) with interchain coupling [27,28], 3D VRH [29,30], charging energy limited tunneling (CELT) model [31] and others. For detailed reviews see [7,32]. Usually these models suppose that there are conducting regions with insulating separation. The size of PANI conducting regions was estimated to have size 4.98 nm [32] and 8 nm [33] with separation distance 2.8 nm [32] and 1.6 nm [33]. Taking into account that size of PANI unit is about 2 nm (see Fig. 1b), we assume that doped PANI units may be considered as conjugated segment.

The details of atomistic simulation of PANI are given in supplementary material. Both the effect of doping level and the effect of structure modifications, e.g. swelling or chain conformations, on conductivity are included using this molecular description. The scheme proposed here is based on the description provided by the Miller–Abrahams equation, which is a popular charge transport model in disordered organic materials [34,35],

$$\omega = \varpi_0 \exp\left[-\frac{\Delta E}{kT}\right] \cdot \exp\left[-\frac{2s}{L}\right] \quad (1)$$

ω is the probability of charge transfer, s is the distance between two conductive units and L is the model parameter which is often called the localization length. When temperature T is constant we can assume that the temperature dependent term $\Delta E/kT$ is constant

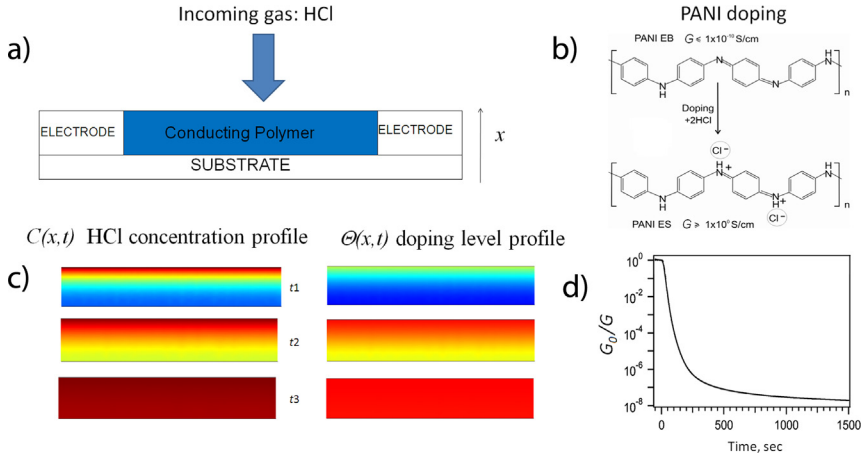

Fig. 1. Schematization of the working scheme of a sensing device. (a) PANI film exposed to an incoming gas, (b) PANI doping reaction with HCl leading to EB and ES forms, (c) gas concentration ($C(x,t)$) and doped level ($\Theta(x,t)$) density profiles, and (d) typical response of a sensing device.