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Modelling electrochemical control of percolation conductivity in short-chain templated conducting polymers

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ABSTRACT

Processible, predoped conducting polymer materials are now commonly formed using a polyelectrolyte backbone as a template material. This results in the conducting portion of the material being composed of a distribution of relatively short-chain oligomers with a corresponding distribution of saturated doping levels. We have investigated the effect of multiple ion doping compensation on the conduction properties of such materials by treating the individual chains as switchable conducting island sites in a percolation matrix. The results of one-, two-, and three-dimensional simulations are compared to experimental results. We show that the measured electrochemical control of material conductivity is best modelled by the simple one-dimensional case which reproduces the characteristic sigmoid-shaped curve. Our findings are consistent with quasi-1D hopping transport between sites, which is the dominant theory for conductivity in this class of materials.

1. Introduction

There have been numerous studies of percolation conduction through many types of homo- and heterogeneous media [1–3]. In recent years there has been a great deal of research into conducting polymers and a large number have been developed for use in a variety of different areas such as anti-static coatings, organic transistors, organic light emitting diodes (OLEDs), etc.

A novel method for producing processible, predoped conducting polymer materials and making them available as either aqueous or solvent-based dispersions has been recently developed by Bayer [4,5]. This method uses a host polyelectrolyte chain, such as polystyrenesulfonic acid (PSSA), as a template for the growth of the conducting polymer, e.g. poly(3,4-ethylenedioxythiophene) (PEDOT) [6], which is then formed into a printable dispersion. This is shown for Bayer's "Baytron P" in Fig. 1. The resultant conducting oligomer chains are ionically bonded to the polyelectrolyte due to electron transfer. This means that the backbone also acts as a dopant since it (normally) accepts electrons from the highest occupied molecular orbital (HOMO) of the chain leaving it p-doped. Studies have indicated that the oligomers grown in this way are relatively short with their length depending on the synthesis conditions. For commercially available Bayer "Baytron P" material they seem to vary between 1000 and 2500 Daltons or lengths of about 8–16 monomer units [7]. As formed, each of these doped oligomer chains can act as a conductive island capable of accepting electrons from neighbouring chains. When they are undoped, however, the HOMO levels are filled and there are no available states so that they cannot accept charge transfer from the HOMO levels of neighbours and conduction is blocked. The chains are short relative to the conjugation length [8] so they will remain strongly conducting even when only singly ionized. The conductivity of the material is therefore dominated by interchain hopping conduction and largely independent of any changes in intrachain conductivity due to doping level. Because of this the chains can be treated as switchable conduction sites that are "on" if they are doped at any level between single ionization and being fully saturated (doping = number of units) and are "off" only if they are completely de-doped with the HOMO level filled.

In this paper we report a simple percolation conduction model and supporting experimental data for the electrochemically controlled response of devices fabricated from templated conducting polymers. This work helps to explain the underlying mechanism responsible for their characteristic behavior and guide material selection and future development. It is shown that the modeled response follows the experimentally determined sigmoid-like characteristics and simulation results corresponding to one-dimensional conduction most closely match measurement.

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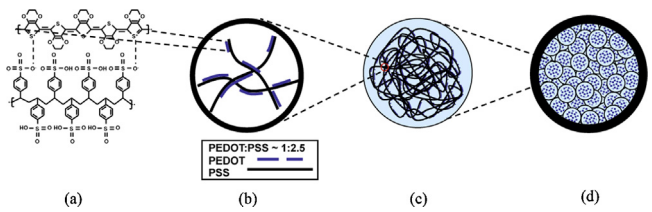

Fig. 1. Templated PEDOT:PSS and its formation into a film. (a) Doped PEDOT chain ionically attached to the PSS backbone. (b) Short PEDOT chains grown *in-situ* on long PSS chains, (c) Water saturated coils dispersed to become processable. (d) Deposited film of dispersed PEDOT:PSS particles.

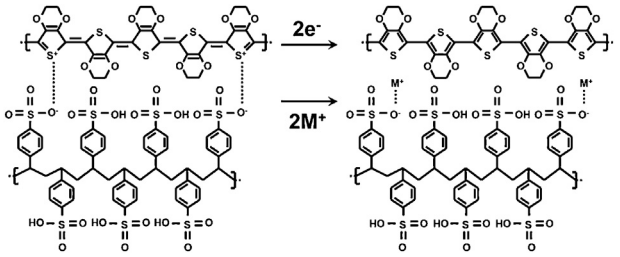

Fig. 2. Intercalation of cations (M+) from the electrolyte causes the normally doped, conducting PEDOT to be reduced to the non-conducting state.

This is consistent with quasi-1D conduction mechanisms that are generally accepted to occur in PEDOT:PSS, though these have not fully explained to date.

2. Simulation method and results

2.1. Assumptions

A number of simplifying assumptions have been made in the implementation of the model system. The system has been represented as a simple *N*-dimensional (ND) regular array of nodes, which has been investigated starting with $N=2$ followed by $N=3$ and finally $N=1$. The electronic transport has been assumed to occur as a site-to-site mechanism with fixed conductance between sites. The sites are assumed to be physically related to the individual oligomer chains and the conductance between sites to the interchain conduction mechanism. In all cases it has been assumed that the conduction is dominated by the interchain portion and that the intrachain conduction is a small factor. This has been taken to be true regardless of the level of doping of the chain i.e. as long as the HOMO 'band' has at least one open state we will assume the site is available. Since the chains are relatively short in comparison to the conjugation length and the interchain mechanism is an average hopping conduction, this is likely a valid assumption. The process modelled is the change in the conductance of a section of material as ions are electrolytically intercalated to compensate the doping. This process is illustrated in Fig. 2 for a short, doubly ionized segment on one electrode with an identical compensated segment at a complementary counter-electrode. With a voltage applied between the two electrodes electrons are transferred between the chains and cations are intercalated from the electrolyte to balance the charge.

It has been further assumed that, as a potential difference is applied between the electrodes, the intercalated ions are distributed randomly when compensating the available doped sites. No consideration has been given to the ion and charge dynamics nor has ion diffusion between chains been taken into account. Finally, there has not been any differentiation between oligomer length and saturated doping level and it has been assumed that the chains are always starting from the fully saturated state when at maximum conductance.

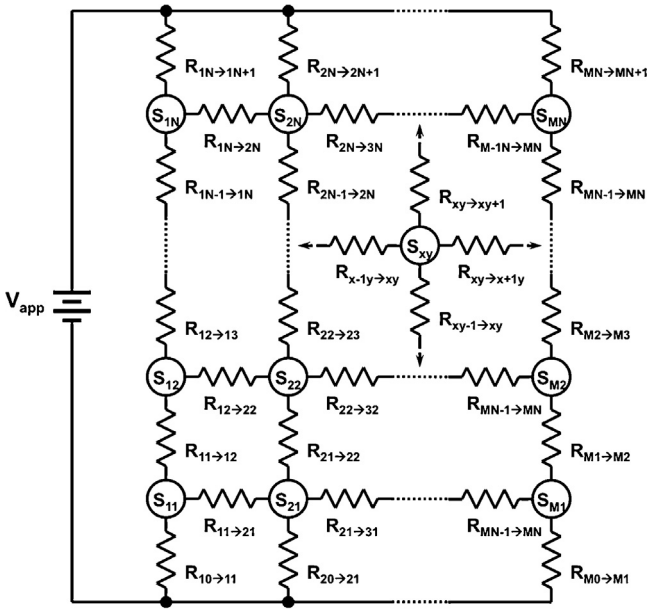

Fig. 3. Grid setup for two-dimensional percolation simulation. The sites, S_{xy} are treated as switches that connect the four incoming connections unless completely de-doped. Inset shows an arbitrary internal node.

2.2. 2D conductivity simulation

2.2.1. Monodispersed oligomers

The simplest problem to investigate is the properties of a two-dimensional (2D) system in which all of the oligomer chains have been grown to the same length on the template chains (although this is impractical in practice). The effect of changing the ratio of a combination of conducting and non-conducting materials on the conductivity of the mixture is a problem that has been previously studied in the literature [9–11]. This is normally used to model the behaviour of conducting composites and is analogous to a special case of the current problem restricted to conducting oligomers of length one, since they can only be singly ionized. The simulation of this simplest case is addressed first. For an array of $N \times M$ sites all the sites initially provide conduction and then each site is turned off at random to simulate the random intercalation of ions which compensate the pre-doped monomer segments (in this special case only one ion is required to block a site by not having any available states at that site). In order to achieve a completely random order of turning off the sites a method due to Newman and Ziff [12] has been used. This is accomplished by creating a vector having a length equal to the total number of sites to be modelled and then filling the sites from the first with a random site greater than or equal to the current site and then swapping the two sites. This process is then repeated for every element. Appendix A illustrates the method in more detail. The 2D model grid was setup as illustrated in Fig. 3. A general square array is shown but for the simulations detailed here all of the interconnecting resistors in the network are of equal value, although there will naturally be a distribution of chain separations and resultant effective hopping resistances. In addition, or perhaps as part of this, the distribution of the number of neighbours will also require consideration (effective coordination number). For the present, both of these are averaged to the uniform grid approximation with equal resistances and a coordination number of four for internal nodes in the 2D case.

Once the random site intercalation order has been determined as outlined above, the effect of intercalating the ions on the overall conductivity of the grid is calculated. This is done by simply alternating between two steps: