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X.-L. Wei and A.J. Epstein

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X.-L. Wei, A.J. Epstein

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The Ohio State University
174 West 18th Avenue
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SIMULATIONS OF THE *IN SITU* CYCLIC VOLTAMMETRY DEPENDENT EPR SPECTRA AND DC CONDUCTIVITY

X.-L. Wei [a], A. J. Epstein [a, b, c]
[a] Chemical Physics Program, [b] Department of Physics, and [c] Department of Chemistry
The Ohio State University, Columbus, OH 43210-1106, USA

Abstract

In situ cyclic voltammetry (CV) dependent EPR and DC conductivity of polyaniline have been reported by many groups. However, the variation of the EPR intensities at two half-wave potentials of the CV scan and the asymmetric CV dependent DC conductivity have remained to be fully accounted for. Here we present in detail a novel quasi-random oxidation model and the related simulation results to interpret the reported in situ experimental results. This model quantitatively describes many phenomena and physical properties found in polyaniline including the origin of the defect states, the variations of the in situ EPR signal during CV potential scan, the effects of the hydrolysis, and the pH-dependent DC conductivity data. The statistical nature of this model suggests its general applicability to the oxidation processes of other conducting polymers. The important roles of nearest neighbor Coulomb interaction and formation of a metallic polaron lattice in the computer modeling are evaluated and discussed.

Keywords: Polyaniline, Electron spin resonance spectra, Cyclic voltammetry, D.c. conductivity, Quasi-random oxidation model, Polaron lattice, Coulomb interaction, Computer simulation.

Introduction

Polyaniline has been an exciting research field for magnetic, electric, and optical studies in both the theoretical and the applied areas. One of the highlights of these research efforts lay in the design and performance of many types of sophisticated *in situ* cyclic voltammetry (CV) dependent experiments, for example, the *in situ* CV/EPR [1-8], *in situ* CV/(DC conductivity) [5, 7-12], and *in situ* CV/optical studies [5, 8, 13-15]. However, many essential questions left as unexplained or remained to be fully accounted for until now. For example, the interpretations on the variation of the EPR intensities at two half-wave potentials of the CV scan and the asymmetric CV dependent DC conductivity have not yet been given until now. In addition, some confusion about conducting mechanisms [4, 7, 8] of emeraldine salt arose from these experiments and remained to be resolved. In this paper, a novel *quasi-random oxidation model* and the related simulation results are presented to account for the *in situ* CV dependent experimental results and to resolve the confusion in conducting mechanisms in conducting polymer materials.

Background

In situ CV/EPR and CV/(DC Conductivity) Spectra. In Figure 1, a typical set of reported *in situ* CV/EPR [2] and CV/(DC conductivity) [7] spectra are shown. We note the following features: (1) The DC conductivity does not rise until the EPR intensity begins to drop, which was suggested to originate from a competition between formation of a bipolaron lattice *vs.* a polaron lattice mechanism [7-9]; (2) the DC conductivity is asymmetric about the vertical axis cross its center of gravity; (3) the EPR peak maxima occur almost coincidentally at the same locations (slightly inward) with those of CV; (4) the two integrated EPR peaks are very different in their intensities (the ratio is about 2 ~ 3) as contrast to the integrated areas of the two CV peaks that are almost equal in size.

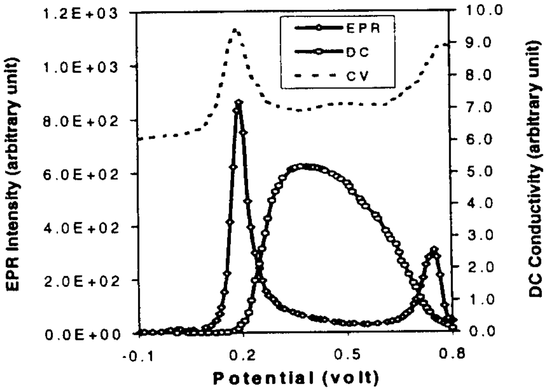

Figure 1. A set of reported *in situ* CV/EPR [2] and CV/(DC conductivity) [7] spectra: All the curves are labeled in the legend box inside the figure.

Quasi-random Oxidation Model. Several assumptions are made in this model [16]: (1) At the early stage of the oxidation process the polymer repeat units are oxidized to polarons; (2) Coulomb repulsion favors the configurations with the largest separation of charged polarons; (3) adjacent pairs of polarons when they do occur have zero magnetic susceptibility [17]; (4) Curie and Pauli susceptibility are separable and are directly related to the CV

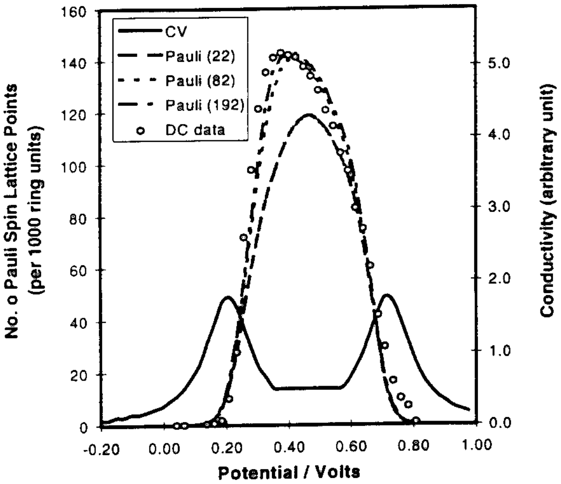

Figure 2. The simulation results of the *in situ* DC conductivity as a function of CV potential scan. Various curves are labeled in the legend table: CV (---), DC conductivity (o) (after Kruszka *et al* [7]), and the number of Pauli spin lattice points for various P_2/P_1 ratios (broken lines).

in situ EPR signal (Curie and Pauli) and DC conductivity (Pauli alone). The detailed discussion can be found elsewhere [19].

Computer simulations. Simulations [19] have been carried out for chain lengths up to 1000 C_6N units. Hundreds (usually 500 or more) of sequential simulations were carried out and their results were averaged. The integrated intensity was normalized to the chain length used in the simulations. Then the normalized oxidation density distribution function was calculated and used in the simulations of CV-dependent spectra. The important contribution of polaron lattice to Pauli susceptibility is included in the simulations at the tenth the susceptibility of room temperature Curie spins [17].

Results and Discussion

The simulation results of CV-dependent EPR spin density converges for an assumed probability ratio of forming 2nd nearest neighbor sites (P_2) to 1st nearest neighbor sites (P_1) of $P_2/P_1 \sim 200$, well agreeing the reported CV-dependent EPR spectra in all features described in previous section [17]. In Figure 1, it is seen that the simulation results of the number of Pauli spin carriers, defined as the number of Pauli lattice points, converge to an asymmetric asymptote with $P_2/P_1 \sim 200$, which fits well to the experimental DC conductivity data (labeled with "o"). This provides evidence for the importance of the polaron lattice formation for high conductivity. In addition, insight can also be drawn for conducting mechanism studies: (1) the DC conductivity is proportional to the number of Pauli spin carriers; (2) the conduction of polyaniline is thus *via* the polaron lattice. Therefore this result disagrees with the bipolaron conduction model for polyaniline samples.

It is noticed that the converged P_2/P_1 ratio yields a dielectric constant ~ 10 [19], a reasonable averaged value of non-conducting and conducting powder samples [20]. Therefore the simulation result is also consistent with the experimental dielectric constant data of PANI. It is worthwhile to note that the presence of the defect states of the base forms of polyaniline and its derivatives is a natural outcome of the *quasi-random oxidation model*, being also a supporting evidence for our model.

Conclusions

A summary of the *quasi-random oxidation model* was presented. The related simulation results showed good agreement with the reported *in situ* CV-dependent spectra. The important role of Coulomb interaction and the formation of polaron lattice were shown.

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