Evolution of Polaron States into Bipolarons in Polypyrrole

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The kinetics of polaron recombination into bipolarons in polypyrrole has been studied by optical-absorption spectroscopy on films doped *in situ* in an electrochemical cell. ESR studies confirm that the metastable states possess spin, while the stable states do not. The data reveal a slow evolution, consistent with polaron-diffusion rates limited by the mobility of the accompanying counterion.

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The observation of high conductivity without ESR absorption[1] in oxidized polypyrrole (PP) films and characteristic optical absorption[2] demonstrate the importance of bipolaron states in this nondegenerate ground-state polymer.[3-5] Bredas *et al.*[6] have shown through band-structure calculations on a deformable polypyrrole chain that both polaron and bipolaron formation are possible on the polymer lattice. Since injection of single charges, for example in electrochemical doping, can only result in polaron formation,[7-9] a strong test of the bipolaron description in this class of materials would be the direct observation of polaron recombination into bipolarons. In this Letter, we report the results of optical and ESR experiments which probe the kinetics of this process.

In situ optoelectrochemical techniques[10] have been used to measure the optical absorption as a function of degree of oxidation (determined by applied voltage) and time. The data reveal electronic states at the predicted[6] polaron energies even at high doping levels. These states evolve with time into electronic levels at predicted bipolaron energies (see Fig. 1). The evolution takes place on time scales typical of mass transport rates, suggesting a novel process wherein diffusion of the counterion is the limiting step in the electronic reaction

$$P_{1/2}^{+} + P_{1/2}^{+} \rightarrow B_0^{++} + \text{phonons}, \qquad (1)$$

where the subscripts indicate the spin of each species. Parallel *in situ* ESR-electrochemical experiments reveal a spin signal which appears for a comparable time after changing the oxidation state of the polymer.

Polypyrrole films were prepared by electrochemical polymerization under dry-box conditions as described elsewhere.[11] These films may be repetitively reduced and reoxidized electrochemically. Samples were prepared on conducting (indium–tin oxide coated) glass at current densities of 0.2 mA/cm^{-2} for ~10 min. The films obtained were ~2000 Å thick based on a density of 1.48 g/cm,[4,12] a ratio of 2.3 electrons per pyrrole unit,[11] and known film area.

It is important to consider the consequences of the nondegenerate ground state of the polypyrrole chain.[3] Removal of a single electron from the chain, accompanied by a lattice relaxation, generates a polaron. Polaron states in the band gap result in three allowed optical transitions (Fig. 1) below the interband transition.[4] In the absence of Coulomb correlations, the sum of the lowest two absorption energies should equal the third. Subsequent removal of electrons may lead to more polarons, or, if pairing of charges is energetically favorable and kinetically achievable, to bipolarons. Soliton formation is prohibited because the creation of two domain walls on a chain results in a region of higher energy between the two charged sites. As a

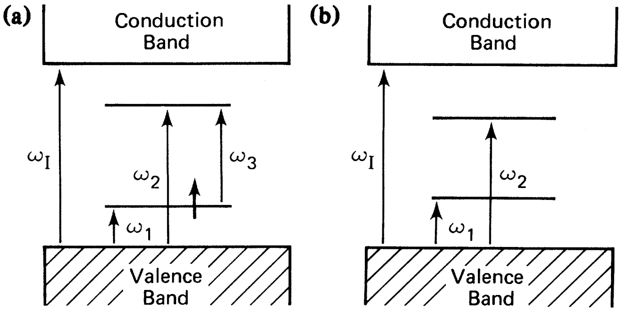

FIG. 1. (a) Energy-level diagram for a polaron state showing allowed optical transitions, ω_1, ω_2, and ω_3. ω_I is the interband threshold. (b) Same for bipolaron state. Note the absence of the transition ω_3.

result, charged defects are bound together as bipolarons (stabilized dications). Bipolaron states in the gap result in only two allowed subgap transitions since the electronic states are either both occupied or, as in the case of polypyrrole which can only be oxidized,[11] both empty.[4]

Previous optical measurements at high doping levels by Yakushi *et al.*[2] reveal two intense absorptions within the PP gap. These have been attributed to the transitions from the valence band into the two wide bipolaron bands which are formed upon doping. At very low dopant concentration, three peaks are observed and explained in terms of polaron states. In this case there is an additional allowed transition, from the occupied lower (bonding) polaron level to the unoccupied antibonding state.

Figure 2 shows the optoelectrochemical data for reduction of polypyrrole film from the oxidized (as-grown) state to nearly neutral. The technique is described elsewhere.[7, 10] The cell is never moved in the course of the experiment. At high doping levels, the spectra reveal absorption maxima at 0.70 and 2.30 eV (± 0.01 eV) with the interband at 3.20 eV (Fig. 2, curves *a*–*d*). Fesser, Bishop, and Campbell (FBC)[4] performed a detailed analysis of the polaron and bipolaron problem for a system with electron-hole symmetry (not strictly true for PP[13]). From their work, we cite four important signatures of optical absorption due to bipolarons: (1) There are two, and only two, absorption peaks in the band gap. (2) The sum of the energies of these two peaks corresponds to the interband transition. (3) The lower-energy peak is more intense. (4) As oscillator strength is transferred from the interband to the gap absorption (with doping), suppression of the interband comes preferentially from the band edge. This results in the apparent shift of the interband transition to higher energy at higher dopant levels.

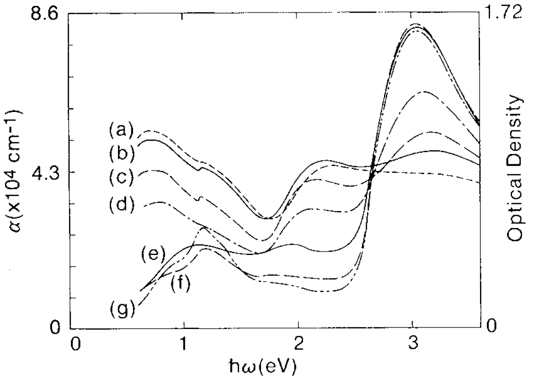

FIG. 2. Sequence of optical spectra of polypyrrole taken during reduction, at various times after a voltage step in the electrochemical cell: *a*, 2.98 V, 1 h; *b*, 2.90 V, 30 min; *c*, 2.80 V, 30 min; *d*, 2.75 V, 1 h; *e*, 2.70 V, 12 h; *f*, 2.40 V, 30 min; *g*, 2.20 V, 30 min. The corresponding dopant concentrations are 20, 15, 11, 9, 5, 2, and ~0.5 mole%, respectively.

The data in Fig. 2 are in good agreement with these signatures. The sum of the two absorption energies corresponds approximately to the interband edge at 3.00 eV. The lower-energy absorption is more intense, and at higher dopant levels, the interband transition shifts to higher energy. The data demonstrate that the transition, at 1.18 eV between localized polaron levels, is observable even at high concentrations when equilibration times (after displacing the cell from equilibrium potential) are kept small. Spectra *b, c, f,* and *g* were taken at $\frac{1}{2}$ h or less after stepping the applied voltage. In the dilute doping regime (*f* and *g*), the absolute intensity of the polaron feature increases, as doping level decreases—the extra oscillator strength coming from the bipolaron signatures.

Spectra taken after 1 h (curves *a* and *d*) show attenuation of the polaron feature which appears only as a shoulder to the lower-energy bipolaron absorption. Spectrum *e*, 12 h after stepping the voltage, reveals *only* bipolarons in the band gap.

Successive spectra over a narrower range below 1.80 eV were taken as a function of time at fixed voltage. The data in Fig. 3 demonstrate this evolution at low doping (2.2 V vs Li). The spectrum shown in Fig. 3, curve *a*, was obtained in equilibrium at 2.4 V; the potential was then stepped to 2.2 V and the spectra *b*–*e* taken after times of 40 min, 1 h 20 min, 4 h 35 min, and 15 h 45 min. Initially (Fig.

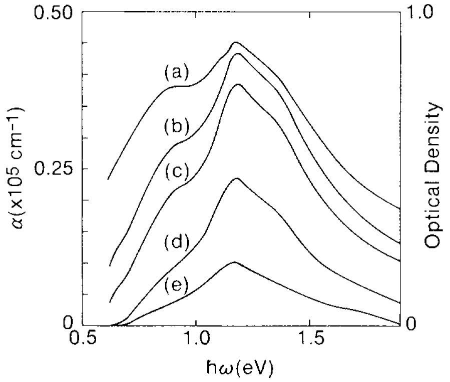

FIG. 3. Successive spectra over the limited range 0.62 to 2.0 eV at various times after a voltage step from 2.40 to 2.20 V: *a*, in equilibrium at 2.40 V; *b*, 40 min after step; *c*, 1 h 20 min; *d*, 4 h 35 min; *e*, 15 h 45 min.

3, curve b) the intensity of the bipolaron feature at 0.8 eV decreases, while the polaron (1.2 V) absorption shows a relatively small change. By the time spectrum c was taken, current had virtually stopped flowing, and the continued evolution of the spectrum reflects the redistribution of charges already present in the sample. After the initial increase of polaron-to-bipolaron ratio (Fig. 3, curves $a-c$), the entire midgap absorption profile decreases in intensity (Fig. 3, curves d and e). Recall that polaron states lead to upper (ω_3) and lower (ω_1) transitions at energies very similar to those of the bipolaron transitions. Then the marked reduction in absorption at the uniquely polaron peak ($\omega_2 = 1.2$ eV), and the relatively smaller decrease at 0.8 eV after 15 h, demonstrate the recombination of polarons into (half as many) bipolarons.

In order to demonstrate that the species created during charge injection or removal have the spin properties expected for polarons, we constructed an electrochemical cell which could be operated in the cavity of an ESR spectrometer. Each time the voltage across the cell was changed, the spin intensity was observed first to increase, and then to decay on a time scale of order 10^3–10^4 sec. Quantitative details of this experiment will be presented in a future publication.

The creation of singly charged polaron states by removal or addition of electrons is expected on the basis of simple ideas of electrochemistry, and the subsequent recombination of free polarons to form bipolarons is a natural consequence of the nondegeneracy of the polypyrrole ground state. However, the fact that these reactions can be observed with optical measurements, and that the latter proceeds at rates characteristic of ionic diffusion, is a novel phenomenon in semiconductor physics. It should be noted that this behavior is not observed in similar nondegenerate ground-state polymers such as polythiophene,[7] or poly(β,β'-dimenthylpyrrole).[14] This may be understood in terms of the degree of structural order of the different materials.[15] For poly(β,β'-dimethylpyrrole),[16] and probably PP and polythiophene, the average chain length is many times the spatial extent of a bipolaron (~ 4 rings).[6] However, even if a chain can accommodate a large number of polarons, the defects must be close enough (within ~ 4 rings) for interaction to occur and/or the mobility along the chain must be high. Alternatively, a polaron can hop to a neighboring chain if the chain (and target polaron) are sufficiently close. The probability of both of these processes depends on structural order (density and perfection of chains). Okuno and Onodera[17] demonstrated that, in the Takayama-Lin-Liu-Maki[18] continuum model, a polaron can move through a soliton with no cost in energy. If this argument carries over to the passage of polarons through bipolarons, then polarons formed on long highly ordered chains will recombine rapidly by the nonadiabatic reaction, Eq. (1). Materials less well ordered and with characteristically short conjugation lengths may exhibit polaron trapping, requiring polaron hopping for recombination to occur. If the distance a polaron must travel (or hop) is large, then the rate of polaron recombination is limited by diffusion of the accompanying anion. In polypyrrole, this diffusion rate is slow enough for optical and ESR observation of the polaron species.

Since polarons and counterions are injected at the electrolyte interface of the polymer, the time for a uniform distribution to be established, after the current stops flowing, depends on the free-diffusion constant of the counterions: $D \sim l^2/\tau$, where l is the thickness of the polymer film (about 2000 Å) and τ is the characteristic time measured in the experiment (10^3 sec). Hence $D \simeq 10^{-12}$ cm^2 sec^{-1}. This is somewhat smaller than the ionic diffusion constant for ClO_4^- in polypyrrole measured electrochemically (i.e., in the presence of an electric field) by Genies, Bidan, and Diaz[19] ($D_0 \sim 2.5 \times 10^{-10}$ cm^2 sec^{-1}). However, it has been shown theoretically[20] that the diffusion rate in an electric field is considerably enhanced over free diffusion. Indeed Genies found that the larger the potential step, the greater the observed diffusion rate.

In summary, we have shown that electrochemical oxidation or reduction of polypyrrole gives rise, initially, to an excess concentration of polarons. The evolution of the optical spectrum and ESR intensity, after charge injection, demonstrates the recombination of polarons into bipolarons, on a time scale of several hours. This slow process is consistent with the time required for ionic (mass) transport, and therefore we believe that counterion diffusion is the kinetically limiting step in polaron recombination, and that thermodynamic equilibrium is not achieved during the observation time of several hours.

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