Contribution of Photogenerated Solitons to Photovoltage in Polyacetylene

In a recent Letter[1] Weinberger concluded that, although there is a strong suggestion that photogenerated charged soliton pairs contribute to photoconductivity,[2-4] they cannot produce the observed photovoltaic response of $(CH)_x$ devices. This conclusion cannot be sustained, however, because it is based on a confusion between the chemical potential of the solitons and the energy level they provide for electrons. I show below that the photovoltage arising from charged soliton conduction is the same as that which would arise from band electron and hole conduction.

Let the chemical potentials be μ_{S^+}, μ_{S^-}, and μ_{S^0} for positive, negative, and neutral solitons, respectively. The relations that hold between these potentials in thermal equilibrium are derived from the "chemical reactions" that can take place. A pair of charged solitons can exchange charge to become neutral solitons, leading to

$$\mu_{S^+} + \mu_{S^-} = 2\mu_{S^0}. \tag{1}$$

Other reactions are the combination of an electron with a positively charged soliton or a hole with a negatively charged soliton to form a neutral soliton, giving

$$\mu_{S^+} + \mu_n = \mu_{S^0}, \tag{2}$$

$$\mu_{S^-} + \mu_p = \mu_{S^0}. \tag{3}$$

Combining Eqs. (1)–(3) we obtain

$$\mu_{S^-} - \mu_{S^+} = \mu_n - \mu_p = 2\mu_n. \tag{4}$$

In the absence of illumination, in an intrinsic region, which we shall assume the junction region to be, the condition $n = p = n_i$, the intrinsic number of carriers, requires that μ_n and $-\mu_p$ be at midgap. When the Fermi energy is at midgap, by symmetry ρ_{S^-}, the number of S^-'s, equals ρ_{S^+}, the number of S^+'s, and $\mu_{S^-} = \mu_{S^+}$. According to Eq. (4) we must then take $\mu_n = -\mu_p = 0$ at midgap. In an n-type region μ_n is above midgap and μ_{S^-} exceeds μ_{S^+} by $2\mu_n$ according to Eq. (4). From Eq. (1) μ_{S^-} is as far above μ_{S^0} as μ_{S^+} is below it. In a p-type region $\mu_n < 0$ and the reverse is true: $\mu_{S^+} > \mu_{S^-}$. Again μ_{S^0} lies halfway between μ_{S^+} and μ_{S^-}, at a distance $|\mu_n|$ from either.

Under illumination n and p and therefore ρ_{S^+} and ρ_{S^-} increase and quasi chemical potentials may be defined for all. The electric field in the junction region will make holes and S^+'s move toward the p region, and electrons and S^-'s move toward the n region. The injection will tend to lower the junction barrier and change the carrier concentrations, particularly for the minority carriers since their populations were small to begin with. As stated by Weinberger,[1] the output voltage V of the device is the free-energy change when a particle is extracted from the reservoir at the higher chemical potential and reinjected in the reservoir at the lower chemical potential. If the current were due to solitons, the transfer of an electron from an S^- on the n side to an S^+ on the p side would result in a change from S^- to S^0, with a free energy decrease $\mu_{S^-} - \mu_{S^0} = \mu_n(n)$, and from S^+ to S^0, with a further free energy decrease $\mu_{S^+} - \mu_{S^0} = |\mu_p(p)|$. Thus the total free energy change per carrier, or the photovoltage, is $\mu_n(n) + |\mu_p(p)|$, the same as if the current were carried by free electrons and holes.

I conclude that the observed photovoltage in $(CH)_x$, just as the photocurrent, can be accounted for by a soliton mechanism for conduction. This could involve moving solitons in the junction region and intersoliton hopping of electrons in the n and p regions, or hopping throughout.

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