Florida State University Libraries

1998

Correlation of Seebeck Coefficient and Electric Conductivity in Polyaniline and Polypyrrole

N. Mateeva, H. Niculescu, Joseph B. Schlenoff, and L. Testardi

Correlation of Seebeck coefficient and electric conductivity in polyaniline and polypyrrole

N. Mateeva, H. Niculescu, J. Schlenoff, and L. R. Testardi

Correlation of Seebeck coefficient and electric conductivity in polyaniline and polypyrrole

N. Mateeva, H. Niculescu,[a)] J. Schlenoff,[b)] and L. R. Testardi[c)]

TecOne, Inc., 1803 Sageway Drive, Tallahassee, Florida 32303

We have measured the Seebeck coefficient and electric conductivity in the air-stable conducting polymers polyaniline and polypyrrole at different doping levels. We find, at 300 K, the general correlation that the logarithm of the electrical conductivity varies linearly with the Seebeck coefficient on doping, but with a proportionality substantially in excess of a prediction from simple theory for a single type of mobile carrier. The correlation is unexpected in its universality and unfavorable in its consequences for thermoelectric applications. A standard model suggests that conduction by carriers of both signs may occur in these doped polymers, which thus leads to reduced thermoelectric efficiency. We also show that polyacetylene (which is not air stable), does exhibit the correlation with the expected proportionality, and, thus, its properties could be more favorable for thermoelectricity. © *1998 American Institute of Physics.* [S0021-8979(98)05906-4]

I. INTRODUCTION

Conducting polymers possess several attractive features for use as thermoelectric elements. They are cheap, lightweight, and flexible. They are, furthermore, easily made uniaxially anisotropic (e.g., by stretching), thus opening up the possibility of applications utilizing anisotropic thermoelectricity.[1] The main disadvantage of conducting polymers is an apparent very low thermoelectric efficiency index $ZT = (S^2 \sigma T)/\kappa$, where S is the Seebeck coefficient (thermoelectric power), σ and κ are the electrical and thermal conductivities, and T is the absolute temperature.[2,3] However, most doping research in conducting polymers is concerned with achieving the maximum electrical conductivity[4] which is not the best state for thermoelectric applications. It is necessary to investigate conducting polymers which are less conducting (less doped) than the maximum conducting state in order to determine their potential for thermoelectric applications. A further disadvantage of conducting polymers is that many of these materials are not air stable.

II. PRIOR WORK

There are only a few studies[5] which have reported σ and S over a sufficiently wide doping range in a conducting polymer to determine thermoelectric application potential. In what follows we draw upon the 1985 work of Reynolds, Schlenoff, and Chien[5] (RSC) who measured these properties at 300 K for polyacetylene, which is not air stable, using perchlorate-ion solution, electrochemical oxidation. Their results, given as a function of dopant concentration in the original report, but replotted in Fig. 1 in the parametric form to be used through this article, show a linear relation between log σ & S over a wide range in σ & S which can be expressed by $\log_e(\sigma/\sigma_{max}) = -\beta\{S/(k/e)\}$. In this relation the pure number $\beta = 1$, $\sigma_{max} = 10$ S/cm (for RSC polyacetylene), and $k/e (= 86.17 \ \mu$V/K) is Boltzmann's constant divided by the electronic charge, the natural microscopic measure for S.

We show below that this is the general behavior expected from statistical mechanics for a material having any σ_{max} and current carriers of one sign only in small concentration. A further result of this graphical presentation is that plots of $\log(\sigma)$ vs S [and $\log(ZT)$ vs S] will shift rigidly in the vertical direction with fractional changes in σ_{max} at the same S, thus allowing a simple determination of the behavior with higher σ_{max}. The σ vs S behavior of the best thermoelectric materials today lies above the RSC data by about three decades in σ.

We have calculated the doping dependence of ZT in polyacetylene using the RSC[5] data and assuming $\kappa = 0.01$ W/cm K ($\kappa < 0.005$ W/cm K is typical for nonconducting polymers[4]). (These ZT results are given in Fig. 8.) The maximum ZT occurs at $S \approx 170 \ \mu$V/K ($\approx 2k/e$) & $\sigma \approx 1$ S/cm as expected [see Eqs. (2) and (3) below], but has a value only slightly greater than 10^{-3} there, nearly three orders of magnitude below the value for the best thermoelectric materials today.

Recently, however, there have been reports[4] of polyacetylene with $\sigma > 10^3$ larger than those used for Fig. 8. This increase has been the result of new dopants and new preparation methods. If $\beta = 1$ for these materials, then they could have ZT>1 at 300 K, a value larger than that for any known material. However, no report of the σ vs S behavior of these high σ materials in a more lightly doped state has appeared. We chose not to investigate these new forms of conducting polyacetylene because they are neither air stable nor easily synthesized.

III. SYNTHESIS

A. Materials and reagents

We chose to investigate the air-stable conducting polymers polyaniline, which is easily synthesized, and polypyr-

---

[a)]Also at The Florida A&M University/Florida State University College of Engineering, Tallahassee, Florida
[b)]Also at The Chemistry Department of Florida State University, Tallahassee, Florida
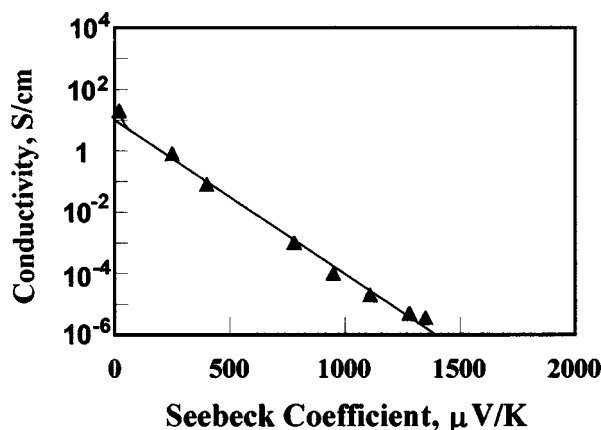[c)]Electronic mail: ltestard@phy.fsu.edu

FIG. 1. Log (conductivity) vs Seebeck coefficient for polyacetylene [from Reynolds, Schlenoff, and Chien (see Ref. 5)]. the straight line is given by $\log_e(\sigma/\sigma_{max}) = -S/(k/e)$.

role which is already commercially available in convenient form. All reagents for the synthesis or doping and dedoping of these materials were used as purchased and without further purification.

B. Synthesis of polyaniline at −25 °C

Synthesis of polyaniline at low temperatures (−20–30 °C) followed the procedure of Adams *et al.*[6] and Monkman *et al.*[6] These authors report that their method results in a high molecular weight polymer with improved mechanical and electrical properties. A typical synthesis was performed as follows:

10 g (0.107 mole) aniline were added to 107 mL 1 M HCl in which 32.64 g LiCl (15 wt %) were then dissolved. The *p*H was adjusted to 1 and the reaction mixture was cooled to −25 °C. 24.4 g (0.107 mole) of $(NH_4)_2S_2O_8$ were then dissolved in 44 mL of H_2O. This solution was pre-cooled to 0 °C and added, dropwise, to the continually stirred aniline solution for 1 h at −25 °C. The reaction heat evolved 2.5 h after addition of the last portion of the oxidant and the temperature rose to −3 °C for 20 min. The reaction mixture was stirred for 24 h at −25 °C. The resulting dark green residue was collected in a Buchner funnel and washed with 4×100 mL 1 M HCl. The product was then suspended in 300 mL 5 M NH$_4$OH and deprotonated for 24 h. The resulting emeraldine base was filtered, washed with 10×100 mL distilled water, then 2×200 mL isopropanol, and finally dried in the air. The final yield was 8 g (80%).

C. Synthesis of polyaniline at 0 °C

Synthesis of polyaniline at 0 °C followed the procedure of MacDiarmid *et al.*[7] A typical synthesis was performed as follows:

20 mL (0.219 mole) aniline were dissolved in 300 mL 1 M HCl and the solution was precooled to 0 °C. 11.5 g (0.0504 mole) of $(NH_4)_2S_2O_8$ were dissolved in 200 mL 1 M HCl, precooled to 0 °C and then added for 1 min to the continually stirred aniline solution. The reaction mixture was stirred for 1.5 h at 0 °C. The residue was collected in a Buch-

ner funnel and washed with 5×100 mL 1 M HCl. The washed residue was then suspended in 250 mL 0.1 M NH$_4$OH, and the *p*H was adjusted to 8.0 by adding several drops of 5 M NH$_4$OH. The mixture was stirred overnight. The resulting emeraldine base was collected in a Buchner funnel, washed with 5×100 mL 0.1 M NH$_4$OH, 3 $\times 100$ mL distilled H$_2$O and 3×100 mL isopropanol. During the washing the level of the liquid was kept above the level of the precipitate in order to avoid cracking of the precipitate cake. The product was dried in the air. The final yield was 18 g (90%). (We did not find significant differences in the stretching and doping properties of the polyaniline films as prepared by the two different methods of synthesis of the emeraldine base powder.)

D. Film casting for polyaniline

A 2% solution of polyaniline in N-methyl pyrrolidinone was stirred for 1 h at room temperature, then placed in an ultrasonic bath for 30 min and stirred again for 2 more hours. The mixture was filtered through glass wool in order to remove any lumps. A 0.5 cm layer of filtered product was placed in the casting substrate (often ably performed by a flat-bottomed, teflon-coated kitchen sauce pan). The liquid was evaporated at 60 °C in a closed environment with the aid of an aspirator. The resulting films typically had thicknesses of ≈0.05–0.1 mm.

E. Film stretching for polyaniline

The cast films were stretched up to 3× their initial length under infrared lamp heating in the range of 120–180 °C. The stretching was completed in less than 2 min.

F. Doping and dedoping procedures for polyaniline and polypyrrole

Polyaniline films were doped by immersion in aqueous solutions of the dopant acid. A wide range of concentrations of the following acids were used: acetic acid, vinegar, camphor sulphonic acid (CSA), citric acid, lemon juice, fluoroboric acid, hydrochloric acid, methane sulphonic acid, molybdophosphoric acid, oxalic acid, perchloric acid, phosphoric acid, *p*H$_3$ buffer solution, sulfuric acid, and tungstosilicic acid. Most measurements were made on different samples (but often from the same synthesis batch) which were individually doped in solutions of differing concentrations. We also used serial doping where a single sample was doped, measured, then doped to higher strength, and this cycle repeated until the maximum doping had been reached.

Polypyrrole samples in the form of a polypyrrole coating (~1 μm thick) on polyester fabrics (commercially available under the name MILLIKEN CONTEX FABRIC and kindly provided by Dr. Andrew Child of Milliken Research Corporation) were investigated. These were used to investigate the thermoelectric properties of polypyrrole at different doping levels. Gradient-dedoped samples were obtained by inserting a 15 cm long strip of the polypyrrole coated fabric slowly (~5 cm/h on average) into a solution of 5 M NH$_4$OH. This provided a convenient ''functional gradient'' in the level of dopant and in the magnitudes of the electrical conductivity
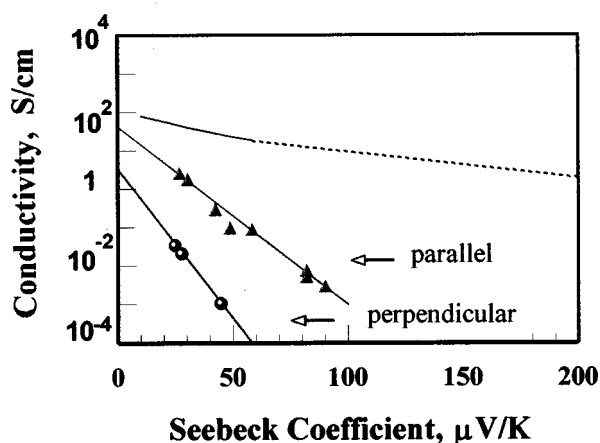
FIG. 2. Log (conductivity) vs Seebeck coefficient for 2.5× stretched polyaniline samples serially doped in oxalic acid. Data are for parallel- and perpendicular-to-stretch samples. The line above the data roughly gives σ vs S for polyacetylene (RSC[5]).

FIG. 3. Log (conductivity) vs Seebeck coefficient for 2.5× stretched polyaniline samples serially doped in citric acid. Data are for parallel- and perpendicular-to-stretch samples. The line above the data roughly gives σ vs S for polyacetylene (RSC[5]).

and Seebeck coefficient. Limited studies of redoped polypyrrole were also carried out. Since the thickness of the polypyrrole coating could not be determined accurately, it was not possible to obtain the electrical conductivity magnitudes accurately from our measurements alone. The values for σ reported in this study were obtained by scaling the measured conductances to the initial state conductances and taking the initial state conductivity to be 80 S/cm, as estimated by The Milliken Research Corporation. Errors in the initial state σ do not affect the slope β in the $\log(\sigma)$ vs S correlation reported below. The absolute values for σ, however, may be in error by a factor of 2, based on uncertainty estimates of σ by The Milliken Research Corporation.

IV. MEASUREMENT RESULTS

Figure 2 shows the σ vs S behavior found for our polyaniline samples which were stretched to $\approx 2.5\times$ their original length and subsequently doped serially in oxalic acid. Our S values were measured relative to Cu or Au electrodes and corrected to the absolute Seebeck coefficient scale[3] (by adding 1.8 μV/K) for the graphical presentations and analytical formulas in this article. All data in this report were taken at 300 K.

The data for 2.5× parallel-to-stretch and perpendicular-to-stretch samples doped with oxalic acid both follow the correlation:

$$\log_e(\sigma/\sigma_{max}) = -\beta\{S/(k/e)\}, \tag{1}$$

where $\beta_{\parallel} \approx 9$ and $\sigma_{max\parallel} \approx 33$ S/cm for the parallel-to-stretch case, and $\beta_{\perp} \approx 15$ and $\sigma_{max\perp} \approx 2.7$ S/cm for the perpendicular-to-stretch case. The line above the data gives the approximate σ vs S behavior found in polyacetylene by RSC,[5] and about which more will be said below. Note that the horizontal (S) scale in Fig. 2 (and all following figures) is 10× smaller than that in Fig. 1.

Figure 3 shows the σ vs S behavior found for a stretched polyaniline sample cut adjacent to that which provided the data in Fig. 3, but which was serially doped in citric instead of oxalic acid. These citric acid doping data follow the same
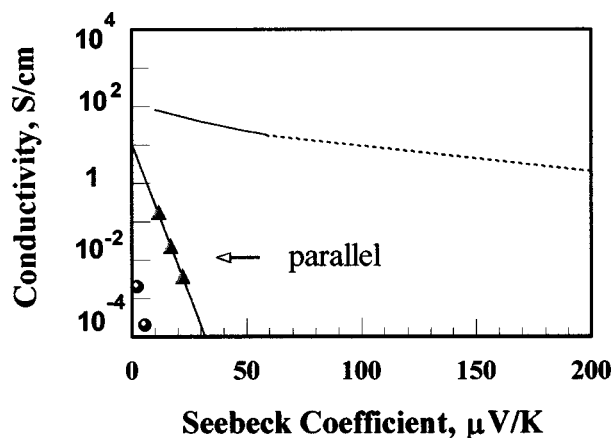
general correlation as those for the oxalic acid samples, but with $\beta_{\parallel} \approx 32$ and $\sigma_{max\parallel} \approx 13$ S/cm in Eq. (1) for the 2.5× parallel-to-stretch samples. (The lower points on this plot are for the perpendicular-to-stretch samples, and yield $\beta_{\perp} > 32$.)

We thus find $\beta \gg 1$ in stretched polyaniline with both oxalic and citric acid doping. These values of β are substantially larger than the value of unity found in unstretched, perchlorate-doped polyacetylene by RSC.[5] Note also that the β's are anisotropic in stretched polyanaline for both oxalic and citric acid doping, and the magnitudes of the β's are different in the two cases.

The anisotropy in σ_{max} with oxalic acid doping is in approximate accord with the anisotropy in σ found in HCl-doped polyaniline by Epstein *et al.*[4] The large value of β, and its anisotropy, are newly reported features.

The linear $\log(\sigma)$ vs S behavior found for the serially doped, stretched (anisotropic) state in polyaniline is readily seen in the unstretched (isotropic) state also. Figure 4 shows the σ vs S behavior found in our unstretched polyaniline samples from a different synthesis, now as individually
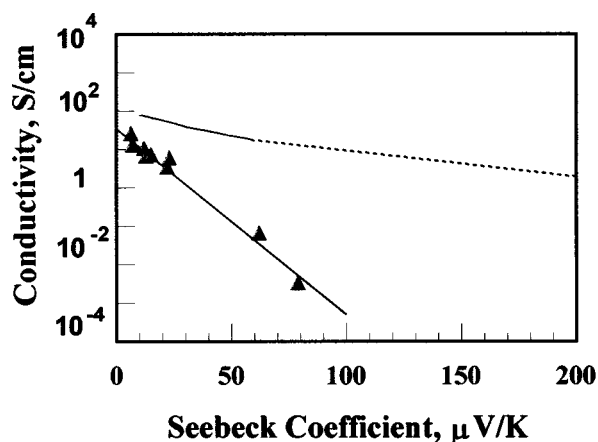

FIG. 4. Log (conductivity) vs Seebeck coefficient for unstretched polyaniline samples individually doped in oxalic acid. The line above the data roughly gives σ vs S for polyacetylene (RSC[5]).
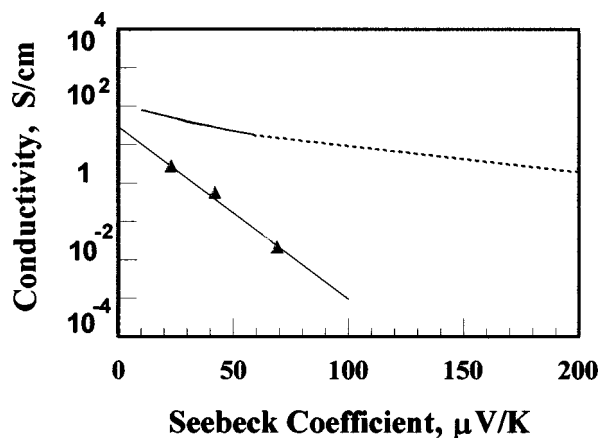
FIG. 5. Log (conductivity) vs Seebeck coefficient for unstretched polyaniline doped in acetic acid. The line above the data roughly gives σ vs S for polyacetylene (RSC[5]).

FIG. 7. Log (conductivity) vs Seebeck coefficient for all data. The line above the data is calculated from band theory assuming a mean free path $= 1$ Å$/(m*/m)$.

doped samples in oxalic acid, and which yields $\beta \approx 9.6$ and $\sigma_{max} \approx 40$ S/cm in Eq. (1).

The value of β from Eq. (1) depends upon the chemical nature of the dopant in the unstretched state as well as in the stretched state. By way of example, the largest values of β in unstretched polyaniline occurred for camphor sulphonic acid (CSA) doped material, where β was ≈ 45, and HCl electrochemically deposited and doped material, where β was ≈ 17. But more typical values for polyaniline (and, with less data, for polypyrrole) were $\beta \approx 9$. Examples follow.

Figure 5 shows the σ vs S behavior found in unstretched polyaniline samples individually doped in acetic acid which yields $\beta \approx 9$ and $\sigma_{max} \approx 40$ S/cm from Eq. (1).

Figure 6 shows the σ vs S behavior found in NH$_4$OH gradient-dedoped, unstretched polypyrrole (MILLIKEN CONTEX FABRIC) which yields $\beta \approx 9$ and $\sigma_{max} \approx 110$ S/cm from Eq. (1).

Finally, Fig. 7 shows the σ vs S data for over 150 samples measured in our studies.

These data are derived from 2 base materials (polyaniline & polypyrrole), 15 different dopants, stretch-oriented and unoriented forms, serially and individually doped and dedoped, and chemically and electrochemically synthesized
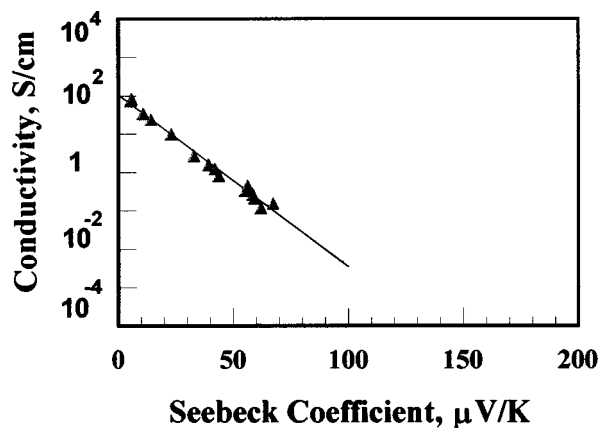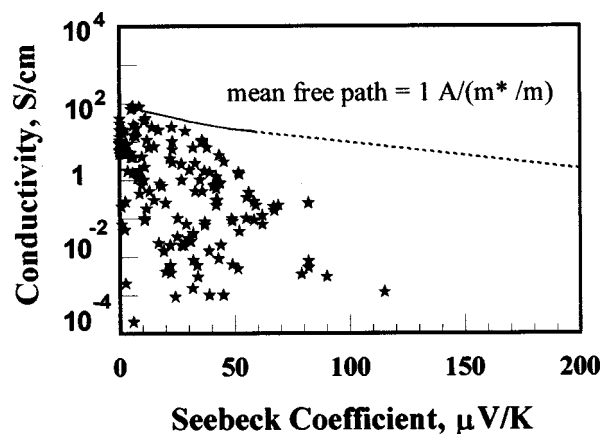
and doped, though not in all combinations. In a more detailed analysis than is allowed by the figure, one can discern the linear trends due to the constant but different β's for the different dopants, some of whose details have been revealed in the previous graphs. The correlation noted in Figs. 2–6 holds whenever we have sufficient data to test it. The near common slope for much of the data in Fig. 7 results from values for β which are often ~ 9.

We can now further identify the line in Figs. 2–5, described as the approximate behavior of RSC[5] polyacetylene. This line, in fact, is the σ vs S behavior calculated from band theory for the case of a constant mean free path, mfp $= 1$ Å$/(m*/m)$, where $(m*/m)$ is the effective mass ratio.[8] Thus the line roughly separates the region of extended states, mfp> 1 Å$/(m*/m)$, which lies above it, from that of localized states, mfp< 1 Å$/(m*/m)$, which lies below it. That conducting polymers in a high σ state lie at a metal-insulator boundary has been noted before.[9] Figure 7 shows evidence in a different form where, among other things, it appears that the less conducting states increasingly depart from the metal-insulator boundary. But a different interpretation is given below.

The common results of these doping studies in polyaniline and polypyrrole are that

(i)   a correlation exists between σ and S such that $\log_e(\sigma/\sigma_{max}) = -\beta\{S/(k/e)\}$,

(ii)   the value of β depends on the chemical nature of the dopant but is always $\gg 1$, and

(iii) the values of β and σ_{max} are anisotropic in a stretched sample of polyaniline with σ_{max} being larger and β being smaller in the direction parallel-to-stretching, compared to that perpendicular-to-stretching.

In a later section we provide an explanation for the $\log_e(\sigma/\sigma_{max}) = -\beta\{S/(k/e)\}$ correlation and a possible, though unexpected, reason for the large β. We next give the consequences of this σ vs S correlation for thermoelectric applications, which are independent of that explanation.

FIG. 6. Log (conductivity) vs Seebeck coefficient for gradient-dedoped polypyrrole.
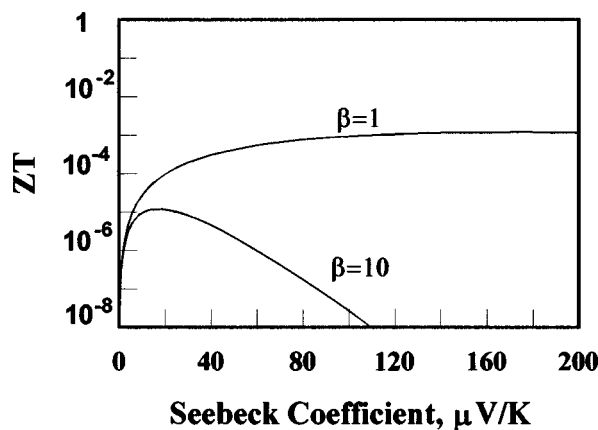
FIG. 8. ZT vs Seebeck coefficient with the empirical σ vs S correlation [Eq. (10)], $\sigma_{max} = 10$ S/cm, $\kappa = 0.01$ W/cm K, and for $\beta = 1$ (RSC[5] polyacetylene) and $\beta = 10$.

V. THE CONSEQUENCES OF THE EMPIRICAL σ VS S CORRELATION FOR THERMOELECTRIC APPLICATIONS

When the thermoelectric efficiency index ZT $= (S^2 \sigma T)/\kappa$ is combined with the empirical σ vs S correlation $\log_e(\sigma/\sigma_{max}) = -\beta\{S/(k/e)\}$, one finds, with the assumption of a constant κ, that ZT will reach a maximum on doping at

$$S(\max \text{ZT}) = (2/\beta)(k/e) \approx (172/\beta)\,\mu\text{V/K}, \quad (2)$$

$$\sigma/\sigma_{max}(\max \text{ZT}) = e^{-2}, \quad (3)$$

and will there have magnitude (at 300 K)

$$\text{ZT(max)} \approx \sigma_{max}/(8 \times 10^5 \kappa \beta^2), \quad (4)$$

where, if σ_{max} is in S/cm, κ must be in W/cm K.

If the thermal conductivity is not constant but is composed of a lattice and an electronic part

$$\kappa = \kappa_1 + \kappa_e = \kappa_1 + C(k/e)^2 \sigma T, \quad (5)$$

then, in the limit $\kappa_1/\kappa_e \ll 1$ (the limit $\kappa_1/\kappa_e \gg 1$ having been treated above),

$$\text{ZT} = [S/(k/e)]^2/C \quad (6)$$

which increases with S up to the point where κ_1/κ_e is no longer $\ll 1$.[10]

The major conclusion of the results above is that the occurrence of the empirical σ vs S correlation with $\beta \gg 1$ is very detrimental to thermoelectric applications. With $\beta \sim 10$, as in our polyaniline and polypyrrole, one needs, for the same ZT, electrical conductivities which are $\beta^2 \sim 100 \times$ greater than in the case where $\beta = 1$, as in RSC[5] polyacetylene, other parameters being equal. This is shown in Fig. 8 where, to obtain the magnitudes of ZT, we have used $\sigma_{max} = 10$ S/cm, similar to that for our data and for RSC[5] polyacetylene with $\beta = 1$, and $\kappa = 0.01$ W/cm K ($\kappa < 0.005$ W/cm K is typical for nonconducting polymers[4]). With higher σ, and the same S and β, the ZT curves would be rigidly raised by the relative increase in σ. This is the basis of the prior statement that a reported increase in σ of $>10^3$ over that for RSC[5] polyacetylene, with $\beta = 1$ and at

the same S, would lead to ZT$>$1 (though the large σ may increase κ beyond 0.01 W/cm K). The detrimental effects of $\beta \gg 1$ for thermoelectric applications from the empirical σ vs S correlation. We now expand a standard model to provide an explanation for the correlation.

VI. ON THE CORRELATION OF ELECTRICAL CONDUCTIVITY AND SEEBECK COEFFICIENT

When an electrical current passes between two dissimilar materials, Peltier heat is evolved or absorbed at the (constant temperature) interface at a rate which is proportional to the electrical current. The Peltier proportionality constant Π is thus the heat of transport per unit electric charge e. From the first Kelvin relation $\Pi = ST$, where S is the Seebeck coefficient and T is the absolute temperature, S is thus the entropy of transport per unit electric charge. For a simple system of particles where the fraction of occupied, thermally-available, current carrying states is c, and using k for Boltzmann's constant, we have from statistical mechanics,

$$S = (k/e)\log_e[c/(1-c)]. \quad (7)$$

The electrical conductivity σ of such a system is given by

$$\sigma = \sigma_{max} c(1-c), \quad (8)$$

where, when $c \ll 1$, σ_{max} is the conductivity extrapolated to $c = 1$. σ_{max} is proportional to the mobility of the charge carriers.

For an electrically neutral material there will be contributions to both σ and S from the equal number of $+$ and $-$ charge carriers. For σ, these contributions simply add. For S these contributions add with a weighting proportional to their individual σ's. Since the S's for the two carrier types have opposite algebraic signs, the magnitude of the total S is always smaller, for a given σ, when there are current carriers of both signs compared to the one carrier type case. Under the additional restraint that $c \ll 1$ (the "light doping" limit), we obtain the final results

$$\sigma/\sigma_{max} = c \quad (c \ll 1), \quad (9)$$

$$\log_e(\sigma/\sigma_{max}) = -\beta\{S/(k/e)\} \quad (c \ll 1), \quad (10)$$

where the pure numbers

$$\beta = [\sigma_{max}(+) + \sigma_{max}(-)]/[\sigma_{max}(+) - \sigma_{max}(-)]$$
$$= (r+1)/(r-1) \quad (c \ll 1), \quad (11)$$

$$r = \sigma_{max}(+)/\sigma_{max}(-)$$
$$= \text{mobility}(+)/\text{mobility}(-) \quad (c \ll 1). \quad (12)$$

In conventional extrinsic semiconductors having mobile charge of one sign only, r is taken to be $\gg 1$ (p-type conduction) or ≈ 0 (n-type conduction), and thus $\beta = +1$ or -1, respectively. These conductivity or mobility ratios apply to the charges in extrinsic semiconductors, partly because of the very large mass difference between the electron (or hole) and the parent ionized dopant atom, and partly because the ionized dopant atom is chemically "locked-in place" due to the substitutional nature of the inclusion.

A simple application of this theory, from Eq. (10), is to plot $\log_e(\sigma)$ vs S for a series of lightly doped samples, wherein a straight line will be obtained with slope $-\beta/(k/e)$. This will test if the theory is appropriate and allow the determination of r, the relative conductivities or mobilities of the two charges, via Eq. (12). (In our graphical data displays we use the convenient 10-based logarithms, which requires numerical adjustments to the e-based logarithms in the formulas of this paper). Furthermore, a $\log_e(\sigma)$ axis intercept will be obtained which yields σ_{max}. This then further allows the determination of the fraction of occupied, thermally-available, current carrying sites c via Eq. (9). This is the basis for our graphical presentations in Figs. 1–7.

As c approaches 1, the "light doping" conditions leading to Eqs. (9)–(12) will break down and the straight-line graphical analysis described above will no longer apply. However, the region and magnitude of the breakdown will require more detailed (and model dependent) information than is contained in the simple model above. For the previous treatment, by way of example, the breakdown will lead to an error in σ/σ_{max} of ≥ 0.43 decade $[=\log_{10}(e)]$ at $S \leq (130/\beta)$ μV/K. This may serve as a rough guide to the limits of the "light doping" region for this model.

For band structure models, the "light doping" limit is properly obtained from numerical calculations with parabolic band parameters, assumed scattering laws and general "occupation probability" statistics. This limit can, in fact, be seen in the RSC[5] data plot for polyacetylene in Fig. 1 where it is given by the straight line portion of the σ vs S behavior that was calculated by this method. The "light doping" limit covers most of the range of experimental data and in this region the expected data slope $\beta=1$ is obtained with no further assumptions. Only the datum point with the highest σ falls outside this "light doping" range, and here the calculations are made to fit this, and thereby all data magnitudes, with the assumed scattering law of a constant mean free path (also called acoustic mode scattering) of 0.6 Å/(m^*/m). Note that the "light doping" analysis criterion for the range of S given above would also apply to these data.

For $c \ll 1$, however, all models should yield Eq. (10). The simple particle model of Eqs. (7)–(12) with "light doping," for example, will yield results equivalent to the use of Boltzmann ("nondegenerate") statistics in the band structure models.

Note that with conduction by both charge types, S values are reduced (shifted left in Figs. 2–6) simply by the factor β from the predictions of the single carrier theory for the same σ. With this graphical rescaling, it is seen that much of the σ and S data for all dopants in Fig. 7, then follows the metal-insulator boundary curve as shown. This boundary line is established by the change in c due to doping, and is approximately computed from Eqs. (9) and (10) with a constant σ_{max} equivalent to a mean free path[8] of ~ 1 Å/(m^*/m) for the case $c \ll 1$.

Relevant to the usual interpretations of conducting polymer behavior, we further note that neither the Mott[11] nor the Efros-Shklovskii[12] theories of transport is disordered materials leads to a linear relation between $\log(\sigma)$ and S unless $\log(\sigma/\sigma_{max})*[d \log N(E)/d(E/kT)]_{E=E_f}$ is constant with varying dopant concentration. [In this expression, $N(E)$ is the density of charge carrying states as a function of energy E, and E_f is the Fermi energy.] This constraint appears unexpected.

VII. CONCLUSIONS AND FINAL COMMENTS

Our central finding is the correlation $\log_e(\sigma/\sigma_{max}) = -\beta\{S/(k/e)\}$ at 300 K for polyanaline and polypyrrole. This correlation, because of $\beta \gg 1$, is unexpected from conventional single carrier theory, and is detrimental for thermoelectric applications.

One theory which can account simply for the empirical correlation admits current conduction by "carriers" of both signs with nearly equal conductivities.[13]

Finally, for $\beta \approx 9$, which characterizes many of our isotropic samples, we further conclude that if "ambipolar" carriers are present in both polyanaline and polypyrrole, the carrier electrical conductivities are often in the ratio $r = \sigma_{max}(+)/\sigma_{max}(-) \approx 1.25$. It is this near equality of "ambipolar" conductivities which leads to substantial "internal short circuiting" of the Seebeck effect (the cause of $\beta \gg 1$), and a much reduced thermoelectric efficiency for these air-stable materials. The presence and near parity of the "ambipolar" conductivities does not, however, occur in polyacetylene (which is not air stable) according to this interpretation of the $\sigma - S$ correlation and the data of RSC.[5] Thus polyacetylene, possibly because of conduction with carriers of one sign only, may hold a critical but unrecognized key for conducting polymer thermoelectricity. The search for an economical, tractable and air-stable analog to high σ polyacetylene for this purpose would warrant effort.

ACKNOWLEDGMENTS

[1] For a more detailed discussion of thermoelectric effects in anisotropic materials, see J. F. Nye, in *Physical Properties of Crystals* (Clarendon, Oxford, 1985) Chapter XII, and C. A. Domenicali, Phys. Rev. **92**, 877 (1953). For references to recent experimental observations, see L. R. Testardi, Appl. Phys. Lett. **64**, 2347 (1994). A fuller account of the advantages of anisotropic thermoelectricity in device applications will be given in a future publication by L. R. Testardi.

[2] See, for example, *Thermoelectricity: Science and Engineering*, edited by R. Heikes and R. Ure, Chap. 11 by R. W. Ure and R. R. Heikes (Interscience, New York, 1961), Chap. 11.

[3] See, for example, *CRC Handbook of Thermoelectrics*, edited by D. M. Rowe, Chap. 5 by C. M. Bhandari and D. M. Rowe for band structure calculations of the thermoelectric parameters, and Chap. 32 by A. T. Burkov and M. V. Vedernikov for the absolute Seebeck coefficients of the elements (CRC, Boca Raton, 1995).

[4] See, for example, *Physical Properties of Polymers Handbook*, edited by J. Mark, Chap. 34 by R. S. Kohlman, J. Joo, and A. J. Epstein for electrical properties of conducting polymers, and Chap. 10 by Y. Yang for thermal

conductivities of polymers, (AIP, New York, 1996).

[5] For references and analysis of prior studies of the Seebeck coefficient and electric conductivity in conducting polymers, see A. B. Kaiser, Phys. Rev. B **40**, 2806 (1989). In the present article we use the findings of J. R. Reynolds, J. B. Schlenoff, and C. W. Chien, J. Electrochem. Soc. **132**, 1131 (1985).

[6] P. L. Adams, J. Laughlin, and A. P. Monkman, Synth. Met. **76**, 157 (1996); A. P. Monkman, P. N. Adams, P. J. Laughlin, and E. R. Holland, *ibid.* **69**, 183 (1995).

[7] A. G. MacDiarmid, J. C. Chiang, A. F. Richter, N. L. D. Somasiri, and A. J. Epstein, in *Conducting Polymers*, edited by L. Alcacer (Reidel, Dordrecht, Netherlands, 1987), p. 105.

[8] The RSC[5] behavior for polyacetylene corresponds more nearly to a mean free path$=0.6$Å/(m^*/m). The effective mass ratio (m^*/m) used for Fig. 8 and in its following text is a combination of inertial and density of states effective masses for ellipsoidal Fermi surfaces, a detail not warranting elaboration in the present case. However, if the volume density of the conducting states is small compared to the mean atomic density, then it is well to point out that one would expect (m^*/m) to be <1, leading to a correspondingly larger calculated mean free path.

[9] C. O. Yoon, M. Reghu, D. Moses, A. J. Heeger, Y. Cao, T-A Chen, X. Wu, and R. D. Rieke, Synth. Met. **75**, 229 (1995).

[10] The numeric parameter C in Eq. (14) is not a constant with doping in the band structure model, however. It varies, for example, from 2 to $\pi^2/3$ from the nondegenerate to the degenerate doping range when the mean free path is constant (a case also called acoustic mode scattering). This variation is not accounted for above, nor do we pursue calculations of the more general expression for κ [Eq.(5)]. Such detail is unwarranted without a better understanding of the empirical σ vs S correlation, since the unexpected values for β may imply new thermal conduction routes with undetermined values of C (see footnote 13 below). We therefore choose to assume a constant total thermal conductivity in what follows.

[11] See, for example, N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Materials*, (Oxford University Press, London, 1979).

[12] See, for example, B. I. Shlkovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer, Berlin, 1979). Thermal generation of current carrying pairs would also contribute to the temperature dependence of the electrical conductivity, a much studied behavior in conducting polymers.

[13] Our measurements cannot tell us if the charge carriers are ''electron-and hole-like'' or anions and cations. However, recent PIXE measurements of our HCl doped PAN show, as expected, that Cl is not mobile with current transport, indicating electron- and hole-like conduction in at least this case. A further consequence of ''ambipolar'' conduction with importance for thermoelectric applications is the possibility that the charge pairs are thermally generated and have a binding energy E_g. This will lead to a temperature dependent concentration of the pairs, and thus provide an additional heat transfer mode when a temperature gradient is present. The resulting addition to κ will be of the form given by Eq. (5), but where C (~ 1 for ''unipolar'' conduction) will now be enhanced by a factor $\sim (E_g/kT)$ with ambipolar conduction, thus leading to a reduced ZT. No test of this, or estimate of the enhanced C, can be made from only our measurements of σ and S at 300 K.