DOE/ER/12171--1

**THERMOELECTRIC BEHAVIOR OF CONDUCTING POLYMERS:
ON THE POSSIBILITY OF "OFF-DIAGONAL" THERMOELECTRICITY**

N. Mateeva, H. Niculescu*, J. Schlenoff**, and L. Testardi
TecOne, Inc., 1803 Sageway Drive, Tallahassee, FL 32303

ABSTRACT

Non-cubic materials, when structurally aligned, possess sufficient anisotropy to exhibit thermoelectric effects where the electrical and thermal paths can be orthogonal due to "off-diagonal" thermoelectricity (ODTE). We discuss the benefits of this form of thermoelectricity for device applications and describe a search for suitable thermoelectric properties in the air-stable conducting polymers polyaniline and polypyrrole. We find, at 300K for "diagonal" (ordinary) thermoelectricity (DTE), the general correlation that the logarithm of the electrical conductivity varies linearly with the Seebeck coefficient on doping, but with a proportionality in excess of a prediction from theory. The correlation is unexpected in its universality and unfavorable in its consequences for applications in DTE & ODTE. A standard model suggests that conduction by carriers of both signs occurs in these polymers, which thus leads to reduced thermoelectric efficiency. We also discuss polyacetylene (which is not air-stable), where this "ambipolar" conduction does not occur, and where properties seem more favorable for thermoelectricity.

INTRODUCTION

The Seebeck coefficient, S , like the electrical conductivity, σ , and the thermal conductivity, κ , is an anisotropic property in structurally ordered materials with symmetry less than cubic. Thus the performance of any such material as a thermoelectric element is also anisotropic. However, it is necessary, with anisotropic S , to further define the mode of thermoelectricity by consideration of the relative directions of the electrical & thermal gradients (or currents) in an anisotropic medium.

The ordinary form of thermoelectricity can be called "diagonal" thermoelectricity (DTE). In DTE, the electrical and thermal paths are parallel. DTE utilizes the diagonal components of S in its matrix representation. DTE can occur in any material irrespective of its symmetry. All thermoelectric devices today use DTE. However, confusion can arise from use of the term "anisotropic" thermoelectricity since it is sometimes applied to ordinary thermoelectricity (DTE) but implemented in different directions for an anisotropic material.

There is another form of thermoelectricity, which we call "off-diagonal" thermoelectricity (ODTE), and where anisotropy leads to new configurations. In ODTE the electrical and thermal paths are not parallel. ODTE utilizes the off-diagonal components of S in its matrix representation. This can lead to substantial improvements in the ease and efficiency of thermoelectric implementation. ODTE, which is rooted in anisotropy, only occurs in non-cubic materials with oriented structures, and, depending on the symmetry, only in certain directions.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Figure 1 shows the orientations of the electrical and thermal currents for Peltier DTE and ODTE.

Figure 1. Schematic diagram of electrical (I) & thermal (Q) currents and impedances Z in “diagonal” and “off-diagonal” Peltier thermoelectricity.

An example of the differences in implementation is as follows. Because the electrical & thermal current paths in Peltier DTE are parallel, the ratio of the electrical & thermal impedances, Z, is given by κ/σ , irrespective of geometry. Since κ/σ is normally set by the optimum thermoelectric material state, and since the ratio of electrical & thermal impedances in common power sources and heat transfer environments is much greater than those of available device materials, one must utilize other means to achieve the desired impedance matching. The usual solution is to build thermoelectric modules with hundreds of thermoelectric elements electrically in series but thermally in parallel. This requires a complex assembly, often with forced-air convection for heat disposal. One can obtain this impedance ratio in Peltier ODTE with a single strip which is ~ 20 times longer than it is thick, given the same κ/σ , and thus achieve a gain in simplicity over DTE.

If, in addition, the ODTE material is flexible (as may be favored by the length/thickness $\gg 1$ strip geometry of Figure 1), there are further benefits of special note for ODTE applications.

- 1) Good shape conformation to the source object for heat pumping or power generation will lead to more compact and efficient operation with faster response.
- 2) Enveloping thermal contact will reduce the passive insulation requirements.
- 3) The large heat transfer area will reduce or eliminate the need for forced-air convection.
- 4) Storage can be much more convenient (for example, a flexible cooling/heating strap can be readily accommodated in the glove compartment of a car or ambulance).
- 5) Multi-stage heat pumping, which is complicated in rigid DTE, may be achieved by the simple procedure of tailored, (electrically insulated) multi-turn wrapping.

These advantages can compensate for the minor, extra plug-energy in small, consumer-oriented thermoelectric applications due to their comparative inefficiency, and add convenience.

Figure 2 shows the differences in rigid DTE & flexible ODTE device geometry in schematic form.

Figure 2. Schematic representation of Single Stage and Multi Stage thermoelectric modules using conventional, rigid thermoelectricity (upper) and "off-diagonal", flexible Peltier thermoelectricity where electrical and thermal currents are orthogonal.

Figure 3 shows some possible Peltier thermoelectric applications with flexible ODTE.

Figure 3. Some possible applications of flexible “off-diagonal” Peltier thermoelectricity.

THEORY OF “OFF-DIAGONAL” THERMOELECTRICITY

Irreversible thermodynamics applied to anisotropic systems shows¹ that off-diagonal terms in the Seebeck coefficient matrix will occur for all triclinic and monoclinic symmetry classes even in their standard axes system orientations, and will also occur for all non-cubic systems having a non-standard axes system orientation. The gradient of the electrical potential ϕ is then related to the gradient of temperature T in the absence of electrical current flow, by the matrix equation

$$\nabla\phi = S'\nabla T \quad (1)$$

where the ϕ 's are measured along leads of identical composition at points of equal temperature, and S' is the Seebeck coefficient matrix relative to those leads in the coordinate system of $\nabla\phi$ and ∇T . The off-diagonal (ODTE) terms in S' can lead to thermoelectric voltages transverse to the temperature gradients (Transverse Seebeck Effect) and total heat pumping transverse to the electrical current density (Transverse Peltier Effect) in sheets that are orders of magnitude larger than those arising from the diagonal terms (DTE) as seen in the following examples.

The Transverse Seebeck Effect

A sheet of uniaxial symmetry material having length x_1 , thickness x_3 , with its unique axis at angle θ from the 3 toward the 1 principal axes, when heated with constant temperature gradient in the x_3 direction will produce Seebeck voltage differences V_3 and V_1 , (measured with leads of identical composition at points of equal temperature, and using the $x_1 - x_3$ coordinate system)

$$V_3 = \int (\partial\phi/\partial x_3) dx_3 = S_{33}' \Delta T_3 \quad \begin{array}{c} \xrightarrow{x_1} \\ \xrightarrow{V_1} \end{array} \quad (2)$$

$$V_1 = \int (\partial\phi/\partial x_1) dx_1 = S_{13}' \Delta T_3 (x_1/x_3) \quad \uparrow \theta / \left[\begin{array}{c} \text{//////} \\ \text{//////} \\ \text{//////} \end{array} \right] \uparrow \Delta T_3, x_3, V_3 \quad (3)$$

Here ΔT_3 is the temperature difference in the x_3 direction (i.e., thru the thickness of the sheet),

$$S_{33}' = (1/2)(S_{33} - S_{11})\cos(2\theta) + (1/2)(S_{33} + S_{11}) \quad (4)$$

$$S_{13}' = (1/2)(S_{33} - S_{11})\sin(2\theta) \quad (5)$$

and the unprimed S's refer to the (assumed diagonal) matrix component values of the Seebeck coefficient in the principal axes system. For anisotropic materials one may expect $|S_{13}'| \sim |S_{33}'| \sim |S_{33}| \sim |S_{11}| \sim |S_{11}'|$ for $2\theta \sim 90^\circ$. This will lead to an ODTE voltage difference V_1 in the x_1 direction which can be $\sim (x_1/x_3)$ larger than the DTE (ordinary thermoelectric) voltage difference V_3 in the x_3 direction.

For a sheet 1mm thick and 100 cm long this (x_1/x_3) factor amounts to an increase in thermoelectric voltage difference V_1 of 1000X over V_3 in the x_3 DTE mode, given corresponding equal $S_{13}' = S_{33}'$. By way of example, for $S_{13}' \sim 10^{-4}$ V/K (which can be expected for a strongly anisotropic thermoelectric material) this yields 0.1 volts V_1 for each 1K of ΔT_3 in the present example. The voltage increase in the ODTE mode is accompanied by a $(x_1/x_3)^2 = 1000^2$ increase in electrical impedance compared to the x_3 DTE mode.

The Transverse Peltier Effect

An electrical current density j_1 in the x_1 direction of the above sheet will produce a Peltier thermal current density q_3 in the x_3 direction having magnitude, in the absence of an x_3 temperature gradient, (from the current analog of Eq. 1)

$$q_3 = j_1 S_{13}' T \quad \begin{array}{c} \xrightarrow{j_1} \\ \left[\begin{array}{c} \text{//////} \\ \text{//////} \\ \text{//////} \end{array} \right] \uparrow h_3 \end{array} \quad (6)$$

For a sheet 1 mm thick & 100 cm long, this (x_1/x_3) factor leads to an increase in ODTE total heat pumping of 1000X over that in the x_1 DTE operation, given corresponding equal $S_{11}' = S_{13}'$. By way of example, for $S_{13}' \sim 10^{-4}$ V/K, a sheet 1 cm wide & $I_1=1$ A, one obtains total heat pumping in the x_3 direction = 30 Watts at 300K. The heat pumping increase in the ODTE mode is accompanied by a $(x_1/x_3)^2 = 1000^2$ decrease in thermal impedance compared to the x_1 DTE mode.

Joule heating from the electrical resistance of the sheet and thermal conduction through the sheet, which are omitted from Eqs. 1 to 6, will limit the efficiency of the thermoelectric performance in heat pumping and power generation. The analysis for optimizing thermoelectric device efficiency with Joule heating and thermal conduction losses has been made for ordinary one-dimensional (DTE) devices^{2,3}. We extend this analysis to the two-dimensional ODTE case below.

The large thermoelectric voltages and total heat pumping obtained in the ODTE mode above result not from new properties but from utilizing the sheet geometry to obtain beneficial impedance transformations. Thus, the relatively low electrical and high thermal impedances, usually associated with one-dimensional DTE devices configured to have small (x_1/x_3) values, are now changed to much higher electrical & lower thermal impedances. This allows more efficient and convenient conversion between electrical and thermal energies because the electrical and thermal impedances of the thermoelectric element can, via the element's shape, be independently matched more closely to common power sources and heat transfer environments, respectively.

THE THERMOELECTRIC FIGURE OF MERIT FOR ODTE APPLICATIONS

The theory of ordinary thermoelectric (DTE) devices shows^{2,3} that their efficiency increases with the dimensionless material efficiency index $ZT_{DTE} = S^2 \sigma T / \kappa$ where S is the isotropic Seebeck coefficient, σ is the isotropic electrical conductivity, T is the absolute temperature, and κ is the isotropic thermal conductivity. From the nearly free electron model of conductors it can be shown^{2,3} that the figure of merit Z_{DTE} varies with carrier concentration and reaches a maximum value for σ less than the maximum σ achievable with doping. The highest values of ZT_{DTE} for room temperature thermoelectric applications have remained ≈ 1 since 1957³.

The efficiency index for DTE can be readily extended to ODTE. If we consider the common case of anisotropic S , σ and κ matrices which are simultaneously diagonal in the principal axes orientation (e.g., uniaxial symmetry), then the angular dependence of ODTE ZT is given by

$$ZT_{ODTE}(\theta) = (S_{33} - S_{11})^2 T \tan^2(\theta) / [\rho_{11}\kappa_{33} + (\rho_{11}\kappa_{11} + \rho_{33}\kappa_{33})\tan^2(\theta) + \rho_{33}\kappa_{11}\tan^4(\theta)] \quad (7)$$

where the electrical current flows parallel to the 1 axis, the heat flows parallel to the 3 axis, and θ is the rotation angle about the 2 axis measured relative to the principal axes orientation. This is the configuration shown in the examples for Eqs. 2 through 6 above with, again, the unprimed matrix component values being those in the principal axes (diagonal) orientation. The resistivity matrix ρ is inverse to the conductivity matrix σ .

The maximum ZT_{ODTE} then occurs at an angle

$$\theta(\max ZT_{\text{ODTE}}) = \tan^{-1}(\rho_{33}\kappa_{11}/\rho_{11}\kappa_{33})^{1/4} \quad (8)$$

at which angle there will be found the maximum magnitude for ZT_{ODTE}

$$ZT_{\text{ODTE}}(\max) = (S_{33} - S_{11})^2 T / [(\rho_{11}\kappa_{11})^{1/2} + (\rho_{33}\kappa_{33})^{1/2}]^2 \quad (9)$$

showing that good ODTE materials must also be good DTE materials. Special note, however, should be taken of the need to select materials with a large anisotropy in S for ODTE applications. Notwithstanding the numerous achievements of materials science, the prediction or development of optimized anisotropy is a difficult problem which has little history of success. Note also that anisotropy in σ and κ , which will likely also occur, is not necessary for ODTE.

ON MATERIALS SELECTION FOR ODTE

Although the theoretical basis for ODTE rests soundly in the irreversible thermodynamics of anisotropic media, and the benefits can be unique, there has been little effort to demonstrate the actual operation. The failure to pursue this path stems mainly from unfamiliarity, and possibly from the perceived need for single crystals of anisotropic materials which (except for triclinic & monoclinic symmetry classes) would also require "off-axis" growth or cuts.

Conducting polymers possess numerous attractive features for use as ODTE thermoelectric elements. They are cheap, lightweight, easily made uniaxially anisotropic (e.g., by stretching) and, with special merit for applications, flexible, thus opening up the possibility of practical ODTE. The main disadvantage of conducting polymers is an apparent very low thermoelectric efficiency index ZT_{DTE} . However, most research in these materials centers on achieving the maximum electrical conductivity⁴ which, as noted above, 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.

There are only a few studies which have reported two of the three relevant thermoelectric parameters - σ and S - over a sufficiently wide doping range in a conducting polymer to determine thermoelectric application potential⁵. Here we draw upon the 1985 work of Reynolds, Schlenoff and Chien⁵ (RSC⁵) who measured these properties 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 Figure 4 in the parametric form to be used through this paper, show a linear relation between $\log \sigma$ & S over a wide range in σ & S which can be expressed by $\log_e(\sigma/\sigma_{\max}) = -\beta \{S/(k/e)\}$ where the pure number $\beta = 1$ and $\sigma_{\max} = 10 \text{ S/cm}$ for RSC⁵ polyacetylene. Here k/e ($= 86.17 \text{ } \mu\text{V/K}$) is Boltzmann's constant divided by the electronic charge, the natural microscopic measure for S .

Figure 4. Log (Conductivity) vs Seebeck coefficient for polyacetylene (from Reynolds, Schlenoff and Chien⁵). The straight line is given by $\log_e(\sigma/\sigma_{\max}) = -S/(k/e)$.

We show below that this is the general behavior expected from statistical mechanics for a material having any $\sigma_{\max}$ and current carrying charge 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 at the same S , thus allowing a simple determination of the results of higher σ . The σ vs S behavior of the best thermoelectric materials today lies above the RSC data by ~ 3 decades in σ .

We have calculated the doping dependence of ZT_{DTE} in polyacetylene using the RSC⁵ data and assuming $\kappa = 0.01$ W/cmK ($\kappa < 0.005$ W/cmK is typical for non-conducting polymers⁴). These ZT_{DTE} results are given in Figure 11. The maximum ZT_{DTE} occurs at $S \approx 170$ μ V/K ($\approx 2k/e$) & $\sigma \approx 1$ S/cm as expected (see Eqs. 11 & 12 below), but has a value only slightly greater than 10^{-3} there, nearly 3 orders of magnitude below the value for the best thermoelectric materials today.

Recently, however, there have been reports⁴ of polyacetylene with $\sigma > 10^3$ larger than those used for Figure 11. This increase has been the result of new dopants and new preparation methods. If $\beta = 1$ for these materials, then they could have $ZT_{DTE} > 1$ at 300K, 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.

SYNTHESIS

I. Materials and Reagents

We chose to investigate the air-stable conducting polymers polyaniline, which is easily synthesized, and polypyrrole which is already commercially available in convenient form. All reagents for the synthesis or doping & dedoping of these materials were used as purchased and without further purification.

II. Synthesis of Polyaniline at -25°C

Synthesis of polyaniline at low temperatures (-20°C to -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 1M HCl in which 32.64 g LiCl (15wt%) were then dissolved. The pH was adjusted to 1 and the reaction mixture was cooled to -25°C. 24.4 g (0.107 mole) of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were then dissolved in 44 mL of H_2O . This solution was precooled to 0°C and added, dropwise, to the continually stirred aniline solution for 1 hour at -25°C. The reaction heat evolved 2.5 hours after addition of the last portion of the oxidant and the temperature rose to -3°C for 20 minutes. The reaction mixture was stirred for 24 hours at -25°C. The resulting dark green residue was collected in a Buchner funnel and washed with 4x100 mL 1M HCl. The product was then suspended in 300 mL 5M NH_4OH and deprotonated for 24 hours. The resulting emeraldine base was filtered, washed with 10x100 mL distilled water, then 2x200 mL isopropanol, and finally dried in the air. The final yield was 8 g (80%).

III. 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 1M HCl and the solution was precooled to 0°C. 11.5 g (0.0504 mole) of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were dissolved in 200 mL 1M HCl, pre-cooled to 0°C and then added for 1 minute to the continually stirred aniline solution. The reaction mixture was stirred for 1.5 hours at 0°C. The residue was collected in a Buchner funnel and washed with 5x100 mL 1M HCl. The washed residue was then suspended in 250 mL 0.1M NH_4OH , and the pH was adjusted to 8.0 by adding several drops of 5M NH_4OH . The mixture was stirred overnight. The resulting emeraldine base was collected in a Buchner funnel, washed with 5x100 mL 0.1M NH_4OH , 3x100 mL distilled H_2O and 3x100 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.)

IV. Film Casting for Polyaniline

A 2% solution of polyaniline in N-methyl pyrrolidinone was stirred for 1 hour at room temperature, then placed in an ultrasonic bath for 30 minutes 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 to 0.1 mm.

V. Film Stretching for Polyaniline

The cast films were stretched up to 3X their initial length under infra-red lamp heating in the range of 120°C to 180°C. The stretching was completed in less than 2 minutes.

VI. 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, pH3 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 micron 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/hour on average) into a solution of 5M NH_4OH . This provided a convenient "functional gradient" in the level of dopant and in the magnitudes of the electrical conductivity 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.

MEASUREMENT RESULTS

Figure 5 shows the σ vs S behavior found for our polyaniline samples which were stretched to $\approx 2.5X$ their original length and subsequently doped serially in oxalic acid. Our S values were measured relative to our Cu or Au electrodes and corrected to the absolute Seebeck coefficient scale³ (by adding $1.8\mu\text{V/K}$) for the graphical presentations and analytical formulas in this paper. All data in this study were taken at 300K.

Figure 5. Log (Conductivity) vs Seebeck coefficient for 2.5X 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 (RSC⁵).

The data for 2.5X parallel-to-stretch and perpendicular-to-stretch samples both follow the correlation

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

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 RSC⁵, and about which more will be said below. Note that the horizontal (S) scale in Figure 5 (& all following Figures) is 10X smaller than that in Figure 4.

Figure 6 shows the σ vs S behavior found for a stretched polyaniline sample cut adjacent to that which provided the data in Figure 5, but which was serially doped in citric instead of oxalic acid.

Figure 6. Log (Conductivity) vs Seebeck coefficient for 2.5X stretched polyaniline samples serially doped in citric acid. Data are for parallel- & perpendicular-to-stretch samples. The line above the data roughly gives σ vs S for polyacetylene (RSC⁵).

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. 10 for the 2.5X 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 RSC⁵. Note also that the β 's are anisotropic in stretched polyaniline for both oxalic and citric acid doping, and the magnitudes of the β 's are different in the two cases.

The anisotropy in $\sigma_{\max}$ with oxalic acid doping is in approximate accord with the anisotropy in σ found in HCl-doped polyaniline by Epstein et. al⁴. 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 7 shows the σ vs S behavior found in our unstretched polyaniline samples from a different synthesis, now as individually doped samples in oxalic acid, and which yields $\beta \approx 9.6$ & $\sigma_{\max} \approx 40$ S/cm in Eq. 10.

Figure 7. 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 (RSC⁵).

The value of β from Eq. 10 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 8 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. 10.

Figure 8. Log (Conductivity) vs Seebeck coefficient for unstretched polyaniline doped in acetic acid. The line above the data roughly gives σ vs S for polyacetylene (RSC⁵).

Figure 9 shows the σ vs S behavior found in NH_4OH gradient-dedoped, unstretched polypyrrole (MILLIKEN CONTEX FABRIC) which yields $\beta \approx 9$ and $\sigma_{\text{max}} \approx 110 \text{ S/cm}$ from Eq. 10.

Figure 9. Log (Conductivity) vs Seebeck coefficient for gradient-dedoped polypyrrole.

Finally, Figure 10 shows the σ vs S data for over 150 samples measured in our studies.

Figure 10. Log (Conductivity) vs Seebeck coefficient for all data. The line above the data is calculated from band theory assuming a mean free path = $1 \text{ Å}/(m^*/m)$.

These data are derived from 2 base materials (polyaniline & polypyrrole), 15 different dopants, stretch-oriented & unoriented forms, serially & individually doped and dedoped, and chemically & electrochemically synthesized & doped, though not in all combinations. One can discern in the plot the linear trends due to the constant β 's, some of whose details have been revealed in the previous graphs. The correlation noted in Figures 5 - 9 holds whenever we have sufficient data to test it. The near common slope for much of the data results from values for β which are often ~ 9 .

We can now further identify the line in Figs 5 - 8, described as the approximate behavior of RSC⁵ polyacetylene. This line, in fact, is the σ vs S behavior calculated from band theory for the case of a constant mean free path, $mfp = 1 \text{ Å}/(m^*/m)$, where (m^*/m) is the effective mass ratio⁸. Thus the line roughly separates the region of extended states, $mfp > 1 \text{ Å}/(m^*/m)$, which lies above it, from that of localized states, $mfp < 1 \text{ Å}/(m^*/m)$, which lies below it. That conducting polymers in a high σ state lie at a metal-insulator boundary has been noted before⁹. Figure 10 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 $\sigma_{\max}$ are anisotropic in a stretched sample of polyaniline with $\sigma_{\max}$ being larger and β being smaller in the direction parallel-to-stretching, compared to 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.

THE CONSEQUENCES OF THE EMPIRICAL σ vs S CORRELATION FOR THERMOELECTRIC APPLICATIONS

When the thermoelectric efficiency index $ZT_{\text{DTE}} = (S^2 \sigma T)/\kappa$ 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_{DTE} will reach a maximum on doping at

$$S(\max ZT_{\text{DTE}}) = (2/\beta) (k/e) \approx (172/\beta) \mu\text{V/K} \quad (11)$$

$$\sigma/\sigma_{\max} (\max ZT_{\text{DTE}}) = e^{-2} \quad (12)$$

and will there have magnitude (at 300K)

$$ZT_{\text{DTE}}(\max) \approx \sigma_{\max} / (8 \cdot 10^5 \kappa \beta^2) \quad (13)$$

where, if $\sigma_{\max}$ 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

$$\kappa = \kappa_1 + \kappa_e = \kappa_1 + C (k/e)^2 \sigma T \quad (14)$$

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

$$ZT_{\text{DTE}} = [S/(k/e)]^2 / C \quad (15)$$

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

The numeric parameter C in Equation 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 non-degenerate 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 (Equation 14). 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 "CONCLUSIONS" Section below). We therefore choose to assume a constant total thermal conductivity in what follows.

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 equal ZT_{DTE} , electrical conductivities which are $\beta^2 \sim 100X$ greater than in the case where $\beta = 1$, as in RSC⁵ polyacetylene, other parameters being equal. This is shown in Figure 11 where, to obtain the magnitudes of ZT_{DTE} , we have used $\sigma_{max} = 10$ S/cm, similar to that for our data and for RSC⁵ polyacetylene with $\beta=1$, and $\kappa = 0.01$ W/cmK ($\kappa < 0.005$ W/cmK is typical for nonconducting polymers⁴). With higher σ , and the same S & β , the ZT_{DTE} 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 RSC⁵ polyacetylene, with $\beta=1$ and at the same S , would lead to $ZT_{DTE} > 1$ (though the large σ may increase κ beyond 0.01 W/cmK).

Figure 11. ZT_{DTE} vs Seebeck coefficient with the empirical σ vs S correlation (Eq. 10), $\sigma_{max}=10$ S/cm, $\kappa=0.01$ W/cmK, & for $\beta=1$ (RSC⁵ polyacetylene) & $\beta=10$.

Since the off-diagonal terms in S rarely exceed the diagonal terms by great amounts (the detailed data of Figs. 5 & 6 confirm this), the failure to achieve large ZT_{DTE} 's, because of the large β , makes further analysis for ODTE in our polyaniline and polypyrrole of little value, and is omitted.

The detrimental effects of $\beta \gg 1$ for thermoelectric applications result from the empirical σ vs S correlation. We now expand a standard model to provide an explanation for the correlation.

ON THE CORRELATION BETWEEN 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 $\Pi = S T$, 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,

$$S = (k/e) \log_e[c/(1-c)] \quad (16)$$

The electrical conductivity σ of such a system is given by

$$\sigma = \sigma_{\max} c(1-c) \quad (17)$$

where, when $c \ll 1$, $\sigma_{\max}$ is the conductivity extrapolated to $c = 1$. $\sigma_{\max}$ 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

$$\sigma/\sigma_{\max} = c \quad (c \ll 1) \quad (18)$$

$$\log_e(\sigma/\sigma_{\max}) = -\beta \{S/(k/e)\} \quad (c \ll 1) \quad (19)$$

where the pure numbers

$$\beta = [\sigma_{\max}(+) + \sigma_{\max}(-)] / [\sigma_{\max}(+) - \sigma_{\max}(-)] = (r+1) / (r-1) \quad (c \ll 1) \quad (20)$$

$$r = \sigma_{\max}(+) / \sigma_{\max}(-) = \text{mobility}(+) / \text{mobility}(-). \quad (c \ll 1) \quad (21)$$

In conventional extrinsic semiconductors 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. However, in what follows we will assume that electrical transport in polymers made conducting by doping with ionizable molecules may occur with both charge types, thus allowing all values of r . (This can then also include the case of unequal numbers of + and - charge carriers.)

A simple application of this theory, from Equation 19, is to plot $\log_e(\sigma)$ vs S for a series of lightly doped samples, wherein a straight line should 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 Equation 21. (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 $\sigma_{\max}$. This then further allows the determination of the fraction of occupied, thermally-available, current carrier sites c via Equation 18. This is the basis for our graphical presentations in Figures 4 - 10.

As c approaches 1, the "light doping" conditions leading to Equations 18-21 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 $\sigma/\sigma_{\max}$ of ≥ 0.43 decade ($=\log_{10}(e)$) at $S \leq (130/\beta) \mu V/K$. 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 RSC⁵ data plot for polyacetylene in Figure 4 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 $0.6 \text{ \AA}/(m^*/m)$. 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 Equation 19. The simple particle model of Equations 16 to 21 with "light doping", for example, will yield results equivalent to the use of Boltzmann ("non-degenerate") statistics in the band structure models.

Note that with conduction by both charge types, S values are reduced (shifted left in Figures 5 to 10) 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 & S data for all dopants in Fig 10 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. 18 & 19 with a constant $\sigma_{\max}$ equivalent to a mean free path⁸ of $\sim 1 \text{ \AA}/(m^*/m)$ for the case $c \ll 1$.

Relevant to the usual interpretations of conducting polymer behavior, we further note that neither the Mott¹⁰ nor the Efros-Shklovskii¹¹ theories of transport in 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.

CONCLUSIONS AND FINAL COMMENTS

Our central finding is the correlation $\log_e(\sigma/\sigma_{\max}) = -\beta \{S/(k/e)\}$ at 300K for polyaniline & polypyrrole. This correlation, because of $\beta \gg 1$, is detrimental for DTE and ODTE applications.

We know of no theory which can account simply for the empirical correlation other than one which admits current conduction by "carriers" of both signs with relative conductivities not greatly different from unity. Our central conjecture, then, is that "ambipolar-like" conduction is the cause of the empirical correlation found in polyaniline & polypyrrole. Our measurements cannot tell us if the charge carriers are "electron- & hole-like" or anions & 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 present¹². The resulting addition to κ will be of the form given by Eq. 14, 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 & S at 300K.

Finally, for $\beta \approx 9$, which characterizes many of our isotropic samples, we further conclude that if "ambipolar" carriers are present in both polyaniline and polypyrrole, then the 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 our interpretation of the σ - S correlation and the data of RSC⁵. Thus polyacetylene, because of current 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

The authors wish to thank Prof. A. Monkman of Durham University for helpful comments, Dr. Andrew Child of The Milliken Research Corporation, Spartanburg, S.C. for helpful discussion as well as the polypyrrole-coated Milliken Contex Fabric samples, Dr. Sene Bauman and the PIXE Analytical Laboratory of Tallahassee, FL for technical assistance, and The Advanced Energy Projects Division of The Department of Energy for their support of this work.

* Also at The Florida A&M University/Florida State University College of Engineering, Tallahassee, FL.

**Also at The Chemistry Department of Florida State University, Tallahassee, FL.

REFERENCES

1. For a more detailed discussion of the "off-diagonal" thermoelectric effects in anisotropic materials, see "Physical Properties of Crystals", J. F. Nye, Chapter XII, Clarendon Press, (1985) 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. Magnetic fields can also lead to "off-diagonal" terms in S and thermoelectric effects which are phenomenologically similar, in part, to those described in the present paper. "Off-diagonal" thermoelectricity induced by magnetic fields, furthermore, can occur in materials of any symmetry. However, the microscopic origins of these effects are different and the required field magnitudes for large effects can be substantial.
2. See, for example, "Thermoelectricity: Science and Engineering", edited by R. Heikes and R. Ure, chapter 11 by R. W. Ure and R. R. Heikes, Interscience Publishers, N.Y., (1961).
3. See, for example, "CRC Handbook of Thermoelectrics", edited by D. M. Rowe, Chapter 5 by C. M. Bhandari and D. M. Rowe for band structure calculations of the thermoelectric parameters, and Chapter 32 by A. T. Burkov and M. V. Vedernikov for the absolute Seebeck coefficients of the elements, CRC Press, Boca Raton, (1995).
4. See, for example, "Physical Properties of Polymers Handbook", edited by James Mark, Chapter 34 by R. S. Kohlman, J. Joo and A. J. Epstein for electrical properties of conducting polymers, and Chapter 10 by Y. Yang for thermal conductivities of polymers, American Institute of Physics, (1996).
5. For references and analysis of prior studies of the Seebeck coefficient and electric conductivity of conducting polymers see A. B. Kaiser, Phys. Rev. **B40**, 2806, (1989). In the present paper 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, Synth. Met., **69**, 183 (1995).
7. A. G. MacDiarmid, J. C. Chiang, A. F. Richter, N. L. D. Somasiri and A. J. Epstein in "Conducting Polymers", L. Alcacer, Editor; Reidel: Dordrecht (Netherlands), 105 (1987).
8. The RSC⁵ behavior for polyacetylene corresponds more nearly to a mean free path = $0.6\text{\AA}/(m^*/m)$. The effective mass ratio (m^*/m) used for Figure 10 & in its following text is a combination of inertial & density of states effective masses for ellipsoidal Fermi surfaces, a detail not warranting elaboration in the present case.
9. C. O. Yoon, M. Reghu, D. Moses, A. J. Heeger, Y. Cao, T -A Chen, X. Wu, and R. D. Rieke, Synthetic Metals, **75**, 229, (1995).
10. See, for example, "Electronic Processes in Noncrystalline Materials", N. F. Mott and E. A. Davis, Oxford University Press, London, (1979).
11. See, for example, "Electronic Properties of Doped Semiconductors", B. I. Shklovskii and A. L. Efros, Springer, Berlin, (1979).
12. Thermal generation of current carrying charge pairs would also contribute to the temperature dependence of the electrical conductivity, a much studied behavior in conducting polymers.