Thermoelectric Power Factor for Electrically Conductive Polymers

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Abstract

In conventional semiconductors, increasing the doping will reduce the Seebeck coefficient, and there is an optimum doping concentration for thermoelectric cooling or power generation applications. An overview of the experimental results for the power factor (electrical conductivity times the square of Seebeck coefficient) for various electrically conductive polymers is presented. Even though the Seebeck coefficient decreases with doping, the power factor keeps increasing. Various mechanisms of electron transport in polymers are described and the doping dependence of the power factor is analyzed.

Introduction

Traditionally, polymer materials have been used for properties other than electronic and optoelectronic. Particularly advantageous properties of macromolecular materials include chemical inertness, electrical insulation, and especially ease of processing. The use of polymers as electronic materials started with the discovery in 1977 that conjugated polymers, a few of which are represented in Fig. 1, can be chemically oxidized or reduced (doped) in any of several simple ways to induce high levels of electrical conductivity [1-24]. The common electronic feature of pristine (undoped) conducting polymers is the π-conjugated system which is formed by the overlap of carbon p_z orbitals and alternating carbon-carbon bond lengths [2,3,24]. Approximately twenty prototypes of conjugated polymers are known as conductive polymers. Among them, the heavily

Fig. 1 The structure of polymer chain:
(a) Trans-polyacetylene (PA),
(b) Poly para-phenylene (PPP),
(c) Poly para-phenylenevinylene (PPV).

doped polyacetylene is unique, since it has the simplest backbone structure and it shows the highest conductivity approaching that of metals. The maximum reported conductivity is $\sigma_{max} \sim 60{,}000$ S/cm for the iodine-doped polyacetylene [9].

In this article we will evaluate the potential of electrically conductive polymers for thermoelectric cooling or power generation applications. Since the lattice thermal conductivity dominates over the electronic contribution for most materials used for room temperature applications, the single "electronic" parameter that describes the efficiency of a thermoelectric cooler or a power generater is the *thermoelectric power factor*. This is defined as $S^2\sigma$, where S is the Seebeck coefficient and σ the electrical conductivity. In conventional semiconductors or metals, increasing electrical conductivity decreases the Seebeck coefficient. This is mainly due to the three dimensional nature of electronic density-of-states [see e.g. A. Shakouri and C. Labounty's article in this proceeding]. For these conventional materials, there is an optimum electrical conductivity at about 1000 S/cm that gives the highest values of the power factor. In this article we will see that the power factor for highly doped conjugated polymers keeps increasing with the increase in electrical conductivity for the highest values achieved to date.

Theoretical description

The doping procedures for polymers differ from conventional ion implantation used for three-dimensional semiconductors. The doping process is carried out electrochemically or by exposing the films to vapors or solutions of the dopant. The negative or positive charges initially added to the polymer chain upon doping do not simply begin to fill the rigid conduction or valence bands. The strong coupling between electrons and phonons causes lattice distortions around the doped charge. This leads to formation of new quasi-particles such as solitons, polarons and bipolarons [17,24].

There is a large anisotropy in the electronic structure of conjugated polymers. This is a consequence of the chain-like form of the molecules, having a strong *covalent* bonding along the chain and comparatively weak bonding of *van der Waals* type between the chains. As an example, the width of the electronic states in polyacetylene is of the order of 10eV along the chain, but only some 0.1eV perpendicular. Conjugated polymers are often considered to originate from a one-dimensional system with one electron per carbon atom. It can be shown that such a system can not exist as a one-
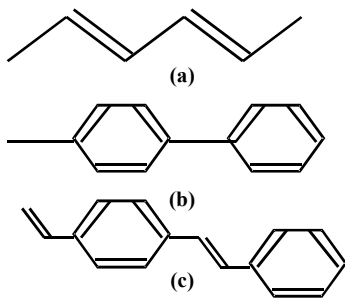
dimensional metal with a half-filled band, but rather as an insulator with a gap forming at the Fermi level. The reason for this is either Peierls instability, or electron correlation, or a combination of both. The quasi-one-dimensional structure of conjugated polymers resembles the conventional semiconductor in exhibiting an energy gap of 1-3eV. [2,4,7,17,20,24].

In order to understand various parameters that influence electronic properties of conjugated polymers, electrical conductivity and Seebeck coefficient as a function of temperature have been extensively studied. Typical experimental results are shown in Figs. 2 and 3 [4,7,24]. For lightly and moderately doped polymers, the conduction is dominated by thermal activation or by variable-range hopping (VRH) [7,24]. In this case the electrical conductivity can be written as:

$$\sigma = \sigma_0 \exp[-(T_0/T)^\gamma]$$

where σ_0 is weakly temperature dependent, T_0 is related to the localization length, and $\gamma \sim 0.25-0.5$. The Seebeck coefficient follows a temperature dependence given by:

$$S = (k_B^2/2e)(T_0 T)^{1/2} (\frac{d \ln N(E)}{dE})_{E=E_f}$$

where $N(E)$ is the density-of-states. This variable range hopping thermopower has been reported in lightly doped polyacetylene, [3,4] and in lightly doped PANi [6-8], especially in pressed powder pellet samples.
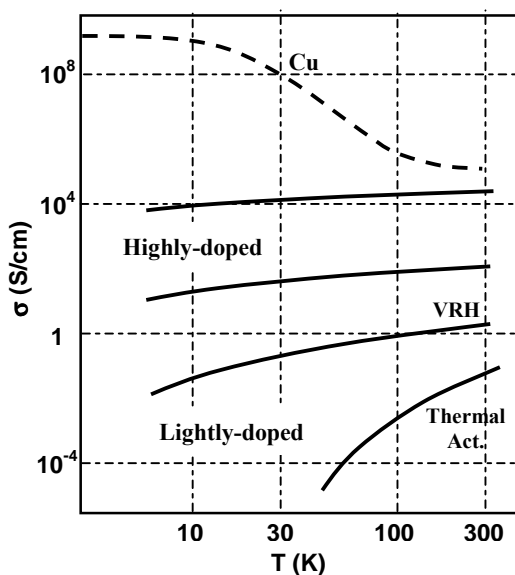
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In highly doped polymers with metallic behavior, the conduction is described either by VRH with smaller T_0 (weaker localization due to improved intrachain and interchain order [24]) or by fluctuation-induced tunneling (Sheng's model [4,7,10,12,14,15]). In the latter case the conductivity is given by:

$$\sigma = \sigma_0 \exp[-T_1/(T + T_0)]$$

The Seebeck coefficient is dominated by the diffusion thermopower contribution, i.e.:

$$S(T) = -\frac{(\pi k_B)^2}{3e} T[\frac{d \ln \sigma(E)}{dE}]_{E=E_f}$$

where $\sigma(E)$ is the differential conductivity. This equation shows that the Seebeck coefficient has a *linear* relation with temperature, this behavior has been observed in highly doped polyacetylene [2-4] and in some cases for PANi [5].

In highly doped samples, the apparent contradiction between the *nonmetallic* temperature dependence of conductivity and the *metallic* behavior of thermopower can be resolved by a heterogeneous polymer model. Conjugated polymer is made of fibrillar polymer strings with high intrinsic electrical conductivity separated by low conductivity barriers. These barriers dominate electrical conductivity, but since the thermopower is a zero current transport coefficient, it is insensitive to complex morphological interruptions of the system (i.e. "contact resistances") [13-15].
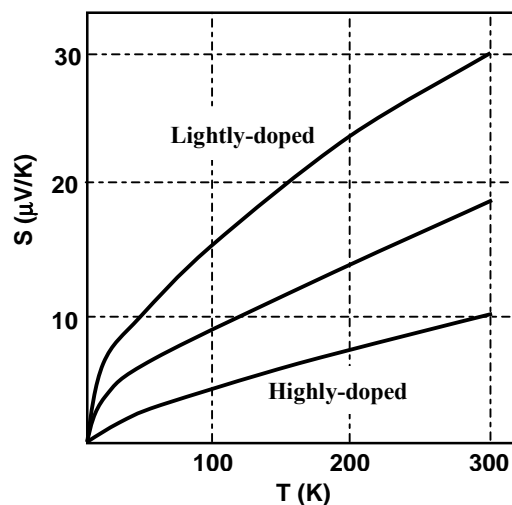

Fig. 2 Typical electrical conductivity of conjugated polymers as a function of temperature [4,7,13].

Fig. 3 Typical Seebeck coefficient of conjugated polymers as a function of temperature [4,7,13].

Review of experimental results

Table 1 lists electrical conductivity, Seebeck coefficient, thermoelectric power factor ($S^2\sigma$), thermal conductivity and thermoelectric figure-of-merit (Z) for various metals and semiconductors. Figure 4 shows the thermoelectric power factor as a function of electrical conductivity. We can see that there is an optimum conductivity on the order of 1000 S/cm that gives the highest power factor (with the exception of Ni, Co, Cr, Sb and Bi). This is mainly due to the three dimensional nature of electronic density-of-states. Increasing the doping, increases the number of carriers contributing to the conduction process. As the Fermi energy is pushed inside the conduction band, the number of electronic states above and below Fermi energy (within $k_B T$) becomes more equal, thus reducing considerably the average transport energy of carriers (the Seebeck coefficient).

Figure 5 shows the thermoelectric power factor versus electrical conductivity for various conjugated polymers (see also Table 2). It is of particular interest to point out that the power factor keeps increasing as the conductivity increases and no saturation is observed.

Conclusion

Highly iodine-doped polyacetylene has thermoelectric power factor ($S^2\sigma$) that approaches that of the best thermoelectric materials. However the aging and instability even in an inert environment is a serious drawback that limits the use of conjugated polymers in thermoelectric cooling or power generation applications. It is interesting to note that unlike conventional semiconductors and metals, the power factor keeps increasing with doping up to the highest values achieved to date (10^5 S/cm). This can be an indication of low dimensional nature of electron transport along 1D chains of polymers.
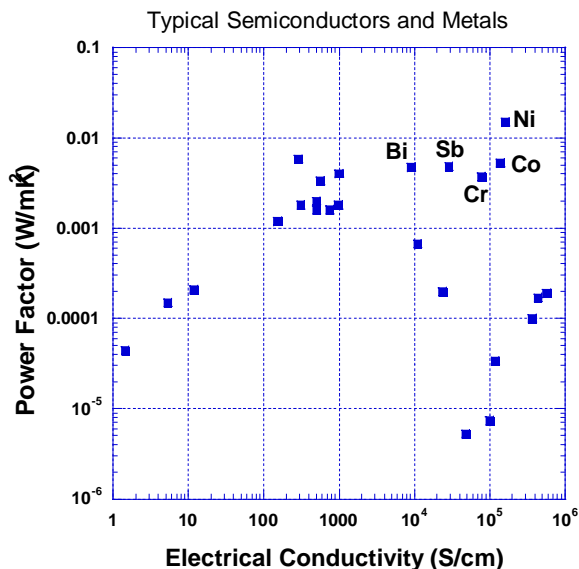
Fig. 4 Power factor as a function of electrical conductivity for various semiconductors and metals (see Table 1).

Table 1: Properties of some semiconductor and metals.

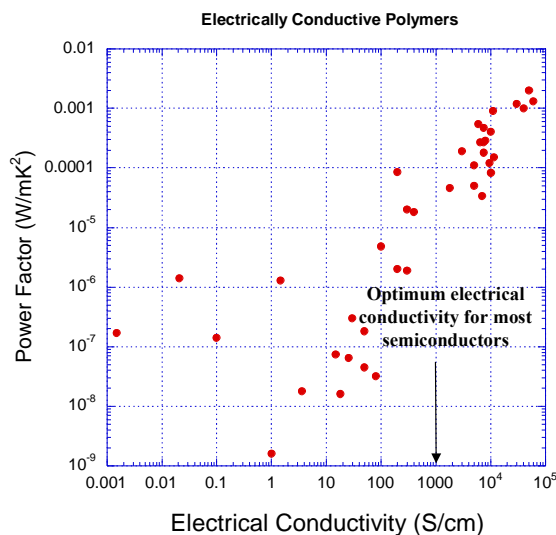| Material	σ	S	$S^2\sigma$	β	Z	Ref.
	1/Ωcm	μV/K	W/mK²	W/mK	/K	
Bi$_2$Te$_3$ polycryst	1000	200	4.0e-03	1.6	3.0e-3	Atramed
SiGe (p) 400K	758	144	1.6e-03	4.8	3.3e-4	CRC 95
SiGe (n) 400K	990	-136	1.8e-03	4.45	4.1e-4	CRC 95
SiGe (p)1200K	313	240	1.8e-03	4.38	4.2e-4	CRC 95
SiGe (n)1200K	562	-242	3.3e-03	4.20	7.8e-4	CRC 95
Al	366300	-1.66	1.0e-04	237	4.2e-7	CRC 95,91
Au	440529	1.94	1.7e-04	315	5.4e-7	CRC 95,91
Bi (polycrystal)	9091	-72	4.7e-03	7.9	5.9e-4	Kaye 60
Co	160256	-30.8	1.5e-02	100	1.5e-4	CRC 95,91
Cr	77519	21.8	3.7e-03	90.3	4.1e-5	CRC 95,91
Cu	580000	1.83	1.9e-04	398	4.8e-7	CRC 95,91
Eu	11111	24.5	6.7e-04	13.9	4.8e-5	CRC 95,91
Ge			4.0e-03	63	6.3e-5	Rowe 83
Ge (thin film) n	1.45	-548	4.4e-05	64	6.8e-7	CRC 95
Ge (thin film) p	12	420	2.1e-04	64.4	3.3e-6	CRC 95
In	119474	1.68	3.4e-05	81.8	4.2e-7	CRC 95,91
InAs n	500	-180	1.6e-03	59.2	2.7e-5	CRC 95
InAs p	500	200	2.0e-03	25	8.0e-5	CRC 95
InSb			8.0e-03	16.0	4.7e-4	Rowe 83
Ir	100200	0.86	7.4e-06	80.4	9.2e-8	CRC 95,91
Ni	138889	-19.5	5.3e-03	90.5	5.9e-5	CRC 95,91
Pb	48426	-1.05	5.3e-06	35.2	1.5e-7	CRC 95,91
PbTe n or p			2.6e-03	2.0	1.2e-3	Rowe 83
Sb (polycrystal)	28570	41	4.8e-03	24.4	2.0e-4	Kaye 60
Si			2.0e-03	113	1.5e-5	Rowe 83
Si	286	450	5.8e-03	145	4.0e-5	CRC 95
Te (annealed)	154	274	1.2e-03	12	1.0e-4	Kaye 60
Te (polycrystal)	5.3	526	1.5e-04	12	1.3e-5	Kaye 60
Ti	23810	9.1	2.0e-04	21.9	9.1e-6	CRC 95,91

Fig. 5 Power factor as a function of electrical conductivity for various conjugated polymers (see Table 2).

Table 2 Electrical conductivity and Seebeck coefficient for a few electrically conductive polymers. 7th and 8th columns show the anisotropy of electrical conductivity and the thermopower in stretched conductive polymers.

Polymer	Abr.	Doped	σ 1/Ωcm	S μV/K	$S^2\sigma$ W/mK^2	σ// σ|	S// S|	Comment	Ref
Polyacytelene	PA		6405	20.6	2.7e-04				Park 91
Polyaniline	PA		18	3	1.6e-08				Zipperling 95
Polyacytelene	PA	FeCl$_4$	7530	15.3	1.8e-04				Park 91
Polyacetylene	PA	FeCl$_4^-$	10200	9	8.3e-05	46	2.2	dry 9μ thick	Pukacki 94
Polyacytelene	PA	Iodine	11110	28.4	9.0e-04				Park 91
Polyacetylene	PA	Iodine	8020	19	2.9e-04	87	1.4	wet 35μ thick	Pukacki 94
Polyacetylene	PA	Iodine	7490	19	2.7e-04	58	1.4	dry 9μ thick	Pukacki 94
Polyacetylene	PA	Iodine	50000	20	2.0e-03			Size 1x10mm^{2}x1μ, Aging: conductivity reduces by a factor of 5,20,50 after 500,2000,2300h resp.	Kaneko 93
Polyacytelene	PA	Iodine	60000	15	1.3e-03				Nogami 90
Polyacytelene	PA	Iodine	40000	16	1.0e-03				Nogami 90
Polyacytelene	PA	Iodine	30000	20	1.2e-03				Nogami 90
Polyacetylene (Pristine)	PA	Iodine	~0.1	~120	1.4e-07		iso	Doping Conc. 0.8%	Pukacki 92
Polyacetylene (Pristine)	PA	Iodine	~200	~65	8.5e-05	4.3	iso	Doping Conc. 3%	Pukacki 92
Polyacetylene (Pristine)	PA	Iodine	~0.07				iso	Doping Conc. 3%, 5%sp^3	Pukacki 92
Polyacetylene (Pristine)	PA	Iodine	~0.001				iso	Doping Conc. 3%, 15sp^3	Pukacki 92
Polyacetylene (Pristine)	PA	Iodine	~6000	~30	5.4 e-04	5.3	iso	Doping Conc. 15%	Pukacki 92
Polyacetylene (Pristine)	PA	Iodine	~300	~26	2.0 e-05		iso	Doping Conc. 15%, 3%sp^3	Pukacki 92
Polyacetylene (Pristine)	PA	Iodine	~400	~21	1.8 e-05	3.2	iso	Doping Conc. 15%, 5%sp^3	Pukacki 92
Polyacetylene (Pristine)	PA	Iodine	~2			2.5	iso	Doping Conc. 15%, 15sp^3	Pukacki 92
Polyacetylene (Pristine)	PA	Iodine	~7500	~25	4.7 e-04	5.2	iso	Doping Conc. 22%	Pukacki 92
Polyacetylene (Pristine)	PA	Iodine	~10000	~20	4.0e-04	6.8	iso	Doping Conc. 28%	Pukacki 92
Polyacetylene	PA	K	5000	10	5.0e-05	30			Park 95
Polyacytelene	PA	MoCl$_5$	1.5e-03	1077	1.7e-07			Doping Conc. 0.06 (aging effect)	Park 91
Polyacytelene	PA	MoCl$_5$	2.1e-02	820	1.4e-06			Doping Conc. 0.13	Park 91
Polyacytelene	PA	MoCl$_5$	1.47	93.9	1.3e-06			Doping Conc. 0.47	Park 91
Polyacytelene	PA	MoCl$_5$	9580	11.4	1.2e-04			Doping Conc. 6.9	Park 91
Polyacetylene	PA	Na	1800	16	4.6e-05	50			Park 95
Polyacytelene	PA	NbCl$_5$	11560	11.4	1.5e-04				Park 91
Polyacetylene	PA	Rb	3000	25	1.9e-04	40			Park 95
Polyacytelene	PA	ZrCl$_4$	4990	14.8	1.1e-04				Park 91
Polyaniline	PAN		7000	7	3.4e-05				Monkman 95
Polyaniline oligo-aniline	PAN		1	-4	1.6e-09			Self assembly	Paloheim 95
Polyaniline	PAN	CSA	200	10	2.0e-06				Wang 95
Polyaniline/PMMA	PAN	CSA	300	8	1.9e-06				Yoon 94
Polyaniline/PMMA	PAni		30	10	3.0e-07			Doping Conc. 60% (commercial)	Zipperling 95
Polyaniline/PETG	PAni		3.6	7	1.8e-08			Doping Conc. 60% (commercial)	Zipperling 95
Polyaniline	PAni	Proton	50	6	1.8e-07	10			Holland 95
Polypyrrole	PPy		26	5	6.5e-08				Maddison 88
Polypyrrole	PPy		50-200	3-7	4.5e-08				Masubuc. 95
Polypyrrole	PPy	polyani	15	7	7.4e-08				Chauvet 94
Polythiophene	PT	PF$_6^-$	100	22	4.8e-06				Masubuc. 95

Acknowledgments

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