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A Chemical Kinetics Perspective on Thermoelectric Transport

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Abstract. There is a growing community of chemists and materials scientists exploring thermoelectric properties of organic, polymeric, hybrid, and composite materials. Many of these materials are nondegenerate semiconductors, meaning that the Fermi and transport charge transport energy levels are significantly offset. Others are ionic conductors. While the meaning of the essential parameters electrical conductivity (σ) and Seebeck coefficient (S, the voltage difference per degree of temperature difference) are accessible, the origins of S are not readily apparent to one trained mainly in chemistry. The purpose of this manuscript is to illustrate S as being the result of a steady state difference between concentrations of two designations of charge carriers, those on hotter and those on colder sides of a material sample, analogous to the equilibrium among interconverting chemical species that differ in enthalpy and entropy. The ion-based Seebeck coefficient, also known as the Soret effect, can be explained using principles similar to those applicable to electrons and holes. We hope that this analysis leads to wider understanding of the origins of S through an explanation using the language of chemical kinetics and thermodynamics, and appreciation of ways that thermoelectric efficiency can be enhanced in emerging materials.

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Background and introduction. There are many emerging semiconducting material systems for thermoelectric applications.[1-7] The most developed and widely applied materials are inorganic compound semiconductors, the major theme of a recent extensive review.[2] A recognized thermoelectric figure of merit is ZT = (Sσ^2 T)/κ where S is the Seebeck coefficient, σ is electronic conductivity, conductivity, T is temperature in Kelvin, and κ is thermal conductivity.[2] S is the voltage per unit temperature difference across a material. As an example, bismuth telluride (parent formula Bi_2Te_3, often with altered stoichiometry and/or dopant elements) can have a figure of merit ZT of 1-1.5, sufficient for practical electricity generation from heat where heat is readily available and other energy sources are not. Conversely, this material can be used for electric-powered cooling where miniaturization or avoidance of mechanical motion are desired. Theoretical calculations project even higher ZT values for Bi_2Te_3 nanostructures. A more recent compound semiconductor is tin selenide (SnSe, often incorporating dopants), from which some higher ZT values were obtained. Many other metal elements (Cu, Ag, Pb, Ge, Zr, etc.) and nonmetals (e.g. Sb, Te) have been the basis for inorganic thermoelectric semiconductors. Some of these, as well as carbon nanotubes, have been used as nanowires or mixed in nanowire or particle form with organic matrices, especially the conductive polymer poly(ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonate (PSS) counterions.

To use mechanically flexible formats, printing processes, common and less toxic elements, and lower processing and operating temperatures, polymer-based thermoelectric materials are of increasing interest.[8] PEDOT-PSS can have ZT >0.1. Some newer, less oxidizable hole-carrying (p-type) thiophene polymers containing dipyrrolopyrrole groups show power factors ($S^2\sigma$) indicating that such a ZT could also be obtained from them.[9] Achieving comparable ZT from electron-carrying (n-type) materials is more challenging, but has been achieved, particularly from a family of nickel coordination polymers.[10, 11]

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A third option for thermoelectric energy conversion is to use ionically conductive polymers.[3] Current is driven and voltage is built up by a combination of temperature-dependent diffusion coefficients in the short term (kinetic limit), and temperature-dependent stability of ion-containing chemical structures in the long term (thermodynamic limit). The voltage arises from what is known as the Soret effect, which can be viewed as an ionic equivalent of a Seebeck coefficient. Continuous power cannot be harvested from an ionic thermoelectric unless the entire electrical circuit is based on ion transport. However, the static voltage built up in an ionic portion of a circuit can be capacitively coupled to an electronic circuit, where it can generate intermittent power or be used to charge a storage capacitor. The absolute voltages can be one or more orders of magnitude higher than obtained via the Seebeck effect at comparable temperatures.

The electronic semiconductors, especially polymeric ones, can have Fermi and transport levels at offset energies. This is the starting point for both classical[12] and contemporary[13, 14] definitions of S, which is concisely expressed as "energy-weighted average of $\sigma E(E, T)$ normalized to thermal energies defined as (kT)."[13] The transport levels generally have higher energies but also higher densities of states and thus greater entropies for charge carriers at those levels. Formal derivations of S include equations with a striking resemblance to those for the entropy of mixing.[14, 15] In this respect, they are analogous to chemical systems in which a higher enthalpy/higher entropy species is in equilibrium with a second species, more "favored" at a cooler temperature. When this kind of "equilibrium", or more properly a steady state, is established for charge carriers at two temperatures on the same material sample simultaneously, the charge density difference for the regions of the two temperatures is associated with the Seebeck effect voltage difference. Our earlier study of polymer blend dielectrics,[16] discussed in more detail below, assumed that the transport level was at the center of a Gaussian distribution of carrier energies, with very little power factor dependence on the width of the distribution (α_0 in that reference) in the range of 1.5-6 times

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kT. Seebeck coefficients in that system were on the order of 200 μV/K, which multiplied by 300 K gives 0.06 eV (2-3 kT) for an approximate difference between the Fermi and transport levels, well within the typical bandwidth of 0.5-1 eV for conducting polymers.[13]

The mathematical definition of S can be obtained from the Boltzmann transport equation (BTE), where the voltage exerted on charge carriers that would normally induce transport in one direction balances the diffusion of the carriers in the opposite direction, with scattering also taken into account.[17-22] Though this may be a fundamental concept, the BTE often appears mathematically complex. A derivation of S in terms of kinetic and equilibrium expressions, while arguable less rigorous or less complete,[23] would be better matched to the training and experience of a typical chemist. This manuscript develops such a derivation, and demonstrates its applicability and self-consistency with a prototypical polymer electronic system. We also show that similar reasoning can be applied to ionic systems.

Model and interpretation. Assume that there is a semiconductor with charge carrier number densities C at two energy levels, Fermi (f) and transport (t). Carriers at each of these energy levels can also be present at two temperatures, hot (h) and cold (c), on two sides of a sample, respectively. Also, we define a carrier level t' to refer to transport level carriers that are relaxed to the vibrational temperature on the cold side, whereas carriers at the t level will be considered at the vibrational temperature of the hot side regardless of which side they are on. This situation is shown schematically in Figure 1.

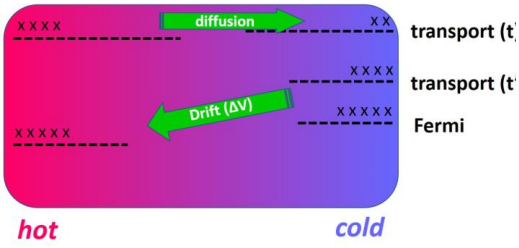

Figure 1. Energy levels, states (dashes) and carriers (x) on hot and cold sides of a sample. C represents the number density of carriers at each temperature and energy level.

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Assume that there are states at the Fermi level

that are (half) occupied. C(f,h) are excited to C(t,h) as below: and establishes a reaction rate expression k_1 C(f,h).

$$C(f,h) \rightarrow C(t,h) \quad (\text{eq. } 1, k_1)$$

The rate constant k_1 incorporates the power from a heater times the efficiency of using the heat to excite carriers, per the energy difference between t and f levels. The heater maintains the hot side temperature We will set C(t,h) to be a constant value equal to the transport level Fermi function value (F(E)) at the hot temperature times the density of states (DOS) at the transport level. It is assumed that the voltage interval by which the density of states is multiplied is the same on the hot and cold sides. An estimate for the DOS at the transport level is the number of molecular orbitals, or associated molecular subunits, at that level. The difference between the Fermi and transport energies can be a measurable property of the material. For example, if hopping transport in the material is not limiting, such as in a single crystal, the temperature dependence of the conductivity could provide this energy difference as an activation energy.[24] The energy difference can also be set by constructing a two-level material composition from major and minor components that determine the transport and Fermi energies, respectively.[16, 25]

The Fermi energy E(f,h) itself can be a known, constant quantity, obtainable, for example, by ultraviolet photoelectron spectroscopy or Kelvin probe measurements,[26-29] or controllable by molecular design. However, since the density of states at the Fermi energy may not be apparent, and the system is not at equilibrium because of the continuing power input, **C(f,h) is unknown,** but not very different from the number of chemical species that could be introduced in a material to stabilize charges at the Fermi level**.** The calculation of the rate of excitation should not require knowledge of C(f,h), but only the utilized power and the energy difference between f and t levels.

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C(t,h) are transported from the hot side of a thermoelectric material to produce an increment in C(t,c) at the cold side with a rate constant k_2.

$C(t,h) \rightarrow C(t,c)$ (eq. 2, k_2)

The carriers C(t,c) are located on the cold side but initially have the hot side temperature. The initial quantity of C(t,c,) is approximately the cold temperature F(E) x DOS at the transport level times exp(-heat capacity x ΔT) to account for cold side thermal excitation. The transport is driven by Fick's First Law diffusion, the rate of which (k_2) is $(\mu_h kT/e)\,(C(t,h) - C(t,c))/L$. The expression $\mu_h kT/e$ is the Einstein relation diffusion coefficient D; μ_h = mobility of hot carriers, k =Boltzmann constant, T = hot side temperature. (C(t,h) – C(t,c)) is the difference charge densities (F(E) times transport level DOS)[30] for the two temperatures. L is the sample length, and e is the charge on an electron.[31-33] Mobility in this expression can include voltage barrier terms in the form of $\exp(-eV_b/kT)$ for hopping past interfaces. The diffusion rate is equivalent to a current density.

C(t,c) relax to C(t',c), for example by transferring some energy to phonons, with a very high rate constant k_3.

$C(t,c) \rightarrow C(t',c)$ (eq. 3, k_3)

For example, time-resolved spectroscopic measurements indicate that the time constants for such relaxations are on the order of nanoseconds.[34-37] Thus, we can assume that C(t,c) remains at its initial value, as any incremental amount of C(t,c) is immediately converted to C(t',c).

The Fermi function F(E) on the cold side uses a Fermi energy that is corrected for **the increased voltage ΔV**, **unknown**, that results from the increase in C(t',c). Because of the condition that C(t,h) is constant, the rate of formation of C(t,c), and thus C(t',c) to which it is instantaneously converted, equals the rate of formation (and consumption) of C(t,h), which is the utilized hot-side power divided by the energy difference between t and f levels, as discussed above for k_1.

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C(t',c) (**unknown,** those just created **ΔC(t',c) (unknown)** plus those already there according to the original cold side Fermi level, $C(t',c)_0$ = F(E) x (DOS) at the cold side transport level, are transported (drift) to regenerate C(f,h) on the hot side with rate constant k_4, driven by Seebeck voltage ΔV/L, which has units of electric field, or force per unit charge. These "cold side charge carriers" have insufficient energy to be at the hot side transport level, so they occupy the Fermi level when they arrive at the hot side.

C(t',c) → C(f,h) (eq. 4, k_4) **k_4 is unknown.**

The sample length term used here is the same one that was used to calculate the charge density gradient for the diffusion current. The voltage is the difference in Fermi energies, ΔV, on the two sides. Energy barriers V_b can also apply to the mobility μ_c for this drift transport, but at lower temperature than for diffusion, so the barrier effect is higher even though the magnitude of each barrier should be the same.

The steady state conditions for this system are as follows: C(f,h) is constant, removed by the heating power, and formed by drift transport of C(t',c) across barriers from the cold side.

k_4C(t',c) = k_1 C(f,h) (5).

C(f,h) in the absence of any thermal gradient would be related by F(E) to C(t,h) by definition (F(E) at the Fermi level is ½).

C(f,h) (no ΔT) = C(t,h) DOS(f)/2 F(t,h) DOS(t) (6)

However, for the case of the thermal gradient, we assume that the C(t,h) that diffuse to the cold side are immediately replaced by excitation of C(f,h) leading to a deficiency of C(f,h) compared to the case without the thermal gradient.

C(f,h) = 0.5 (DOS at Fermi level) – ΔC(t',c) (7)

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As mentioned before, we will set C(t,h) to be a constant value equal to F(E) on the hot side times density of states (DOS) of the transport level.

$C(t,h) = f(t,h)\,DOS(t)$ (8)

The diffusion rate is equal to the rate of C(t,c) relaxing to the level of C(t',c)

$D((DOS)(F(t,h)) - F((t + \Delta V),c))) = k_3C(t,c)$ (9)

C(t',c) is a steady state concentration, formed by the very fast relaxation of C(t,c) and removed by drift transport to form C(f,h) driven by the voltage according to the classic definition of current density. We then set the diffusion expression that initially increases C(t,c) but ultimately is responsible for ΔC(t',c) equal to the drift rate, the essential steady state condition.

$$\mathbf{k_3C(t,c) = k_4C(t',c) = eC(t',c)\mu_c\Delta V/L = e(C(t',c)_0 + \Delta C(t',c))\,\mu_c\Delta V/L}$$ (10a, 10b, 10c)

The Fermi level voltage on the cold side increases by an amount equal to the voltage caused by C(t,c) + ΔC(t',c) where C(t,c) + ΔC(t',c) is in excess over the original $C(t',c)_0$. Carriers on the cold side fill available energy levels according to the Fermi function. They can be quantified by integrating F(E) times density of states with respect to energy over the transport energy band so that the integral equals C(t,c) + C(t',c) = C(t,c) + $C(t',c)_0$ + ΔC(t',c) and solving numerically for the cold side Fermi energy E(f,c), which is equivalent to solving for ΔV. Again, C(t,c) is probably negligible, so C(t,c) + C(t',c) = C(t',c) = $C(t',c)_0$ + ΔC(t',c) .

$C(t',c) = \int DOS(E)\,F(E,c)\,dE$ from E(t) to E(f,c) (11)

However, by employing the value of C(t,c) obtained using the thermal excitation assumption above, the relatively complex equation 11 is not essential.

A high transport energy level will mean a high voltage and a high S, but fewer charge carriers.

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The above derivation has five unknown quantities C(f,h), C(t',c), ΔC(t',c), k_4, and ΔV, and six equations containing them (5, 7, 10a, 10b, 10c, and 10d), all indicated in bold. The remaining variables have a basis in literature for assigning values to them or can be measured. Thus, the Seebeck coefficient S (ΔV/ΔT) can be derived from these mathematical relationships, relying on the principles of chemical kinetics, the laws of diffusion, and the Fermi function. A demonstration of how this could be done is shown in Supporting Information. However, it may be easier to measure S experimentally than some of the other input variables, such as DOS or the energy difference between Fermi and transport energies. Therefore, it should be recognized that measuring S could enable the calculation of one of the other input variables as well. It is also recognized that these equations/ models are not unique, but may be useful for relating bulk-macroscopic observables to an appropriate microscope ensemble average.

Generic calculation. The speed of a charge carrier is μ ΔV/L, mobility times electric field. If the mobility of a carrier is 1 cm^2/Vs and an induced electric field is 1 mV/mm = 0.01 V/cm, reasonable for S of 100-1000 μV/K, ΔT = 10-100 K, and a sample length of 0.1-1 cm, the speed is 0.01 cm/sec, and the transit time is 100 sec across 1 cm or 10 sec across 1 mm. Note that this is indeed much slower than the rate of carrier relaxation (nanoseconds time scale) to a cold side temperature.

The diffusion coefficient is (per the Einstein Relationship) μkT/e = mobility x 0.026 = 0.026 cm^2/s. The rate of electrons moving from the hot to cold sides per second = 0.026 cm^2/s times the difference in (F(E) x DOS for t, per volume-length) on hot and cold sides, converted to coulombs to get current in amps/cm^2. F(E) (Fermi-Dirac distribution) at 0.08 eV = 3kT (the optimum $E_t - E_f$ value for highest power factor[38, 39]) is about 0.05 at room temperature, as illustrated by the graph reproduced in Figure 2.

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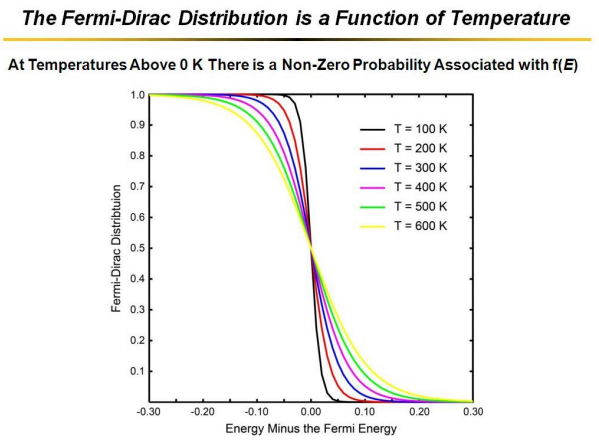

Figure 2. Temperature-dependent Fermi-Dirac distribution reprinted from Bryan Boudouris, "Organic Electronic Devices", Nanohub U (Creative Commons License BY). The x-axis is in units of eV.

For this generic calculation, we use an arbitrary order of magnitude charge density for low-moderately doped polymers of 10^{17}/cm^3.[40, 41] For the present system, this includes Fermi level carriers as well, which could be considered trapped and thus not mobile, so we use 10^{16} (0.002 coulombs)/cm^3) for the part of the charge density that is in the transport level according to the F(E) x DOS. A 100-degree temperature increase (300 to 400 K) increases F(E) by a factor of 2, so the *difference* in charge density between the hot and cold sides is also 10^{16} electrons/cm^3, assuming the densities of states at transport and Fermi levels are the same on each side. To impose the high-T occupancy (C(t, c) + C(t',c))/available states) on the low-T side but keeping the average transport level at the same energy, the Fermi level must increase by 0.02 eV on the cold side. This is equivalent to 200 μV/K, the optimal Seebeck coefficient for highest power factor.[38, 39]

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The rate of electrons moving from the hot to the cold sides per second by diffusion = 0.026 times mobility times 10^{16} electrons/cm^3/0.1 cm = 0.026 volts times 1 cm^2/Vs times 0.002 coulombs/0.1`cm^4 = 5 x 10^{-4} amps/cm^2 assuming a 1 mm sample length.

The rate of electrons moving from cold to hot sides by drift = (0.02 V x 0.002 coulombs/cm^3 times 1 cm^2/Vs)/0.1 cm = 4 x 10^{-4} amps/cm^2, the same order of magnitude.

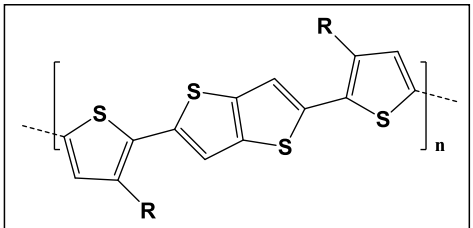

Figure 3. PBTTT, R = dodecyl or dodecylthio.

Polymer blend example. In a recent study, [16] we employed a blend consisting mostly of PBTTT (Figure 3) but with a small amount of an alkylthio-side chain derivative that helped set a Fermi level slightly offset from the transport level mostly defined by the PBTTT. The dopant was NOBF4. The hole mobility for a representative doped blend was 2.5 cm^2/Vs, measured using a field-effect transistor. The difference between transport and Fermi levels was estimated by electrochemistry and activation energy of conductivity to be about 2.5 kT near ambient temperature.

The diffusion coefficient is now calculated using kT/e times this mobility value = 0.026 x 2.5 = 0.065 cm^2/s. F(E) at 0.065 eV = 2.5 kT is about 0.1 at room temperature, based on the graph in Figure 2. We still use 10^{16} electrons (0.002 coulombs)/cm^3 for the part of the charge density that is in the transport level according to the F(E) x DOS, based on the arbitrary initial charge density mentioned above. A 10-degree temperature increase (300 to 310K) that was used in our experiment increases F(E) by a factor of about 1.2, so the estimated difference in charge density between the hot and cold sides per unit length is now 2 x 10^{15} electrons/cm^4 (0.0002 coulombs/cm^4). To impose the high-T occupancy on the low-T side but keeping the average transport level at the same energy, the Fermi energy must increase by 0.002 eV. This is still

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equivalent to 200 μV/K, one tenth the charge density increase for one tenth the temperature increase compared to the generic example discussed above. It is also in the middle of the range of measured S for the material system under investigation, and appropriate for a polymer with conductivity of 0.1-1 S/cm, as we[16] and others[9, 42, 43] have found.

The sample length for the measurements of S was 3 mm (0.3 cm). The rate of electrons moving from the hot to the cold sides per second by diffusion = 0.065 cm^2/s times 2 x 10^{15} electrons/0.3 cm^4 = 0.065 cm^2/s times 3.2 x 10^{-4} /0.3 coulombs/cm^4 = 6 x 10^{-5} amps/cm^2. The rate of electrons moving from cold to hot sides by drift = (0.002 V x 0.0002 coulombs/cm^3 times 2.5 cm^2/Vs)/0.3 cm = 3 x 10^{-6} amps/cm^2, a factor of 20 lower than from the diffusion method, reasonable considering that the charge carrier density estimates were also only orders of magnitude and only the "excess" charge carriers added to the transport level based on the Fermi function were considered to be mobile, as opposed to all the charge carriers initially present on the cold side.

We can also use charge carrier densities based on added dopant quantities and voltages based on our measured values of S. The sample with measured transistor mobility of 2.5 cm^2/Vs had a dopant concentration of 2.6 x 10^{20} cm^{-3}. When this was assumed to be the charge carrier concentration (meaning a 100% doping efficiency, an upper limit of charge carrier concentration), μ calculated from a measurement of σ was 0.02 cm^2/Vs. To calibrate this charge density further, a polymer with mobility of 2.5 cm^2/Vs and conductivity of 0.8 S/cm (the measured values of the sample of interest), the charge density would be 2 x 10^{18} /cm^3, clearly lower. The diffusion coefficient would be 0.02 x kT/e = 0.02 x 0.026 = 5 x 10^{-4} cm^2/s. F(E) sets the excess carrier density on the hot side at 0.2 x 2.6 x 10^{20} = 5 x 10^{19} cm^{-3} (10 coulombs cm^{-3}) . The diffusion transport rate is therefore 5 x 10^{-4} x 5 x 10^{19} /0.3 cm = 8 x 10^{16} electrons/cm^2 s or 0.004 amp/cm^2. The measured Seebeck voltage for a 10 K temperature difference was 0.8 mV. The drift transport rate is 0.02 cm^2/Vs x 10 coulombs cm^{-3} x 8 x 10^{-4} V/0.3 cm = 0.0005 amp/cm^2, this time within a

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factor of ten. If all the carriers, not just the "excess" carriers, were included in the drift calculation, and/or the "excess carrier density" closer to 2 x 10^{18} /cm^3 were used, the two transport rates would be even closer.

Ionic polymer example. Many of same quantities and relationships used for hole and electron "charge carriers" above could also apply to mobile ions, where the Seebeck coefficient arises from what is known as the Soret effect.[44-50] The main difference would be the multiple possible driving forces for such ions. For example, it is possible that heat would "excite" an ion in its surrounding medium to some higher-energy configuration, which would be the equivalent of a "transport level" for holes and electrons. However, there are other possibilities. For example, it is possible that an ion could either increase or decrease organization of its surrounding medium, in which case the "less organized" side would be more favored at higher temperature. Thus, an ion could induce a Seebeck coefficient of either sign, depending on whether it induced greater or lesser organization and would therefore move to the colder or hotter side, respectively. More specific and discontinuous mechanisms are also possible, such as the thermogalvanic driving force from the temperature dependence of reactions at electrodes[51] or the coupling of ionic stability to a local phase change.[52]

Because the treatment used above for electronic carriers is based on chemical kinetic and equilibrium principles, it should also apply to ionic species transported through media. Let us consider a prototypical case of an anion in a polymeric cation host, such as might be found in an ion-exchange membrane. A typical mobility for Cl- ion at high concentration in a polycation is 10^{-6} cm^2/Vs.[53] Again, kT/e = 0.026 V. The diffusion coefficient is 0.026 x 10^{-6} = 3 x 10^{-8} cm^2/s. Unlike in the hole-carrying polymer blend case above, which was governed by the Fermi-Dirac distribution, we have no a priori way to estimate the energy difference between ground and

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transport levels. However, we can reasonably use an estimated S = 0.01 V/K, the same order of magnitude as published values for the ionic Seebeck coefficient of other ionomers.[3, 49, 54-56]

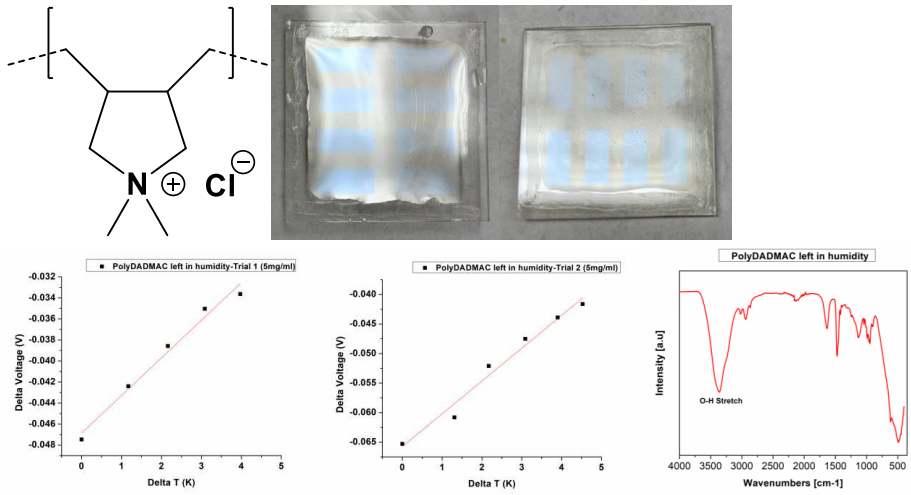

Figure 4. Poly(DADMAC), micrograph of dropcast films before and after drying (2.5 cm on a side), voltage change vs temperature change plots for Seebeck coefficient determinations, and infrared spectra showing the large OH stretching peak for incorporated water.

In an attempt to corroborate this value in a dry film, we measured S of a simple, minimally functionalized polyammonium salt, poly(diallyldimethylammonium chloride) (PolyDADMAC, Figure 4), as a dropcast film from 3-5 mg/mL solutions in water on glass with indium tin oxide (ITO) electrodes. After drying at room temperature and then at 95 degrees C in air and heating several hours at 80 degrees C under vacuum, we obtained Seebeck coefficients of negative 0.001-0.005 V/K, which is only somewhat lower than the published value cited above. Samples left in ambient air sometimes showed positive Seebeck (Soret) coefficients, a possible sign of proton contributions, and indicating the importance of controlled water inclusion/exclusion for assigning Seebeck coefficients to ionic polymers. Data supporting these statements are also shown in Figure 4. Reheating such devices for an additional 1-2 hours at 80 degrees C under vacuum resulted again

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in negative coefficients. Positive coefficients have been previously observed for this polymer under humid conditions.[49]

Again using the published 0.01 V/K value, for a 10 K temperature difference, $\Delta V = 0.1$ V (4 kT) across a sample, which we will again take to be 0.3 cm in length. Using the Boltzmann distribution, the initial thermally excited Cl- concentration on the hot side is fifty times higher than on the cold side! This is an enormously higher ratio than the one for holes in the above example. The initial concentration difference between the ground state and thermally excited state populations is expressed as follows:

$[Cl^-]_t = ([Cl^-]_0 - [Cl^-]_t)\exp(-\Delta G/kT)$ where t refers to transport level ions, 0 refers to original concentration of ions, and ΔG, the free energy difference between thermally excited and ground states, is used instead of ΔE as is appropriate for a chemical equilibrium. This equation applies separately to the hot and cold sides, designated h and c, at which there is a different (temperature-dependent) ΔG, with the temperature dependence expressed as the entropy. Note that the density of states terms in the treatment for holes and electrons expressed the entropy component when we used the Fermi-Dirac distribution.

Using an analogous method to what was used for the electronic transport case, we set

$\mathbf{[Cl^-]_{t,h}} = ([Cl^-]_0 - [Cl^-]_{t,h})\exp(\mathbf{-\Delta G_h}/kT)$ as a constant value.

Because $[Cl^-]_0 >> [Cl^-]_{t,h}$, this simplifies to

- $[Cl^-]_{t,h} = ([Cl^-]_0)\exp(-\Delta G_h/kT)$ where $-\Delta G_h$ is the free energy difference between the two levels at the hot temperature.
- $\mathbf{[Cl^-]_{g,h}} = ([Cl^-]_0 - [Cl^-]_{t,h} - \mathbf{\Delta[Cl^-]_{t,c}})$, expressing the net loss of [Cl-] from the hot side ground state, from excitation and diffusion to the cold side. This loss is not compensated

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by drift back from the cold side, because any such drifted Cl- ions are immediately heated and excited to the transport level.

$[Cl^-]_{t,c}$ = $([Cl^-]_0 - [Cl^-]_{t,c})\exp(-\Delta G_c/kT)$. This is also a constant value. As done earlier, we expect that $[Cl^-]_0 >> [Cl^-]_{t,c}$, so

- $[Cl^-]_{t,c} = ([Cl^-]_0)\exp(-\Delta G_c/kT)$, where $-\Delta G_c$ is the free energy difference between the two levels at the cold temperature. $[Cl^-]_{t,c}$ is defined as the original Cl- ion concentration at the transport level on the cold side. It is in addition to the $\Delta[Cl^-]_{t,c}$ that diffused from the hot side.

We assume that the voltage difference between the hot and cold sides is entirely due to the difference in concentration of transport level ions, because they are farther removed from positive counterions and are mobile. Note that unlike the case of electronic carriers, in which holes and electrons can both move, the polymeric cations are fixed in place by polymer chains.

- $\Delta V = kT/e \ln[([Cl^-]_{t,c} + \Delta[Cl^-]_{t,c}) / [Cl^-]_{t,c}]$, based on the Nernst equation for an electrochemical equilibrium on the cold side. We assume that the hot side voltage is fixed at its original reference value, set to zero, because the decrease in total [Cl-] on the hot side is compensated by its higher temperature. As discussed above, a reasonable value of $\Delta V/\Delta T$ is 10 mV/K.[44] Using a ΔT of 10 K, this results in $\Delta V = 0.1$ V.
- $\Delta V = 0.1\ V = (\Delta G_c - \Delta G_h)/e = 10\ \Delta S/e$ where $(\Delta G_c - \Delta G_h) = \Delta\Delta G = \Delta S \Delta T$ where ΔS is the entropy gained by the Cl- ions when moving from the ground to transport states.

$0.1\ V = kT/e \ln(\Delta[Cl^-]_{t,c} / [Cl^-]_{t,c})$; $\ln(\Delta[Cl^-]_{t,c} / [Cl^-]_{t,c}) = 4$

$\Delta[Cl^-]_{t,c} = 50\ [Cl^-]_{t,c}$

The diffusion and drift rates must be the same at steady state, so

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- D($[Cl^-]_{t,h}$ - $\Delta[Cl^-]_{t,c}$ - $[Cl^-]_{t,c}$) = 3 x 10(-8) cm^2/s ($[Cl^-]_{t,h}$ - $\Delta[Cl^-]_{t,c}$ - $[Cl^-]_{t,c}$) cm^{-4}) (diffusion)

= (0.1)(10^{-6}) ($\Delta[Cl^-]_{t,c}$) / 0.3 charges/cm^2 sec = 3 x 10^{-7} ($\Delta[Cl^-]_{t,c}$) (drift),

making the assumption that $\Delta[Cl^-]_{t,c}$ >> ($[Cl^-]_{t,h}$ - $[Cl^-]_{t,c}$), reasonable considering the result of the interpretation of ΔV.

The above constitute six equations (bulleted) in six unknowns (highlighted in **bold**). The equations can be solved as shown below for the ΔS of the ground and transport states for Cl- in the media.

From the last of the bulleted equations, 10 ($\Delta[Cl^-]_{t,c}$) = ($[Cl^-]_{t,h}$ - $\Delta[Cl^-]_{t,c}$ - $[Cl^-]_{t,c}$)

11 ($\Delta[Cl^-]_{t,c}$) = ($[Cl^-]_{t,h}$ - $[Cl^-]_{t,c}$)

($\Delta[Cl^-]_{t,c}$) = ($[Cl^-]_{t,h}$ - $[Cl^-]_{t,c}$)/11 = ($[Cl^-]_{t,h}$ - [$[\Delta Cl^-]_{t,c}$/50])/11

Multiplying the top and bottom of the last expression by 50 and rounding,

50 $[Cl^-]_{t,c}$ = 0.1 $[Cl^-]_{t,h}$; $[Cl^-]_{t,h}$ = 500 $[Cl^-]_{t,c}$

RT ln 500 = $\Delta\Delta G$ = $\Delta S\Delta T$

$\Delta S\Delta T$ = (2 cal/mol) (300 K) (6) = about 4000 cal/mol or 14,000 J/mol

ΔS = 13 cal/ mol K or 50 J/ mol K.

This shows excellent consistency with the entropy of Cl- association with a weak diacid receptor, determined to be 23 J/mol K.[57] Cl- association in the present system, which is the ground state of a quaternary ammonium polymer, would have stronger per-site attraction but would be expected to be monovalent. A related study of Br- binding to a tetravalent acidic host gave 33 J/mol K.[58] A solution for ΔH for the difference between the ground and transport states for Cl- in the media

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could also be found if one more experimental measurement could be made, such as the rate of evolution of $\Delta[Cl^-]_{t,c}$ using an ion selective electrode.

Summary, Limitations, challenges, and future work. For both electrons/holes and ions, drift speed is decreased by $\exp(-E_b/kT)$ for every barrier. Diffusion and drift are both decreased by the series resistance resulting from the intentional introduction of domains that form obstacles. The figure of merit for selective hot vs cold transport in a multidomain system is the barrier decrease term $\exp(-E_b/k\Delta T)$ divided by the series resistance transport decrease, a concept sometimes expressed as "energy filtering".[59-61] This would appear in the present model as a contribution to the temperature dependence of the mobility.

The model so far only considers two levels with uniform bandwidth, and an approximate graphical portrayal of the Fermi distribution. More advanced density of states profiles applied to the explicit Fermi level distribution and further details about the relaxation of cold side charge carriers would afford greater accuracy. The model does not consider phonon thermal conductivity, which significantly affects ZT in polymers. However, the model reiterates the parameters that determine power factor and that require further optimization. For electronic conductors, the Fermi level offset from the transport level is indeed 2.5kT for maximum power factor assuming temperature-independent mobility, as this optimizes the S-σ tradeoff. However, the implementation of energy filtering concepts through rational design of nano-inclusions,[59-61] especially for polymers, affords an additional way to increase S beyond that tradeoff. Energy filtering in ionic polymers does not seem to have been explored yet.

Even if μ is temperature-independent, its increase would proportionally increase the power factor and thus ZT. Recent investigations of chemical dopants that preserve molecular ordering and maintain or even increase μ,[9, 62-64] while initially aimed at higher σ for its own sake, would also lead to improved thermoelectric behavior when the Fermi level remains appropriately offset from

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the transport level. Field-effect doping,[62, 65-67] if implemented in a practical way, would avoid dopant-induced structural disruption that decreases mobility and allows high-mobility molecular semiconductors to be used. For ionic thermoelectrics, the decades-long efforts to increase conductivity for battery electrolytes and fuel cell membranes[68-71] could contribute material design ideas for higher power factor ionic circuits when ground and transport levels are offset. Alternatively, larger Soret effects for capacitive energy conversion could result from improved understanding of ion complexation thermodynamics in ion-transporting media. Larger entropy increases from thermally induced decomplexation should increase attainable static voltage.

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1. M. Lindorf, K. A. Mazzio, J. Pflaum, K. Nielsch, W. Brutting and M. Albrecht, Journal of Materials Chemistry A **8** (16), 7495-7507 (2020).
2. J. T. Wei, L. L. Yang, Z. Ma, P. S. Song, M. L. Zhang, J. Ma, F. H. Yang and X. D. Wang, Journal of Materials Science **55** (27), 12642-12704 (2020).
3. X. Wu, N. W. Gao, H. Y. Jia and Y. P. Wang, Chemistry-an Asian Journal **16** (2), 129-141 (2021).
4. W. R. Zhao, J. M. Ding, Y. Zou, C. A. Di and D. B. Zhu, Chemical Society Reviews **49** (20), 7210-7228 (2020).
5. A. K. Menon, E. Uzunlar, R. M. W. Wolfe, J. R. Reynolds, S. R. Marder and S. K. Yee, Journal of Applied Polymer Science **134** (3), 44402 (2017).
6. Y. Sun, C. A. Di, W. Xu and D. B. Zhu, Advanced Electronic Materials **5** (11), 1800825 (2019).
7. H. L. Jin, J. Li, J. Iocozzia, X. Zeng, P. C. Wei, C. Yang, N. Li, Z. P. Liu, J. H. He, T. J. Zhu, J. C. Wang, Z. Q. Lin and S. Wang, Angewandte Chemie-International Edition **58** (43), 15206-15226 (2019).
8. H. Y. Yao, Z. Fan, H. L. Cheng, X. Guan, C. Wang, K. Sun and J. Y. Ouyang, Macromolecular Rapid Communications **39** (6), 1700727 (2018).
9. S. Lee, S. Kim, A. Pathak, A. Tripathi, T. Qiao, Y. Lee, H. Lee and H. Y. Woo, Macromolecular Research **28** (6), 531-552 (2020).
10. A. K. Menon, R. M. W. Wolfe, S. Kommandur and S. K. Yee, Advanced Electronic Materials **5** (11), 1800884 (2019).

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AIP Publishing

11. R. M. W. Wolfe, A. K. Menon, S. R. Marder, J. R. Reynolds and S. K. Yee, Advanced Electronic Materials **5** (11), 1900066 (2019).
12. H. Fritzsche, Solid State Communications **9** (21), 1813-1815 (1971).
13. S. A. Gregory, R. Hanus, A. Atassi, J. M. Rinehart, J. P. Wooding, A. K. Menon, M. D. Losego, G. J. Snyder and S. K. Yee, Nature Materials, just accepted.
14. S. D. Kang and G. J. Snyder, Nature Materials **16** (2), 252-257 (2017).
15. P. M. Chaikin and G. Beni, Physical Review B **13** (2), 647-651 (1976).
16. H. Li, E. Plunkett, Z. Cai, B. Qiu, T. Wei, H. Chen, S. Thon, D. H. Reich, L. Chen and H. E. Katz, Advanced Electronic Materials **5**, 1800618 (2019).
17. A. T. Ramu and J. E. Bowers, Applied Physics Letters **101** (17), 173905 (2012).
18. A. T. Ramu, L. E. Cassels, N. H. Hackman, H. Lu, J. M. O. Zide and J. E. Bowers, Journal of Applied Physics **107** (8), 083707 (2010).
19. D. Wang, W. Shi, J. M. Chen, J. Y. Xi and Z. G. Shuai, Physical Chemistry Chemical Physics **14** (48), 16505-16520 (2012).
20. P. Pichanusakorn and P. Bandaru, Materials Science & Engineering R-Reports **67** (2-4), 19-63 (2010).
21. H. C. Lin, N. Goldsman and I. D. Mayergoyz, Solid-State Electronics **35** (6), 769-778 (1992).
22. D. Csontos and S. E. Ulloa, Journal of Computational Electronics **3** (3-4), 215-219 (2004).
23. N. D. Lu, L. Li and M. Liu, Physical Chemistry Chemical Physics **18** (29), 19503-19525 (2016).
24. N. F. Mott and E. A. Davis, *Electronic Processes in Non-crystalline Materials, Second Edition*. (Clarendon, Oxford, UK, 1979).
25. G. Z. Zuo, X. J. Liu, M. Fahlman and M. Kemerink, Advanced Functional Materials **28** (15), 1703280 (2018).
26. B. Philippe, T. J. Jacobsson, J. P. Correa-Baena, N. K. Jena, A. Banerjee, S. Chakraborty, U. B. Cappel, R. Ahuja, A. Hagfeldt, M. Odelius and H. Rensmo, Journal of Physical Chemistry C **121** (48), 26655-26666 (2017).
27. A. M. Shing, Y. Tolstova, N. S. Lewis and H. A. Atwater, Applied Physics a-Materials Science & Processing **123** (12) (2017).
28. Y. Zou, D. Z. Huang, Q. Meng, C. A. Di and D. B. Zhu, Organic Electronics **56**, 125-128 (2018).
29. Y. J. Lin and J. J. Zeng, Applied Physics Letters **102** (18) (2013).
30. H. S. Bennett and H. Hung, Journal of Research of the National Institute of Standards and Technology **108** (3), 193-197 (2003).
31. J. Bisquert, Physical Chemistry Chemical Physics **10** (22), 3175-3194 (2008).
32. J. J. Dong, W. Si and C. Q. Wu, Journal of Chemical Physics **144** (14), 144905 (2016).
33. V. Rani, A. Sharma, S. R. Chaudhuri and S. Ghosh, Applied Physics Letters **118** (8), 083301 (2021).
34. A. Devizis, K. Meerholz, D. Hertel and V. Gulbinas, Physical Review B **82** (15), 155204 (2010).
35. S. Sadasivam, M. K. Y. Chan and P. Darancet, Physical Review Letters **119** (13), 136602 (2017).
36. C. Soci, D. Moses, Q. H. Xu and A. J. Heeger, Physical Review B **72** (24), 245204 (2005).
37. Z. Z. Zhou, H. J. Liu, D. D. Fan, G. H. Cao and C. Y. Sheng, Acs Applied Materials & Interfaces **10** (43), 37031-37037 (2018).
38. M. Hong, W. Y. Lyu, Y. Wang, J. Zou and Z. G. Chen, Journal of the American Chemical Society **142** (5), 2672-2681 (2020).
39. P. Pichanusakorn and P. R. Bandaru, Applied Physics Letters **94** (22), 223108 (2009).
40. D. Mendels and N. Tessler, Journal of Physical Chemistry C **117** (7), 3287-3293 (2013).
41. D. Mendels and N. Tessler, Journal of Applied Physics **117** (10), 105502 (2015).
42. A. M. Glaudell, J. E. Cochran, S. N. Patel and M. L. Chabinyc, Advanced Energy Materials **5** (4), 1401072 (2015).
43. B. Russ, A. Glaudell, J. J. Urban, M. L. Chabinyc and R. A. Segalman, Nature Reviews Materials **1** (10), 16050 (2016).
44. A. Al-zubaidi, X. X. Ji and J. Yu, Sustainable Energy & Fuels **1** (7), 1457-1474 (2017).

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45. S. Duhr and D. Braun, Proceedings of the National Academy of Sciences of the United States of America **103** (52), 19678-19682 (2006).
46. X. Guan, H. L. Cheng and J. Y. Ouyang, Journal of Materials Chemistry A **6** (40), 19347-19352 (2018).
47. D. Niether and S. Wiegand, Journal of Physics-Condensed Matter **31** (50), 503003 (2019).
48. D. Zhao, A. Martinelli, A. Willfahrt, T. Fischer, D. Bernin, Z. U. Khan, M. Shahi, J. Brill, M. P. Jonsson, S. Fabiano and X. Crispin, Nature Communications **10**, 1093 (2019).
49. S. L. Kim, J. H. Hsu and C. Yu, Organic Electronics **54**, 231-236 (2018).
50. W. B. Chang, C. M. Evans, B. C. Popere, B. M. Russ, J. Liu, J. Newman and R. A. Segalman, Acs Macro Letters **5** (1), 94-98 (2016).
51. C. G. Han, X. Qian, Q. K. Li, B. Deng, Y. B. Zhu, Z. J. Han, W. Q. Zhang, W. C. Wang, S. P. Feng, G. Chen and W. S. Liu, Science **368** (6495), 1091-+ (2020).
52. B. Y. Yu, J. J. Duan, H. J. Cong, W. K. Xie, R. Liu, X. Y. Zhuang, H. Wang, B. Qi, M. Xu, Z. L. Wang and J. Zhou, Science **370** (6514), 342-346 (2020).
53. P. Knauth, L. Pasquini, R. Narducci, E. Sgreccia, R. A. Becerra-Arciniegas and M. L. Di Vona, Journal of Membrane Science **617**, 118622 (2021).
54. Q. L. Jiang, H. D. Sun, D. K. Zhao, F. L. Zhang, D. H. Hu, F. Jiao, L. Q. Qin, V. Linseis, S. Fabiano, X. Crispin, Y. G. Ma and Y. Cao, Advanced Materials **32** (45), 2002752 (2020).
55. A. L. Pires, R. S. Costa, C. Pereira and A. M. Pereira, Acs Applied Electronic Materials **3** (2), 696-703 (2021).
56. D. Zhao, H. Wang, Z. U. Khan, J. C. Chen, R. Gabrielsson, M. P. Jonsson, M. Berggren and X. Crispin, Energy & Environmental Science **9** (4), 1450-1457 (2016).
57. K. Kavallieratos, C. M. Bertao and R. H. Crabtree, Journal of Organic Chemistry **64** (5), 1675-1683 (1999).
58. R. C. Jagessar, M. Y. Shang, W. R. Scheidt and D. H. Burns, Journal of the American Chemical Society **120** (45), 11684-11692 (1998).
59. M. N. Hasan, H. Wahid, N. Nayan and M. S. M. Ali, International Journal of Energy Research **44** (8), 6170-6222 (2020).
60. T. G. Novak, K. Kim and S. Jeon, Nanoscale **11** (42), 19684-19699 (2019).
61. J. H. Yang, H. L. Yip and A. K. Y. Jen, Advanced Energy Materials **3** (5), 549-565 (2013).
62. S. Fratini, M. Nikolka, A. Salleo, G. Schweicher and H. Sirringhaus, Nature Materials **19** (5), 491-502 (2020).
63. K. A. Peterson, E. M. Thomas and M. L. Chabinyc, in *Annual Review of Materials Research, Vol 50, 2020*, edited by D. R. Clarke (2020), Vol. 50, pp. 551-574.
64. I. Salzmann, G. Heimel, M. Oehzelt, S. Winkler and N. Koch, Accounts of Chemical Research **49** (3), 370-378 (2016).
65. Y. Kiyota, T. Kawamoto and T. Mori, Journal of Physical Chemistry C **124** (41), 22399-22405 (2020).
66. F. J. Zhang, Y. P. Zang, D. Z. Huang, C. A. Di, X. Gao, H. N. Sirringhaus and D. B. Zhu, Advanced Functional Materials **25** (20), 3004-3012 (2015).
67. Q. Y. Zhang, B. Barrett, A. E. Bragg and H. E. Katz, Acs Applied Electronic Materials **1** (12), 2708-2715 (2019).
68. K. M. Diederichsen, E. J. McShane and B. D. McCloskey, Acs Energy Letters **2** (11), 2563-2575 (2017).
69. J. Escorihuela, R. Narducci, V. Compan and F. Costantino, Advanced Materials Interfaces **6** (2), 1801146 (2019).
70. M. Forsyth, L. Porcarelli, X. E. Wang, N. Goujon and D. Mecerreyes, Accounts of Chemical Research **52** (3), 686-694 (2019).
71. N. N. Krishnan, D. Henkensmeier, J. H. Jang and H. J. Kim, Macromolecular Materials and Engineering **299** (9), 1031-1041 (2014).

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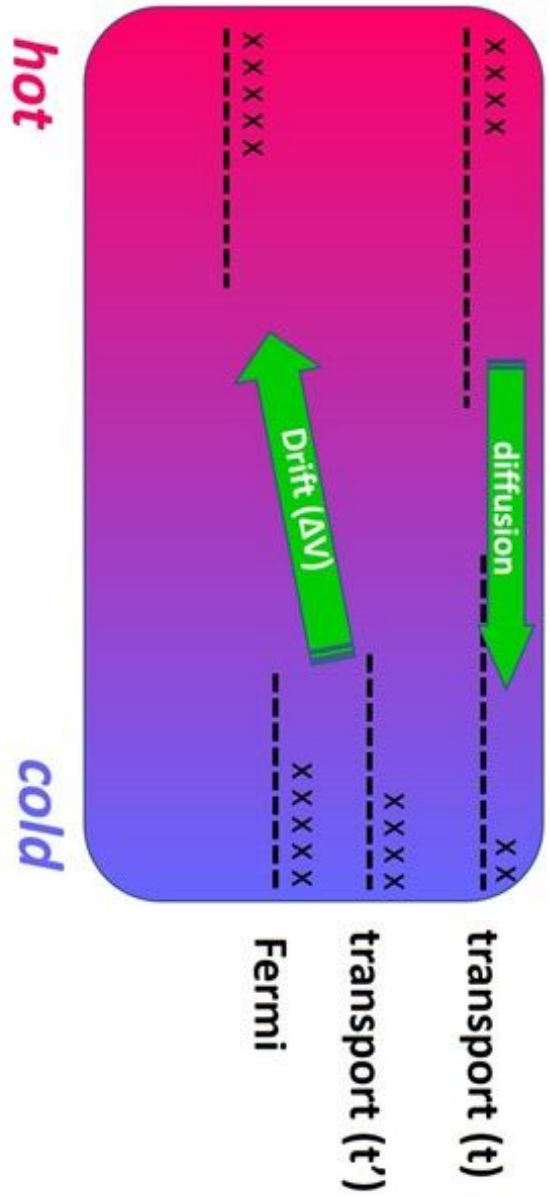

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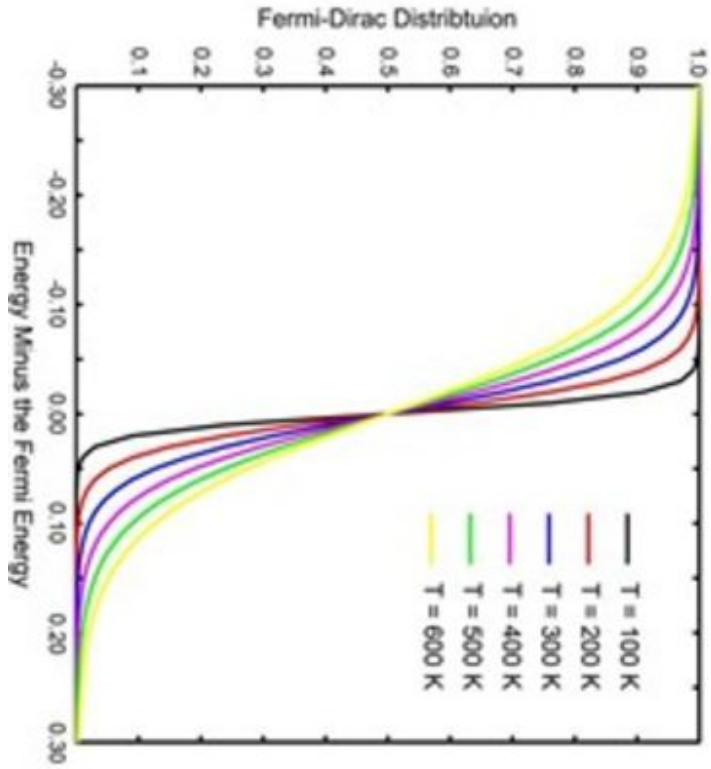
At Temperatures Above 0 K There is a Non-Zero Probability Associated with f(E)



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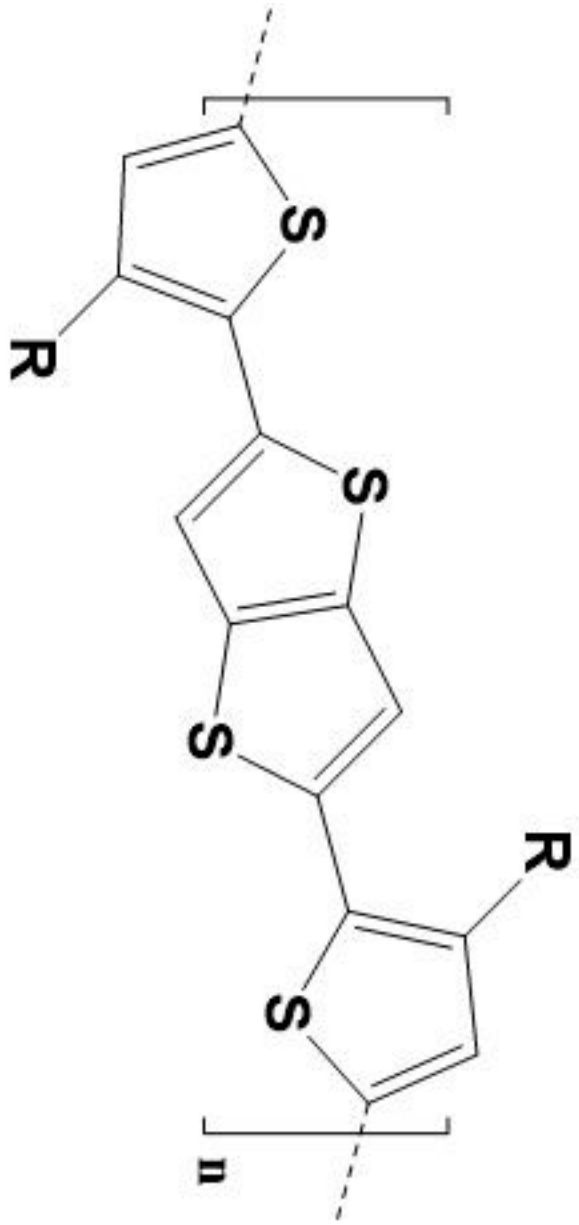

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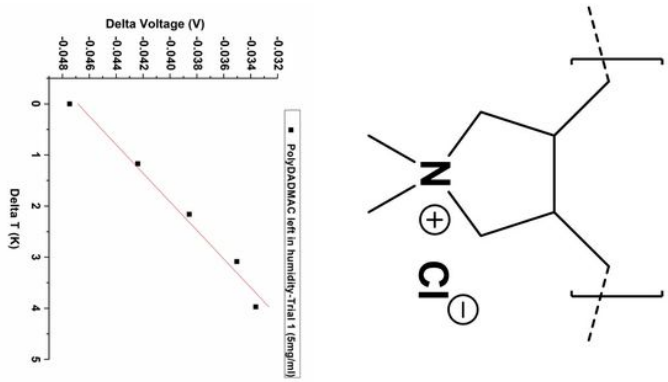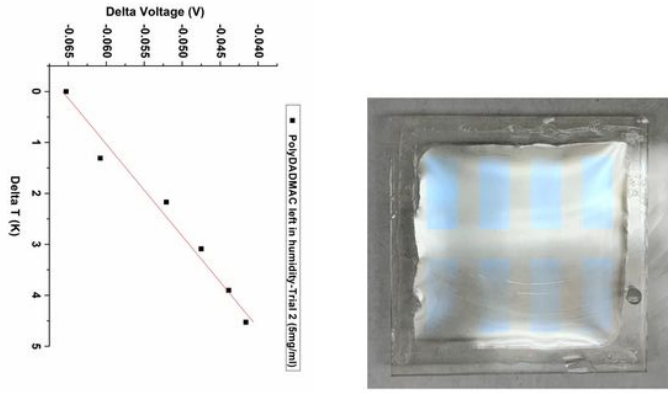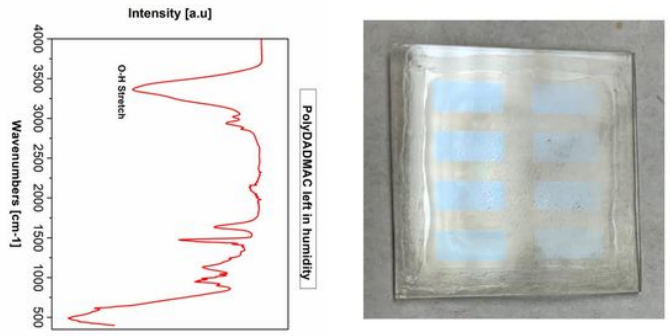
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