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Origin of the material dependence of temperature coefficient of redox potential in conjugated polymers

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The thermal coefficient α ($=dV/dT$) of the redox potential (V) is an important physical parameter for thermal energy harvesting. To clarify the microscopic origin of α in conjugated polymers, we compared α and the physical quantity obtained by a quantum chemistry calculation in typical polymers with small monomer molecular weight. We observed a strong correlation between α and the number (N_{active}) of the active atom, which is defined as the atom whose variation of the Mulliken charge (Δq) at the oxidation process is beyond a threshold (Δq_{th}). We interpreted the material dependence of α in terms of N_{active} , because active atoms have a significant effect on the configuration entropy of the surrounding solvent molecules. © 2021 The Author(s). Published on behalf of The Japan Society of Applied Physics by IOP Publishing Ltd

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It is crucial to develop thermal energy-harvesting devices that produce electrical energy efficiently and inexpensively from environmental waste heat, to realize a “smart” society. Recently, several researchers reported that a battery can be charged by environmental heat by using the difference ($\Delta\alpha$) in the thermal coefficient α ($=dV/dT$) of the redox potential (V) between the cathode and anode materials.^{1–8} The battery can produce electrical energy in thermal cycles between the low (T_L) and high (T_H) temperatures and is called a tertiary battery. In the warming process, the cell voltage (V_{cell}) increases when heated from 0 V to $\Delta\alpha\Delta T$ ($\Delta T = T_H - T_L$). In other words, the battery is charged by the environmental heat. The accumulated electrical energy can be extracted by the discharging process at T_H . Similarly, V_{cell} decreases with cooling from 0 V to $-\Delta\alpha\Delta T$. Shibata et al.⁴ fabricated a tertiary battery consisting of two kinds of cobalt Prussian blue analogs (Co-PBAs) with different α , i.e. $\text{Na}_x\text{Co}[\text{Fe}(\text{CN})_6]_{0.71}$ (NCF71) and $\text{Na}_x\text{Co}[\text{Fe}(\text{CN})_6]_{0.90}$ (NCF90), and aqueous electrolyte. The NCF71/NCF90 tertiary battery produces electrical energy with high thermal efficiency ($\eta = 1\%$) between T_L ($=295$ K) and T_H ($=323$ K). They further increased the V_{cell} with the use of a phase transition of Co-PBA.⁸ The V_{cell} of the $\text{Na}_x\text{Co}[\text{Fe}(\text{CN})_6]_{0.82}$ (NCF82)/NCF90 tertiary battery steeply increased from 0 to 120 mV at ~ 320 K.

From a thermodynamic point of view, α is expressed as $\frac{\Delta S}{e}$, where e (≥ 0) and ΔS are the elementary charge and difference in entropies (S) between the reduced and oxidized states, respectively. Importantly, the redox process in a battery system influences not only the solid electrode, but the electrolyte. In other words, ΔS consists of the solid (ΔS_{solid}) and electrolyte ($\Delta S_{\text{electrolyte}}$) components.⁹ Generally, $\Delta S_{\text{electrolyte}}$ is ascribed to the variation in the configuration entropy of the solvent molecules.

Among the battery materials, conjugated polymers have several advantages for thermal energy harvesting, such as light weight, flexibility and environmental friendliness.^{10–13} Many conjugated polymers, e.g. polyacetylene,¹⁴

poly(p-phenylene) (PPP)^{15,16} and polythiophene,¹⁷ show the reversible redox process among the reduced, neutral and oxidized states. The characteristic of conjugated polymers is that α strongly depends on the main chain structure;¹⁸ $\alpha = 1.08$ mV K^{−1} for poly(3-hexylthiophene-2,5-diyl) (P3HT), 0.38 mV K^{−1} for poly(9,9-dioctylfluorene-co-bithiophene) (F8T2) and 0.19 mV K^{−1} for poly[9,9-dioctylfluorene-co-N-(4-butylphenyl) diphenylamine] (TFB). In our previous work,¹⁸ the material dependence is interpreted in terms of the vibrational entropy of the benzene (C_6H_5) and thiophene ($\text{C}_4\text{H}_4\text{S}$) units. In this model, the main chains of the polymers were approximated to be composed of the C_6H_5 and $\text{C}_4\text{H}_4\text{S}$ units. The model, however, may be too simple to describe the actual materials. In addition, the model is not applicable to other polymers. Therefore, we need to build a more realistic model to comprehend the material dependence of α .

In this work, we investigated four typical conjugated polymers with small monomer molecular weight, i.e. (a) Poly(4-butylphenyl-diphenylamine) (PTAA), (b) poly(2,5-dioctyl-1,4-phenylene) (PPP), (c) poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and (d) P3HT (see Fig. 1). We compared α and the physical quantity obtained by a quantum chemistry calculation on the monomer unit including the side chains. We observed a strong correlation between α and the number (N_{active}) of the active atom, which is defined as the atom whose variation of the Mulliken charge (Δq) at the oxidation process is beyond a threshold (Δq_{th}). We interpreted the material dependence of α in terms of N_{active} , because the active atoms have a significant effect on the configuration entropy of the neighboring solvent molecules.

We prepared PTAA according to methods in the literature.¹⁹ We purchased MEH-PPV from Sigma-Aldrich and PPP from American Dye source, which were all used as received. Polymer films were prepared by casting the polymer solution on a glass substrate coated with indium tin oxide (ITO) electrode (GEOMATEC Co., Ltd.). The

Fig. 1. (Color online) Monomer structure of (a) PTAA, (b) MEH-PPV, (c) PPP and (d) P3HT. Structures were optimized at the B3LYP/6-311G(*p,d*) level. Atom surrounded by a green circle represents the active atoms (see text).

thickness and sheet resistance of the ITO film were 150 nm and $\leq 10 \Omega \text{ sq}^{-1}$, respectively. The thickness of the glass substrate was 0.7 mm. For PTAA and MEH-PPV, 2.5 mg of polymer was dissolved in 0.5 ml of chloroform. The thickness and weight of the films were typically 6 μm and 0.04 mg, respectively. For PPP, 25 mg of PPP was dissolved in 0.5 ml of chloroform to stabilize the redox potential. The polymer weight was evaluated from the weight of the polymer solution cast on the substrate. The areas of the electrodes are about 0.3 cm^2 . The electrochemical measurements were performed using a beaker-type cell with a potentiostat (HokutoDENKO; HJ1001SD8) within an Ar-filled glove box. The cathode, anode and electrolyte were the cast film, Li metal, and ethylene carbonate (EC)/diethyl carbonate (DEC) containing 1 mol/l LiClO_4 , respectively. The charge and discharge rate were 0.3 C for PTAA and PPP and 0.9 C for MEH-PPV. The charge/discharge rate is defined by the reciprocal of the time (*h*) required for full charge/discharge. The corresponding currents were 0.44, 0.56 and 6.20 μA for PTAA, PPP and MEH-PPV, respectively. The upper and lower cut-off voltages were set to be 3.8–4.0 V and 1.0 V vs Li/Li^+ , respectively.

We determined α_{cell} of the beaker-type cell, whose cathode, anode and electrolyte were the cast film, Li metal, and EC/DEC containing 1 mol/l LiClO_4 , respectively. α of the conjugated polymer is expressed as $\alpha_{\text{cell}} - \alpha_{\text{Li}}$, where α_{cell} and α_{Li} are the coefficient of the cell and Li metal, respectively. α_{Li} in EC/DEC containing 1 mol/l LiClO_4 is 0.76 mVK^{-1} .⁹⁾ To avoid the potential fluctuation that is prominent in the as-grown film, the polymers are partially oxidized (arrows in Fig. 2) in the beaker-type cell. V_{cell} was carefully measured against the cell temperature (*T*), which was monitored with a Pt resistance thermometer in the electrolyte. *T* was slowly increased/decreased at a rate of $\pm 0.3 \text{ Kmin}^{-1}$.

Figure 2 shows the charge and discharge curves of the cast films: (a) PTAA, (b) PPP and (c) MEH-PPV. In the PTAA film [(a)], the discharge curve shows a single plateau at 3.7 V, which is assigned to the removal of an electron from the highest occupied molecular orbital (HOMO). Similar single

Fig. 2. (Color online) Charge and discharge curves of the cast films against the charge (*Q*): (a) PTAA, (b) PPP and (c) MEH-PPV. Charge and discharge rate were 0.3 C (PTAA), 0.3 C (PPP) and 0.9 C (MEH-PPV). Arrows indicate the positions where α was determined.

plateaus are observed in the PPP [(b)] and MEH-PPV [(c)] cast films and are assigned to the removal of an electron from the HOMOs. The discharge capacities (Q_{exp}) were evaluated and are listed in Table I together with the ideal value (Q_{ideal}). Except for P3HT, Q_{exp} is much smaller than Q_{ideal} , indicating that these polymers can be only partially oxidized.

Figure 3 shows V_{cell} of the Li/polymer cell against *T*: (a) PTAA, (b) PPP and (c) MEH-PPV. Red and blue marks represent the data observed in the heating and cooling runs, respectively. No thermal hysteresis was observed in V_{cell} , which indicates that the temperature gradient as well as the sample deterioration are excluded. α_{cell} of the Li/polymer cell was evaluated by least-squares fitting (straight lines in Fig. 3). α of the conjugated polymer was obtained using the relation, $\alpha = \alpha_{\text{cell}} + 0.76 \text{ mVK}^{-1}$, and listed in Table I.

First, let us consider the vibrational component (α_{vib}) of α , which is expressed as $\frac{S_{\text{vib}}^{\text{neu}} - S_{\text{vib}}^{\text{oxi}}}{e}$, where $S_{\text{vib}}^{\text{neu}}$ and $S_{\text{vib}}^{\text{oxi}}$ are the vibrational entropies in the neutral and oxidized states, respectively. In the oxidation process, an electron with bonding character is removed from the HOMO. The removal of an electron weakens the force constant between the neighboring atoms and lowers the frequencies of the vibrational modes.^{20–23)} The softening of the modes increases the number of thermally-excited phonons, and hence, increases $S_{\text{vib}}^{\text{oxi}}$. To evaluate $S_{\text{vib}}^{\text{neu}}$ ($S_{\text{vib}}^{\text{oxi}}$), quantum chemistry calculations were performed on the monomer unit with including side

Table I. Observed (Q_{exp}) and ideal (Q_{ideal}) capacities of conjugated polymers together with the temperature coefficient (α) of redox potential. Q_{ideal} was evaluated assuming that one electron can be accommodated/removed per monomer unit. Data of P3HT are cited from Ref. 18.

Polymer	Q_{exp} (mAhg^{-1})	Q_{ideal} (mAhg^{-1})	α (mVK^{-1})
PTAA	39	89.5	0.02
PPP	5	80.6	0.41
MEH-PPV	37	102.9	0.46
P3HT	90	162.5	1.08

Fig. 3. (Color online) Cell voltage (V_{cell}) of the Li/polymer cell against the cell temperature (T): (a) PTAA, (b) PPP and (c) MEH-PPV. Blue and red marks represent the data obtained in the cooling and warming runs, respectively. Straight lines are the results of the least-squares fitting. In (b) PPP and (c) MEH-PP, a decrease in V_{cell} was observed in proportion to time (t) and was corrected with a t -linear function.

chains in the neutral (oxidized) state. The calculations were performed with Gaussian16 at the B3LYP/6-311G(d , p) level.²⁴⁾ After the structural optimization (Fig. 1), the frequencies of the vibrational modes were evaluated (Table S1; supplementary data, available online at stacks.iop.org/APEX/14/037001/mmedia). The number of thermally-excited phonons is proportional to $e^{-\frac{\hbar\omega_i}{k_B T}}$, where $\hbar\omega_i$ and k_B are the vibrational energy of the i th mode and Boltzmann constant, respectively. Hereafter, we use the vibrational energy $x_i (= \frac{\hbar\omega_i}{k_B T})$ as the unit of thermal energy. After a simple calculation, S_{vib} is expressed as $k_B \sum_{i=1}^N \left[\frac{x_i e^{-x_i}}{1 - e^{-x_i}} - \ln(1 - e^{-x_i}) \right]$, where N is the number of vibrational modes. We note that α_{vib} does not include the low-energy lattice modes, e.g. the translational or rotational movement of the entire monomer and movement of the side chain relative to the main chain. In addition, α_{vib} does not include the configuration entropy of the side chains. The reduction process, however, is considered to have a negligible effect on the low-energy lattice mode as well as the configuration entropy of the side chains.

Table II. Vibrational entropies in the neutral ($S_{\text{vib}}^{\text{neu}}$) and oxidized ($S_{\text{vib}}^{\text{oxi}}$) states of monomers at 298.15 K. Vibrational component (α_{vib}) of α is expressed as $\frac{S_{\text{vib}}^{\text{neu}} - S_{\text{vib}}^{\text{oxi}}}{e}$. α is the experimental value. α of P3HT is cited from Ref. 18.

Monomer	$S_{\text{vib}}^{\text{neu}}$ (meVK ⁻¹)	$S_{\text{vib}}^{\text{oxi}}$ (meVK ⁻¹)	α_{vib} (mVK ⁻¹)	α (mVK ⁻¹)
PTAA	3.402	3.289	0.113	0.02
PPP	5.273	5.298	-0.025	0.41
MEH-PPV	3.512	3.574	-0.062	0.46
P3HT	1.803	1.839	-0.036	1.08

In Table II, we listed $S_{\text{vib}}^{\text{neu}}$, $S_{\text{vib}}^{\text{oxi}}$ and α_{vib} , together with the experimental value (α). We found that α_{vib} is an order of magnitude smaller than α , suggesting that α_{vib} at least is not the main origin of the material dependence of α . In addition, the order of S_{vib} is opposite to the order of α , indicating that S_{vib} cannot qualitatively explain the material dependence of α . Therefore, we need to search the origin for the material dependence in another physical parameter. In our previous work,¹⁸⁾ the material dependence was explained by the fact that α_{vib} of thiophane ($\text{C}_4\text{H}_4\text{S}$) is larger than that of benzene (C_6H_5). In this model, the main chains of the polymers were approximated to be composed of the C_6H_5 and $\text{C}_4\text{H}_4\text{S}$ units. In the actual conjugated polymers, however, an electron escapes not only from a single C_6H_5 or $\text{C}_4\text{H}_4\text{S}$ unit, but from many atoms in a strongly material-dependent manner (Table S2). In this sense, this model was too simple to describe the actual materials.

Here, we note that ΔS is dominated by $\Delta S_{\text{electrolyte}}$ in a solute system, e.g. $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ in water.²⁵⁾ In this system, $\Delta S_{\text{electrolyte}}$ is evaluated to be -1.28 mVK^{-1} since ΔS originated in $[\text{Fe}(\text{CN})_6]^{4+}/[\text{Fe}(\text{CN})_6]^{3+}$ is -0.22 mVK^{-1} .^{26,27)} In general, $\Delta S_{\text{electrolyte}}$ is ascribed to the variation in the configuration entropy of solvent molecules around the redox couple. By means of quantum mechanical and molecular dynamics calculations, Prampolini et al.²⁸⁾ investigated the water structure around $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$. They found that water molecules get closer to $[\text{Fe}(\text{CN})_6]^{4-}$ than to $[\text{Fe}(\text{CN})_6]^{3-}$, reflecting the higher charge of $[\text{Fe}(\text{CN})_6]^{4-}$. In order to evaluate the effect of the configuration entropy of the EC and DEC molecules, we experimentally investigated α of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in EC/DEC (Fig. S1; supplementary data). We found that the corresponding α ($=2.21 \text{ mVK}^{-1}$) is large, indicating that the configuration entropy of the EC and DEC molecules significantly changes around $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the redox process. A similar effect is expected even in the polymer system, because most of the polymers are in contact with the electrolyte. In other words, the $\Delta S_{\text{electrolyte}}$ component is expected if the variation (Δq) of the Mulliken charges for the constituent atom at the oxidation process is large. Table S2 (supplementary data) shows the Mulliken charges in PTAA, MEH-PPV, PPP and P3HT in neutral (q^{neu}) and oxidized (q^{oxi}) states. The serial numbers of the atoms are shown in Fig. S2 (supplementary data).

Figure 4(a) shows Δq ($=q^{\text{oxi}} - q^{\text{neu}}$) in the oxidation process for S, N, O (filled symbols) and C (open symbols).

Fig. 4. (Color online) Variation (Δq) of the Mulliken charge in the oxidation process; (a) S, N, O and C and (b) H. Δq s are shown in order of quantity. Open (closed) symbols in (a) represent C (S, N, O). Broken red line means a tentative threshold (Δq_{th}).

Table III. Number (N_{active}) of the active atoms in monomers with different threshold (Δq_{th}).

Δq_{th}	P3HT	MEH-PPV	PPP	PTAA
0.08	3	1	2	1
0.07	5	1	2	1
0.06	6	4	4	1
0.05	8	8	6	1

Δq s are shown in order of quantity. In PTAA (triangles), Δq is very small; Δq s from the largest are 0.10, 0.04, etc. We found that Δq is much enhanced in P3HT (squares); Δq s from the largest are 0.22, 0.12, 0.08, 0.05, etc. A similar trend is observed in Δq for H [Fig. 4(b)]. The atom with large Δq significantly influences the configuration entropy of the surrounding solvent molecules. We will call such an atom an “active atom”. Here, we introduce a threshold (Δq_{th}) to identify an atom with large Δq ($\geq \Delta q_{\text{th}}$). The broken red line in Fig. 4 is an example of Δq_{th} ($=0.06$). In this case, the number (N_{active}) of the active atoms are one for (a) PTAA, four for (b) PPP and (c) MEH-PPV and six for (d) P3HT. The active atoms are indicated by green circles in Fig. 1. The order of N_{active} is the same order as α , suggesting that the material dependence can be ascribed to N_{active} . We recognized that Δq_{th} is only a guide and has no absolute physical meaning. We carefully investigated Δq_{th} -dependence of N_{active} (Table III). We confirmed that the order of N_{active} is insensitive to Δq_{th} .

In conclusion, we compared α and the physical quantity obtained by a quantum chemistry calculation on the monomer unit including the side chains. We observed a strong correlation between α and N_{active} , suggesting that the material dependence of α can be ascribed to the variation in the configuration entropy of the EC and DEC molecules. N_{active} gives us a useful strategy to design and/or search conjugated polymers with high α .

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