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Thermoelectric Conversion by Thin-Layer Thermogalvanic Cells with Soluble Redox Couples

Tamio IKESHOJI
Government Industrial Research Institute, Tohoku, Nigatake 4-2-1, Sendai 983
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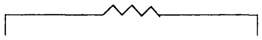
Thermogalvanic cells containing a redox couple of $[Fe(CN)_6]^{4-/3-}$ or $Fe^{2+/3+}$ as an electroactive species were built for thermoelectric conversion from low-grade heat with a temperature less than 100 °C. The distance between high- and low-temperature electrodes was set to 1 mm in order to produce a high power density. Thermoelectric powers, inner resistances, and heat fluxes of the cells, which were placed horizontally (i.e. in which the temperature gradient was vertical) were measured under steady state conditions. Natural convection, which was induced by a temperature difference and current flowing in appropriate directions, produced lower inner resistances than those with no convection by several times. It had only a small effect on thermoelectric powers and heat-transfer coefficients. Thus, both the power densities and the thermal efficiencies increased by nearly one order of magnitude due to the convection. A power density of 2.6 W m^{-2} was obtained during steady state using a cell containing an aqueous solution of 0.13 mol dm^{-3} $K_4[Fe(CN)_6]$ and 0.85 mol dm^{-3} $K_3[Fe(CN)_6]$ at a temperature difference of 72 K and a thermal efficiency of 6.7×10^{-5}; the upper electrode was kept at a lower temperature.

The direct energy conversion of heat to electricity is a very attractive technique. Although a successful effort using an electrochemical system has not been presented yet, it has a higher thermoelectric power than that of metal thermocouples by nearly two orders of magnitude. It is of the order of 1 mV K^{-1}, which is as large as that of semiconductor thermocouples.

Several electrochemical systems for thermoelectric conversion appeared in the 1950s—60s and some of them were patented.[1,2] The systems of this period were mainly designed for high-temperature heat from the nuclear reactors in space crafts. In recent years two new systems have been proposed. One is called AMTEC (alkali metal thermoelectric converter), which is for high-temperature heat.[3] The other is a thermogalvanic cell using an aqueous electrolyte solution in order to convert low-grade heat (for instance, waste heat, geothermal heat, ocean thermal energy, etc).[4-6] Such thermoelectric conversions by electrochemical systems, sometimes called "thermally regenerative electrochemical system," have been reviewed in recent papers.[1,2,7] This paper is concerned with the aqueous thermogalvanic cells for energy conversion from heat sources of less than 100 °C.

A basic electrochemical cell for thermoelectric conversion is a thermogalvanic cell in which two electrodes of an identical type are maintained at a high temperature (T_H) and a low temperature (T_L) as



electrode(T_L)/electrolyte/electrode(T_H),

where "electrolyte" means an electrolyte solution such as molten salt, solid solution, or any other ionic conductors. A big difference in the thermoelectric conversion system using a thermogalvanic cell from that using a semiconductor or metal thermocouple concerns the type of charged species that move in the respective closed circuit. Only electrons move in the latter case, while ions and electrons move in the former thermogalvanic cell. A compound is, thus, accumulated at one of the two electrodes, where a charge-transfer reaction between ions and electrons takes place during operation. At the other electrode this same compound is consumed. These accumulated species must be returned to the latter electrode from the former one in order to continuously produce electricity from the cells. In many cases pumps are used to transfer the accumulated species through an outer circuit of the cells. This method, however, results in the losing of a major merit in that there are no moving parts in the direct thermoelectric conversion system. Another way for continuous operation is to periodically reverse the temperatures of the electrodes.[8]

It was suggested by Burrows that it is possible to return the accumulated species without using a pump if a soluble redox couple is used as the electroactive species with innert electrodes.[5,6] The electroactive species, i.e. the redox couple, are transferred by diffusion or convection in the electrolyte solution. As shown in a schematic diagram of the thermogalvanic cell with a soluble redox couple, $M^{m+/n+}$, in Fig. 1, M^{m+} is reduced to M^{n+} at the electrode of T_H, and the opposite reaction takes place at the electrode of T_L, as

$$M^{m+} + (m-n)e^- \longrightarrow M^{n+} \quad (T_H),$$

and

$$M^{n+} \longrightarrow M^{m+} + (m-n)e^- \quad (T_L),$$

where the thermoelectric power of this cell is assumed to be positive, i.e. the potential of the higher temperature electrode is positive against the lower temperature one. The counter ion, X^-, migrates from the higher-temperature electrode to the lower-temperature one in order to maintain the electroneutrality of the solution. At the T_H electrode, MX_m is consumed and MX_n is accumulated. At the T_L electrode, the opposite species are consumed and accumulated. A concentration polarization, then, arises in the thermogalvanic cell. If MX_n and MX_m are not transferred from one electrode to the other, the potential difference due to this concentration polarization will increase until it becomes equal to the potential difference produced by the thermoelectric power; eventually, current will cease to flow.[8]

Since there is neither a diaphragm nor a membrane in the cell, the accumulated species can diffuse to the opposite electrode. A current corresponding to the amount of the species returned to the electrodes by the diffusion will continue to flow. The amount, however, is usually very small. In Burrows' cell rotating electrodes were used to obtain a higher current than that by diffusion only.[5] In this cell the consumed species is supplied by forced convection. Having a moter to rotate the electrode, the cell unfortunately again loses the big advantage of the direct thermoelectric conversion sysytem. Consequently, a short distance electrode cell, i.e. a thin-layer cell,[9] has been investigated in this study in order to obtain a high power density. Since the thermal efficiency of thermoelectric converters in which heat and electricity pass through the same part in the same direction is not fundamentally changed by their structures,[10] the thin-layer cell is expected to have a high power density without lowering the thermal efficiency.

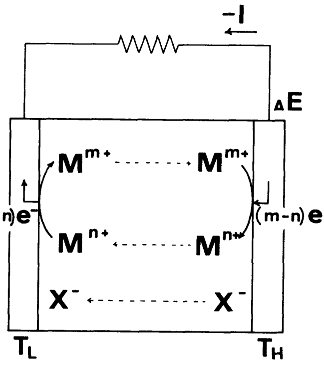


Fig. 1. A schematic diagram of a thermogalvanic cell with a soluble redox couple, $M^{m+/n+}$. T_H And T_L: Temperatures of electrodes ($T_H>T_L$), E: potential at T_H against that at T_L, I: current.

The current at a steady state in a thin-layer cell is, primarily, proportional to the speed of the diffusion determined by the concentration gradient induced by the flowing current. This means that the observed inner resistance of this cell increases from the solution resistance measured by the normal method. If the concentration gradient of the redox species can be diminished by homogenizing, the inner resistance will decrease. This would be possible by a natural convection induced by a temperature and/or concentration gradient in the cell without a motor. However, the convection in the cell has a possibility of enhancing the heat transfer through the cells, which may cause a low thermal efficiency. In this paper some effects to homoginize the redox couple on power densities, thermal efficiencies, etc. in the thin-layer thermogalvanic cells are described. The redox couple of $[Fe(CN)_6]^{4-/3-}$ was used in dilute and saturated solutions. Since a more concentrated solution results in a higher power density,[6] a redox couple of $Fe^{2+/3+}$ was used in a more concentrated solution than the saturated solution of $[Fe(CN)_6]^{4-/3-}$.

Experimental

The thin-layer thermogalvanic cell used in this study is illustrated in Fig. 2. The distance between two platinum plates (ca. 120×120×0.05 in mm) was kept at 1 mm with a byton rubber spacer, which had many holes of ca. 9 mm in diameter. The platinum electrodes were in contact with two heat transfer-plates of copper, of which temperature was kept constant by flowing water from thermostats. The two heat transfer-plates were tightened by electrically insulated bolts. Each hole of a spacer was filled with an aqueous electrolyte solution containing a redox couple ($[Fe(CN_6]^{4-/3-}$ or $Fe^{2+/3+}$). This thermogalvanic cell was horizontally placed and covered with a thermal insulator of polystyrene and polyurethane foams. Since the inner resistance of the cell was very small (<1Ω), a potentiostat or a power supply was used as an electrical load instead of a resistance. The cell voltage was measured through two leads independent of current leads, i.e. 4-probe method.

Three types of aqueous electrolyte solutions were used: a: a dilute solution of mixture of 0.010 mol dm^{-3} $K_4[Fe(CN)_6]$

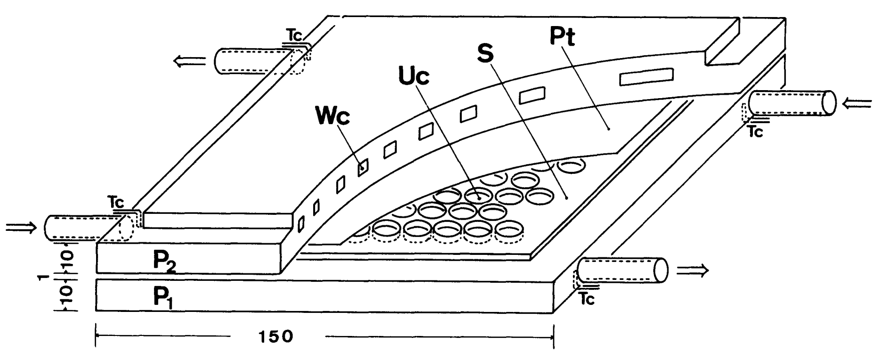


Fig. 2. Thin layer thermogalvanic cell. (Numbers in the illustration is in a unit of mm.) P_1 And P_2: Heat transfer plates, Pt: platinum plate, S: spacer, Tc: thermocouple, Uc: a unit cell, Wc: water channel, ⇨⇦: water inlet and outlet.

and 0.010 mol dm^{-3} $K_3[Fe(CN)_6]$, b: a concentrated solution of mixture of 0.13 mol dm^{-3} $K_4[Fe(CN)_6]$ and 0.85 mol dm^{-3} $K_3[Fe(CN)_6]$, which was made as a saturated solution at 0 °C of their mixture solution, c: a solution of 1.0 mol dm^{-3} $FeCl_2$ and 1.0 mol dm^{-3} $FeCl_3$ in pH 0.6 adjusted by hydrochloric acid. Every chemical used was guaranteed grade.

Notations and Definitions: The potential difference (ΔE) between two electrodes of a cell is defined here as the potential measured for the upper side electrode (temperature T_2) of two horizontal electrodes against the lower one (temperature T_1). The direction of the positive current (I) is defined here from the upper electrode to the lower one through the cell. The temperature difference (ΔT) is defined as T_2-T_1. The thermoelectric power (ε) of the cell is calculated from $\varepsilon=\Delta E/\Delta T$. T_1 and T_2 are the mean values of the temperatures measured by thermocouples placed at the water inlet and outlet in the respective heat-transfer plates, P_1 and P_2. The temperature differences between the inlet and outlet were less than 3 K. Heat transferred through the cell was calculated from a temperature decrease or increase of the flowing water (rates of ca. 15 ml s^{-1}). Heat transfer to the surroundings from the cell was so small that it could be neglected. The current density (i), resistance (R), power density (w), heat flux through the cell (q), and heat transfer coefficient (h) were calculated on a basis of the surface area (A=68.1 cm^2) of the platinum electrodes in contact with the solution as follows (units are shown in parentheses):

i = current through the cell/A (A m^{-2}),

R = cell resistance × A (Ω m^2),

$w = i \times \Delta E$ (W m^{-2}),

q = (heat transferred through the platinum electrode in contact with the solution)/A (W m^{-2}), and

$h = q/\Delta T$ (W K m^{-2}).

Results and Discussion

Thermoelectric Powers. When the temperature of one electrode was increased by changing the water source from a thermostat at ca. 5 °C to another at ca. 40 °C, the potential differences of the cells increased with time (t) as shown in Figs. 3-a, b, and c. In Fig. 3-d, a typical change in the temperature difference with time is shown. It is well known that species in the cell move to the higher or lower temperature electrodes due to Soret diffusion.[11,12] During steady state the Soret diffusion is in equilibrium with the diffusion due to a concentration difference built up by the Soret diffusion. The observed thermoelectric power is, therefore, changed by the potential difference due to this concentration polarization.[11,12] Then, there are two kinds of thermoelectric powers: an initial type (ε_i) defined as the thermoelectric power under the condition of uniform concentration in the cell, i.e. just after the temperature is changed, and a final type (ε_f) at a steady state under no convection, i.e. at time=∞.[11,12] The decreases in $|\Delta E|$ after maximum peaks in case of the cells with the $[Fe(CN)_6]^{4-/3-}$ redox couple (Fig. 3-a(−) and b(−)) are, thus, considered to be due to the Soret diffusion. The first increase in $|\Delta E|$ is toward $\varepsilon_i\Delta T$, and the decrease of $|\Delta E|$ is toward $\varepsilon_f\Delta T$. The fact that there was no decrease of $|\Delta E|$ in Figs. 3-a(+), b(+), and c will be explained later.

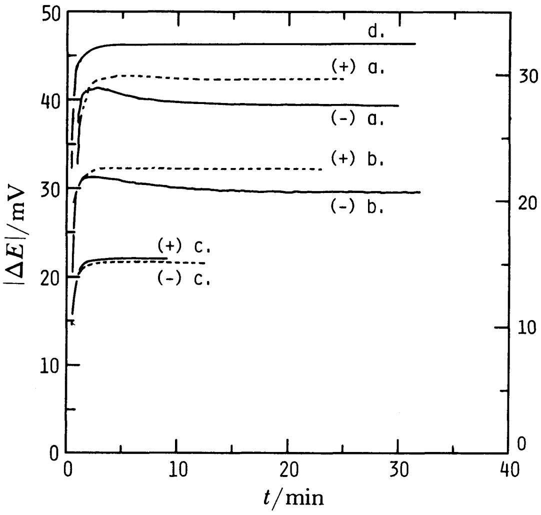


Fig. 3. Variations of potential (a, b, and c) and temperature (d) differences with time. (+): $\Delta E>0$, (−): $\Delta E<0$, min(T_1, T_2)=6.5—6.9 °C, a: cell with dilute $[Fe(CN)_6]^{4-/3-}$ solution, b: cell with concentrated $[Fe(CN)_6]^{4-/3-}$ solution, c: cell with concentrated $Fe^{2+/3+}$ solution, d: a typical temperature difference during the measurement of curve (−)a, ——: changes at $\Delta T>0$, ----: changes at $\Delta T<0$.

In many measurements of the thermoelectric power reported so far, only initial thermoelectric powers have been presented,[13] since it generally takes a long time to attain Soret equilibrium. It is not surprising that Soret equilibrium was attained within a few minutes in the cells used here. This was because of the short distance between the two electrodes. The speed of the Soret diffusion can be evaluated by a characteristic time, τ, calculated from

$$\tau=\frac{d^2}{\pi^2 D},$$

where d is the distance between the electrodes, and D is the diffusion coefficient of the species in the cell.[13] For instance, from $D(K_4[Fe(CN)_6])=1.183\times10^{-9}$ m^2 s^{-1} (0.01 mol dm^{-3}, 25 °C)[15] and d=1 mm τ is about 1.5 min, which is corresponding to the observed speed.

In Fig. 4 thermoelectric powers under steady state conditions in these cells are shown as a function of the temperature differences with initial thermoelectric powers measured using an anti U-shaped cell shown in Ref. 16. Since the steady state thermoelectric powers were larger than $|\varepsilon_i|$ in cells with $[Fe(CN)_6]^{4-/3-}$, $[Fe(CN)_6]^{3-}$ migrates to the higher-temperature electrode and/or $[Fe(CN)_6]^{4-}$ to the lower-temperature one. In the cell with $Fe^{2+/3+}$, Fe^{2+} migrates to the higher-temperature electrode and/or Fe^{3+} to the lower-temperature one.

There is some evidence for natural convection arising in the cell with $[Fe(CN)_6]^{4-/3-}$, which could make

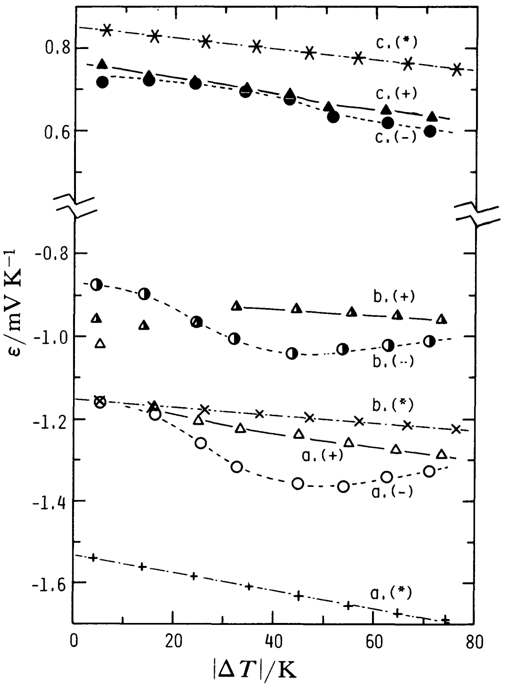


Fig. 4. Initial and steady state thermoelectric powers as a function of temperature difference. Min(T_1, T_2)=4.0—8.0°C, (+): steady state ε at $\Delta T>0$, (−): steady state ε at $\Delta T<0$, (*): ε_i, a, b, and c: see Fig. 3.

the concentration uniform. They were observations that the steady state thermoelectric powers at $\Delta T<0$ shifted toward ε_i from ε_f (as can be seen in Figs. 4-a and b) and that the potential difference at $\Delta T<0$ achieved a steady state with no maximum (Fig. 3). The cause of the convection is considered to be explained as follows.

Natural convection in a pure solvent occurs when the temperature difference in a vertical direction exceeds a point (ΔT_{cr}) calculated from the critical Rayleigh number (Ra_{cr}) as[17]

$$Ra_{cr} = \frac{g\alpha|\Delta T_{cr}|d^4}{a\nu} = 1708,$$

where g, α, a, and ν are the accelation of gravity, the coefficient of volume expansion, the thermal diffusivity, and the kinematic viscosity of the solvent, respectively, and d is the distance of two plates of different temperature, i.e. the distance between the two electrodes. If $|\Delta T|<|\Delta T_{cr}|$, no convection occurs, even when the lower electrode is hotter. The critical temperature difference calculated is ca. −120 K at d=1 mm for pure water. Since the physical constants in this equation do not change much, even for the electrolyte solutions, ΔT_{cr} will not be so different from −120 K in the thermogalvanic cells. However, convection took place from $\Delta T\approx -20$ K in the cell with $[Fe(CN)_6]^{4-/3-}$ (as can be seen in Figs. 4-a and b, in which ε at $\Delta T<0$ was observed to shift toward ε_i, even at $\Delta T=-20$ K. This suggests that the main cause of the convection is not due to a thermal expansion of the solution but, rather, it comes from the electrolyte, since the critical temperature difference may move close to 0 or convection takes place even at $\Delta T>0$ in two-component fluids.[18] The observed small critical temperature difference would, thus, be due to this special convection in the electrolyte solution.

In the case of $Fe^{2+/3+}$, at ε at $\Delta T>0$ is observed to shift toward ε_i as can be seen in Fig. 4-c. As pointed out in the above, convection could abnormally take place at this temperature difference, in which the lower electrode is hotter. Changes of the potential difference with time by increasing of the temperature (see Fig. 3-c), however, didn't show a distinguishable difference between the ΔE–t curves at $\Delta T>0$ and $\Delta T<0$. Clearer experimental evidence concerning the convection at $\Delta T>0$ will be given in the next section.

Inner Resistances. Resistances at $T_1=T_2$: When a small potential difference (=10 mV) was applied to cells at $T_1=T_2$, the current densities (i) through the cells decreased with time in different ways depending on the direction of the currents as shown in Fig. 5. The positive i for the cells with $[Fe(CN)_6]^{4-/3-}$ and the negative i for the cells with $Fe^{2+/3+}$ decreased like an exponential curve to steady state currents. Currents in the opposite direction decreased with oscillation to bigger steady state currents. In the latter case $K_4[Fe(CN)_6]$ and $FeCl_3$ were generated at the electrode of the upper side. The density of the solutions containing these compounds was higher than that of $K_3[Fe(CN)_6]$ or $FeCl_2$ solutions in the same molar concentration, respectively. A natural convection, then, could take place in the cells. It produces a smaller inner resistance during steady state than that of the former case in which the currents were controlled by the diffusion. The convection in the cell with a dilute solution seems to be weak (Fig. 5-a); it took a longer time for the oscillation of the current to start and its steady state current was not so large as that by diffusion. The reason is that the concentration difference induced in the dilute solution by the same applied voltage, which corresponds to the ratio of the concentrations of the oxidized and reduced species of the redox couple, is smaller than that in the cell with a concentrated solution.

Relations between the applied potential difference (ΔE) and the steady state current are shown in Fig. 6, wherein the measurements were performed from +500 mV to −500 mV in ΔE for Fig. 6-a and b and from +500 mV to −500 mV for Fig. 6-c, i.e. from the diffusion state to the convection one. The currents approached limiting values at a large potential difference, in which the concentration of one species of the redox couple was almost zero at one electrode. The currents will not increase beyond the limiting currents, unless another charge-transfer reaction or the stronger convection takes place. At a small potential difference (about less than 50 mV) currents were linearly proportional to ΔE in each side of $\Delta E>0$ and $\Delta E<0$ with different proportional ratios, i.e. different resistances, except at ΔE very close to 0, in which the concentra-

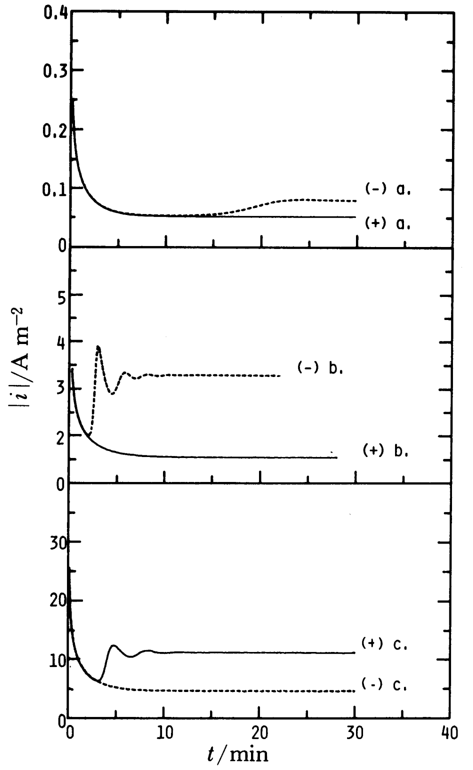


Fig. 5. Current variations with time by applying ±10 mV. (+): $\Delta E>0$ And $i>0$, (−): $\Delta E<0$ and $i<0$, a and b: $T_1=T_2=4.9\,°C$, c: $T_1=T_2=40.6\,°C$, a, b, and c: see also Fig. 3.

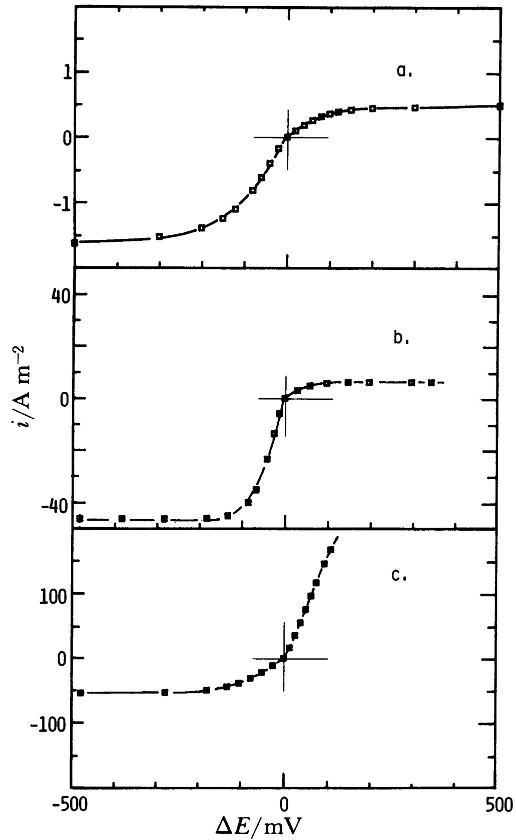


Fig. 6. Relations between steady state current and potential difference applied at $T_1=T_2$. a And b: $T_1=T_2=4.9$—5.0 °C, c: $T_1=T_2=40.6\,°C$, a, b, and c: see also Fig. 3.

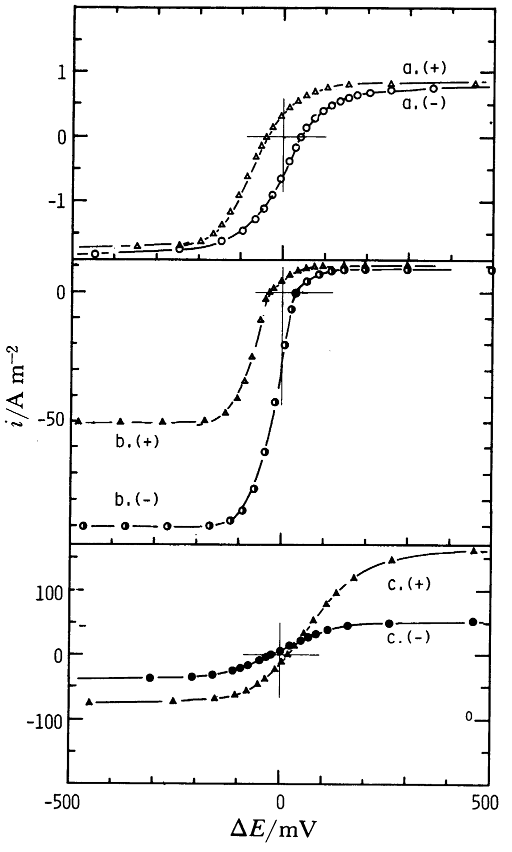


Fig. 7. Relations between steady state current and potential difference applied at $T_1 \neq T_2$. (+): $\Delta T>0$, (−): $\Delta T<0$, a and b: $T_H=39.2\,°C$ and $T_L=6.9\,°C$, c.(+): $T_1=39.1\,°C$ and $T_2=7.6\,°C$, c.(−): $T_1=4.3\,°C$ and $T_2=38.9\,°C$, a, b, and c: see also Fig. 3.

tion difference is so small that no convection arises. Detailed features of $i-\Delta E$ curves and resistances at $T_1=T_2$ are shown in Appendix 1.

Resistances at $T_1 \neq T_2$: In case of $T_1 \neq T_2$ i-ΔE relations can be divided into four regions, due to the signs of ΔT and i, i.e. due to how the convection arises. The results are shown in Fig. 7, wherein the measurements were performed in the same direction for applying ΔE (as in Fig. 6). It is noted here that an observation of the greater current at $\Delta T>0$ than at $\Delta T<0$ in the cell with $Fe^{2+/3+}$ (Fig. 7-c) confirms the previous argument that the convection is induced by $\Delta T>0$.

As already described, it is obvious that there are two causes (the temperature difference and the current) for the onset of convection. Those condisions are summarized as follows.

solutions	ΔT	i
$[Fe(CN)_6]^{4-/3-}$	−	−
$Fe^{2+/3+}$	+	+

When these two causes for the convection were superimposed positively, the biggest currents flowed (i.e. in cases of $\Delta T<0$ and $i<0$ for the cells with $[Fe(CN)_6]^{4-/3-}$ and in case of $\Delta T>0$ and $i>0$ for the cell with $Fe^{2+/3+}$). Under the conditions of the opposite signs in ΔT and i, the smallest currents controlled by the diffusion were observed (i.e. in cases of $\Delta T>0$ and $i>0$ for the cells with $[Fe(CN)_6]^{4-/3-}$ and in case of $\Delta T<0$ and $i<0$ for the cell with $Fe^{2+/3+}$. When the two causes for convection are competitive, the following three states are possible: convection arises, it is diminished, or no convection arises. In cells with $[Fe(CN)_6]^{4-/3-}$, convection became completely diminished at $i\gg 0$, even at $\Delta T<0$. The limiting currents under these conditions were observed to be equal to those controlled by the diffusion. In the same cells at $\Delta T>0$, convection arose at $i\gg 0$. From these relations it is concluded that the condition $i<0$ is more predominant for convection to arise than that of $\Delta T<0$ in these cells. This is especially evident in a cell with a dilute solution as the almost equal negative limiting currents under the convection were observed at both $\Delta T<0$ and $\Delta T>0$. In cells with $Fe^{2+/3+}$ the condition $\Delta T>0$ was more predominant than that of $i>0$. This can be seen in curves at $\Delta T>0$, in which the currents of either $i\gg 0$ or $i\ll 0$ are bigger than those at $\Delta T<0$. More detailed descriptions for $i-\Delta E$ relations are given in Appendix 1.

The resistance during the generation of the electric power, where $i\Delta E<0$, is dependent on which region the $i-\Delta E$ relation belongs to during this condition. In cells with $[Fe(CN)_6]^{4-/3-}$ a negative current flows when a negative temperature difference is applied, i.e. $\Delta T<0$ and $i<0$. These two conditions are positive for convection to arise (as already described). Therefore, in this case the resistance was much smaller than that obtained under the opposite conditions ($\Delta T>$, $i>0$). In the cell with $Fe^{2+/3+}$ a negative current flowed when a positive temperature difference was applied, i.e. $\Delta T>0$ and $i<0$. Since only one of these two conditions ($\Delta T>0$) is positive for the convection, the resistances were not so small in comparison with that obtained under the opposite conditions ($\Delta T<0$, $i>0$).

The resistances measured by applying half of $\varepsilon\Delta T$, at which maximum power densities were obtained, are shown as a function of ΔT in Fig. 8. A typical change in the resistances with ΔT was observed in the cell with a dilute $[Fe(CN)_6]^{4-/3-}$ solution, in which the difference between the resistances at $\Delta T<0$ and $\Delta T>0$ increased with increasing $|\Delta T|$. This would be a reflection of a stronger convection at a bigger $|\Delta T|$.

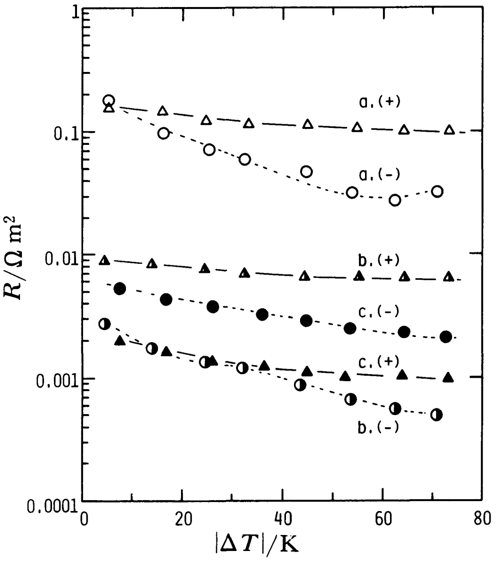


Fig. 8. Steady state resistances as a function of temperature difference. (+) And (−): see Fig. 7, a, b, and c: see Fig. 3.

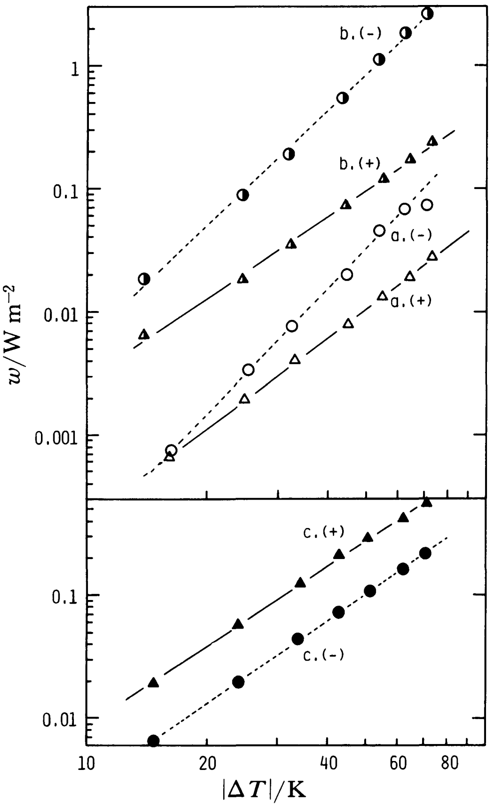


Fig. 9. Maximum power densities as a function of temperature difference. (+): $\Delta T>0$, (−): $\Delta T<0$, a, b, and c: see Fig. 3.

Power Densities. Effects of Convection: In the region of $i\Delta E<0$ (Fig. 7) where the cells have electrical works to the surroundings, currents changed linearly with ΔE, i.e. the resistances were constant. Since the maximum power density (w) is obtained when the electrical load is equal to the inner resistance (R), it can be expressed as

$$w=\frac{\varepsilon^2\Delta T^2}{4R}, \tag{1}$$

where R is assumed to be independent on the potential differences. The power densities obtained by applying $\varepsilon\Delta T/2$, which corresponds to the electrical load$=R$, are shown in Fig. 9. Those of the convection cells were larger than those of the diffusion cells at equal temperature differences due mainly to $1/R$ rather than ε. The differences between convection and diffusion cells are within 10% in ε, but is 4-times greater in $1/R$ for convection cells. The biggest power density obtained in these measurements was 2.6 W m^{-2} by a cell with a concentrated $[Fe(CN)_6]^{4-/3-}$ solution at $\Delta T=-72$ K. A greater power density might be possible at greater temperature differences; however, it would become difficult to apply a temperature differences of nearly 100 °C or more than 100 °C. The biggest power density obtained in these measurements by a cell with $Fe^{2+/3+}$ was 0.56 W m^{-2} (at $\Delta T=71$ K), less than the above cell because of a smaller $|\varepsilon|$, though the concentration was higher than the former cell and the inner resistance was of the same order.

It is possible to imagine an ideal state in which the inner resistnace is equal to the AC resistance (R_{AC}). This state can be achieved by a strong convection, which would also make the thermoelectric power close to ε_i. The ideal power density (w_{id}) is, then, calculated by inserting ε_i and R_{AC} instead of ε and R, respectively, into Eq. 1. At this ideal state, where the current does not decrease from the initial current, the power density in cells with $[Fe(CN)_6]^{4-/3-}$ can increase up to 40 W m^{-2}, which is higher than the observed power density (by 20 times). These estimations are summarized in Table 1. It is necessary to consider the size of ε_f and ε_i to conclude that convection always makes the power density bigger. In all the cells measured here $|\varepsilon_f|$ was smaller than $|\varepsilon_i|$; however, this relation can not be extended to all kinds of thermogalvanic cells. Some cases of $|\varepsilon_f|>|\varepsilon_i|$ were reported, but the difference between them was negligibly small: usually ca. 0.1—0.5 mV/K.[11] Therefore, it can be stated in a practical sense that convection can produce a higher power density in any type of thermogalvanic cell.

ΔT Dependence: If ε and R were not dependent on ΔT, the power densities should increase by a power of two from Eq. 1. However, the observed power densities fit lines with slopes of 2—3 in log-log plots of w and $|\Delta T|$ (Fig. 9). In the whole region of ΔT used here, $1/R$ increased by ca. 3—4 times in convection cells but only by ca. twice in diffusion cells. In the same region of ΔT the changes of ε were as small as ca. 20% in convection cells and ca. 10% in diffusion cells. The increase of $1/R$ with $|\Delta T|$, therefore, has greater affects on the power densities than on the changes of ε with $|\Delta T|$.

Heat Transfer. In thermoelectric converters the heat supplied to the high-temperature electrode is different from that taken away from the low-temperature electrode. The difference between two thermal energies is converted into electrical work. In the case of thermogalvanic cells, the heat flux supplied to the electrode at T_H is the sum of a heat flux (q_c) transferred by conduction and convection through the cell and that ($q_{e,H}$) transported by electrolyte and electrochemical reactions. The two heat fluxes can be expressed as[10]

$$q_c = h\Delta T, \tag{2}$$

and

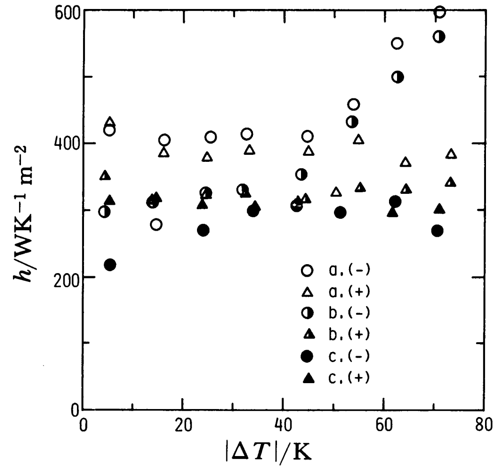


Fig. 10. Heat transfer coefficients as a function of temperature difference at no current. (+) and (−): see Fig. 9, a, b, and c: see Fig. 3.

$$q_{e,H} = -T_H i, \tag{3}$$

where h is the heat-transfer coefficient through the cell. The heat taken away from the cell at the low-temperature electrode is also the sum of q_c and the heat flux ($q_{e,L}=-T_L i$) transported by electrochemical processes. The difference between two heat fluxes, $q_{e,H}$ and $q_{e,L}$, is equal to the electrical work of this cell, $-\varepsilon\Delta Ti$. A part of this work is converted into Joule heat in the cell.

Heat fluxes q_c and $q_{e,H}$ passing through a distance of 1 mm are estimated as $q_c=609$ W m^{-2} and $q_{e,H}=0.3$ W m^{-2} from $h=k$(the thermal conductivity of pure water)$=0.609$ W K^{-1} m, $\varepsilon=1$ mV K^{-1} the solution resistivity=1 Ωm, $\Delta T=1$ K, and $T_H=300$ K. From $q_{e,H}\ll q_c$, the heat flux, q, transferred from the high-temperature electrode to the low one will be

$$q \approx q_c = h\Delta T.$$

Heat transfer coefficients obtained from $h=q/\Delta T$ in case of no current are shown as a function of the temperature difference in Fig. 10. In the cells with $[Fe(CN)_6]^{4-/3-}$, the heat-transfer coefficient started to increase at $\Delta T\approx-50$ K owing to the convection due to the temperature difference. In cells with $Fe^{2+/3+}$ it did not increase at both regions of $\Delta T>0$ and $\Delta T<0$. Although there was a possibility for the heat flux to increase by convection due to the current, no increase was observed within the experimental error (less than 40 W m^{-2} in q corresponding to 0.5—20 W K m^{-2} in h) during the measurement of Fig. 7.

Thermal Efficiencies. The thermal efficiency (η) at the maximum power of this cell can be calculated from Eqs. 1, 2, and 3 as

$$\eta = \frac{w}{q_c + q_{e,H}} = \frac{T_H - T_L}{T_H}\frac{1}{2}\left(\frac{1}{1+2/ZT_H}\right),$$

Table 1. Observed and Ideal Characteristics of the Thin-Layer Thermogalvanic Cells

	T_L	$\|\Delta T\|$	ε_d	ε_c	ε_i	R_d	R_c	R_{AC}[d)]	w_d	w_c	w_{id}	h_d	h_c	η_d	η_c	η_{id}	Z_d	Z_c	Z_{id}
	°C		mV K^{-1}			10^{-3} Ωm^2			W m^{-2}			W K^{-1} m^{-2}		10^{-6}			10^{-6}/K		
a. Dilute[a)] $[Fe(CN)_6]^{4-/3-}$	5.5	72	−1.29	−1.33	−1.69	81	30	1.6	0.028	0.074	2.2	383	596	0.98	1.8	82	0.054	0.099	4.7
b. Cocentrated[b)] $[Fe(CN)_6]^{4-/3-}$	5.4	72	−0.96	−1.01	−1.22	5.2	0.49	0.046	0.24	2.6	40	340	560	9.6	670	1660	0.053	3.7	95
c. Concentrated[c)] $Fe^{3+/2+}$	6.3	71	0.60	0.63	0.75	2.1	0.97	0.18	0.22	0.56	3.9	269	300	11	26	205	0.63	1.4	12

a), b), and c): See Fig. 3-a, b, and c, respectively, d): Measured at 40°C. Meanings of suffixes; AC: measured by alternating current, c: measured under convection, d: measured under diffusion (or weak convection in the cell with $Fe^{2+/3+}$), i: initial, id: ideal.

and

$$Z = \varepsilon^2/hR,$$

where the term, $(T_H - T_L)/T_H$, is the thermal efficiency of the Carnot cycle, and Z is called a figure of merit.[10)] Under the condition $q = q_c$, η will be

$$\eta = \frac{w}{q} = \frac{T_H - T_L}{T_H}\frac{ZT_H}{4}. \tag{4}$$

The highest thermal efficiency obtained in these measurements was 6.7×10^{-5} by the cell with the concentrated $[Fe(CN)_6]^{4-/3-}$ solution at $\Delta T = -72$ K (i.e. under the convection) with the biggest figure of merit, 3.7×10^{-6} K^{-1} (Table 1). In any cell a higher η and a bigger Z were obtained by convection cells than those by the diffusion cells. Though the heat-transfer coefficient increased with $|\Delta T|$ in the range of $\Delta T < -50$ K, the thermal efficiencies did not decrease except at one point, since increase in the electric work compensates for the heat leak across the cells. This can be proved generally, as described in Appendix 2.

The thermal efficiencies calculated from the measured power densities and heat fluxes are shown in Fig. 11 as a function of the temperature difference. From Eq. 4, they should increase linearly in the first order with the temperature difference, if the three constants, h, R, and ε, were not dependent on the temperature difference of the cell. The observed thermal efficiencies are on straight lines of slope greater than 1 in $\log(\eta)$-$\log(|\Delta T|)$ plots. This means that the higher thermal efficiencies (than those expected from the small temperature difference) were obtained at a greater temperature difference. This is mainly because of the lower resistance among the three factors (h, R, and ε) at large temperature differences.

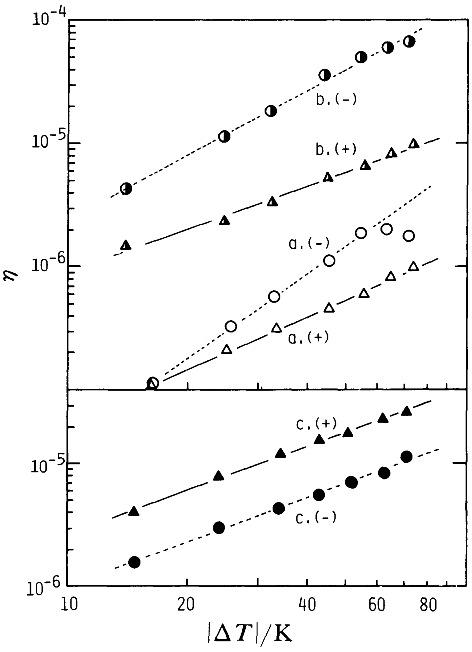


Fig. 11. Thermal efficiencies measured for the cell operating at temperature difference ΔT. (+) And (−): see Fig. 9, a, b, and c: see Fig. 3.

Conclusion

It was confirmed that in thin-layer thermogalvanic cells with soluble redox couples a natural convection induced by a temperature difference and by a concentration change due to current produces a small inner resistance under steady state conditions without sacrificing the thermal efficiency. An $[Fe(CN)_6]^{4-/3-}$ couple with K^+ is more suitable than an $Fe^{2+/3+}$ couple with Cl^-, since the convection induced by two causes is superimposed positively in the former case but it is reciprocal in the latter case. In addition, the former cell exhibits a bigger thermoelectric power than the latter. Minimizing the inner resistance during steady state conditions close to the AC resistance as possible is important for obtaining a high performance thermogalvanic cell. It is also necessary to find a redox couple with a higher thermoelectric power.

Appendix 1

***i–ΔE* Relations at Small $|\Delta E|$ and Isothermal Resistances.** The i–ΔE curves measured by small potenital differences at $T_1 = T_2$ are shown in Fig. 12, in which the transition points from the diffusion states to the convection states can be clearly seen as inflection points (ΔE_{in}) in those curves; $\Delta E_{in} = -6$ mV for the cell with the dilute $[Fe(CN)_6]^{4-/3-}$ solu-

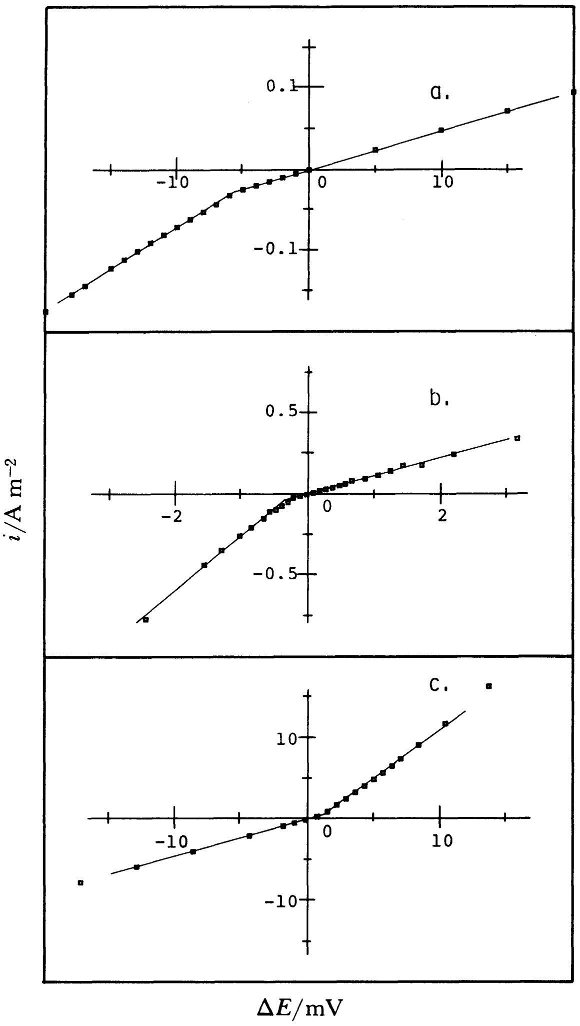


Fig. 12. Relations between steady state current and small potential difference applied at $T_1=T_2$. See Fig.6.

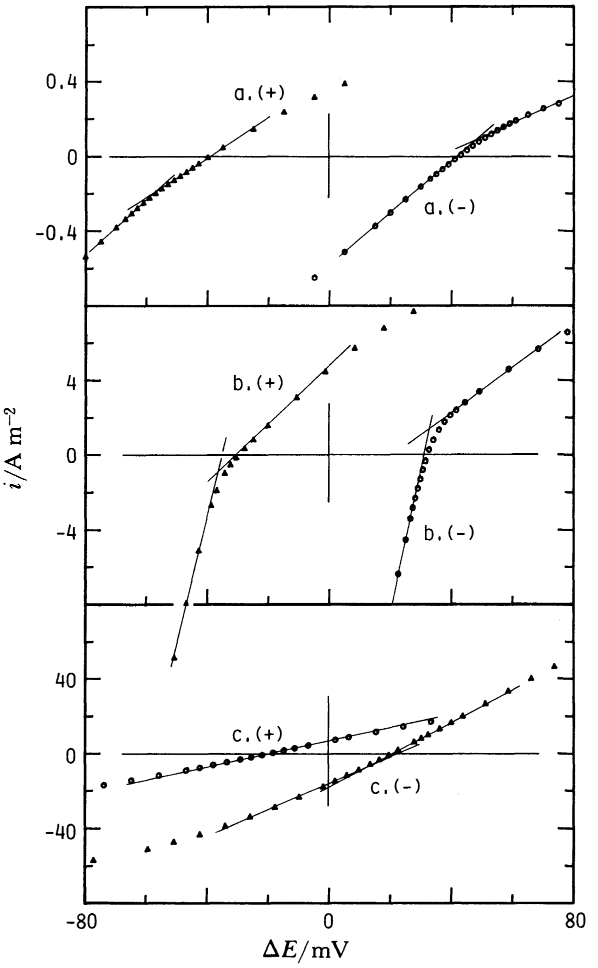


Fig. 13. Relations between steady state current and small potential difference applied at $T_1 \neq T_2$. See Fig. 7.

tion, $\Delta E_{in}=-0.3$ mV for the concentrated $[Fe(CN)_6]^{4-/3-}$ one, and $\Delta E_{in}=2$ mV for the concentrated $Fe^{2+/3+}$ one. In case of low concentration, this inflection point was farther from $\Delta E=0$ than that of the concentrated solutilon, for the same reason as described for weak convection in a cell with a dilute solution.

The $i-\Delta E$ curves measured by small potential differences at $T_1 \neq T_2$ are shown in Fig. 13. The inflection points near $i=0$ in the $i-\Delta E$ curves (Fig. 13-c) of the cell with $Fe^{2+/3+}$ were not observed clearly. The reason for this may be due to the fact that a change of ΔE from $-$ to $+$ produces a small change in the state of this cell, such as from diffusion to weak convection or from weak convection to strong convection. In cells with $[Fe(CN)_6]^{4-/3-}$ a change of ΔE from $+$ to makes it from diffusion to convection at the both directions of the temperature difference. Therefore, the clearer inflection points were observed in the latter cells. They moved to a somewhat more positive or negative potential difference than $\varepsilon_f \Delta T+\Delta E_{in}$, which is an expected inflection point by assuming no convection due to the temperature difference.

In Fig. 14 three kinds of resistances at $T(=T_1=T_2)$, the steady state resistances under diffusion with no convection (R_d), those under the convection (R_c), and AC resistances measured at 1 or 5 kHz (R_{AC}), are shown. The steady state resistances were calculated from changes in the steady state currents at $|\Delta E|=5\rightarrow 10$ mV. The AC resistances had a small frequency dispersion. Since both resistances (R_d and R_{AC}) are related to the diffusion coefficients, they decreased with an increase in the temperature with almost the same slope in log(R) vs. $1/T$ curves; 0.66 ± 0.04, 0.72 ± 0.09, and $1.1\pm0.1 \times 10^3$ K for Fig. 14-a(+, *), b(+, *), and c(−, *), respectively. Since the resistances under convection (R_c) are related not only to R_d and R_{AC}, but also to the convection speeds, there is a possibility of having different features in log(R) vs. $1/T$ curves. However, they exhibited similar slopes in log(R) vs. $1/T$ curves; 0.55, 0.58, and 1.0×10^3 K for Fig. 14-a(−), b(−), and c(+), respectively.

Appendix 2

Thermal Efficiency in the Convection Cells. It is first assumed that a volume, V, of the solution in contact with the electrode at T_H is moved to the electrode at T_L within time Δt; heat flux under this condition can increase by

$$\Delta q_{convection}=V\rho c(T_H-T_L)/\Delta t,$$

where ρ and c are the density and the heat content of the solution, respectively. If all electroactive species transferred

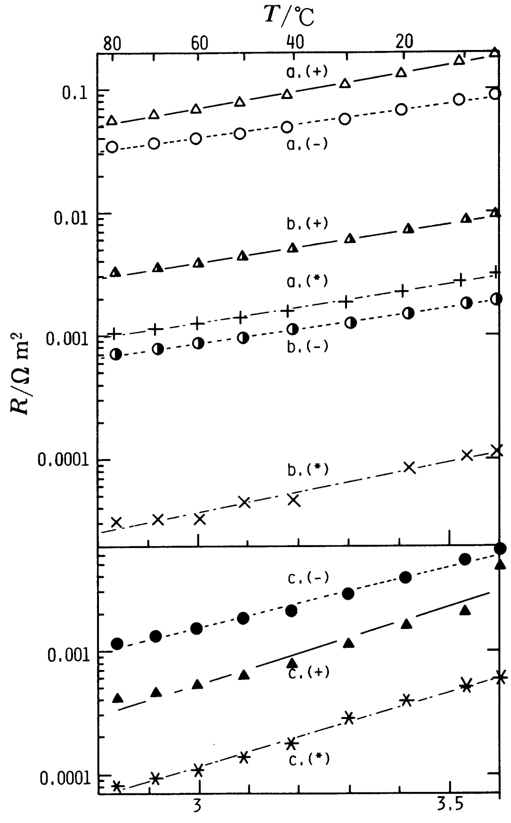


Fig. 14. Steady state and AC resistances as a function of temperature. ($T_1=T_2$) (+): Steady state R at $\Delta E>0$, (−): steady state R at $\Delta E<0$, (*): R_{AC} at 1 kHz (a and b) or 5 kHz (c). a, b, and c: see Fig. 3.

by this movement have a one-electron charge-transfer reaction with the electrodes, it can result in a current increase

$$\Delta i = FCV/\Delta t \quad (F\text{: Faraday constant}),$$

where C is the concentration of the electroactive species. The efficiency of increased work against the increased heat flux due to the convection is

$$\eta_{\text{convection}} = \frac{\varepsilon \Delta T \Delta i}{\Delta q_{\text{convection}}} = \frac{F\varepsilon C}{\rho c}.$$

If the efficiency of cells without convection (η_d), which can be roughly estimated as

$$\eta_d = \frac{(\varepsilon \Delta T)(FDC/d)}{k\Delta T/d} = \frac{F\varepsilon DC}{k} \quad (k\text{: thermal conductivity of the solution}),$$

assuming that the current is equal to the limiting current, FDC/d, is larger than $\eta_{\text{convection}}$, i.e. if

$$\frac{\eta_{\text{convection}}}{\eta_d} = \frac{a}{D} > 1,$$

where $a=k/\rho c$ (thermal diffusivity), the convection will make the thermal efficiency higher than that by the diffusion cell. Since the thermal diffusivity of the pure water is 1.45×10^{-7} m^2 s^{-1} and the diffusion coefficients of many ions in water are in range of 10^{-10}—10^{-8} m^2 s^{-1},[15] it is concluded that the convection always improves the thermal efficiency. If the convection is very strong, however, improvement may be impaired, since the current is limited by $\varepsilon_i \Delta T/R_{AC}$ under this condition. It is necessary to more rigorously determine how convection effects the heat transfer and the electrical resistance. This might be a new type of Benard problem[18] having not only the temperature difference but also the concentration difference induced by the current.

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