

Comparative Studies of a Thermoelectric Converter by a Thermogalvanic Cell with a Mixture of Concentrated Potassium Ferrocyanide and Potassium Ferricyanide Aqueous Solutions at Great Temperatures Differences.

Reinaldo Simões Gonçalves*

Universidade Federal de Santa Maria, Caixa Postal 5061
CEP 97119 - Santa Maria, RS, Brasil

and

Tamio Ikeshoji

Government Industrial Research Institute, Tohoku
Nigatake 4-2-1, Miyagino-ku, Sendai 983, Japan

Received: april 27, 1992.

São mostrados alguns efeitos da concentração do par redox $[\text{Fe}(\text{CN})_6]^{4-/3-}$ na termocela operada com grandes diferenças de temperaturas entre os eletrodos. Todos os dados confirmam que a solução 0,4 M do par é melhor do que 0,8 M. A maior densidade de potência (22.0 W/m^2) foi obtida em soluções 0,4M e um gradiente de temperatura de 137,5 graus. Em soluções mais concentradas podem ocorrer os processos de formação de par iônico ou precipitação do sal.

It is presented some effects of the high concentration of the redox couple $[\text{Fe}(\text{CN})_6]^{4-/3-}$ on the thermocell that operated great temperature difference between the electrodes. All data confirms that a 0.4 M redox couple solution is better in this system than a 0.8 M one. Highest power density (22.0 W/m^2) was obtained in 0.4 M solutions with temperature difference at 137.5 K. At more concentrated solutions, the processes of ionic-pair formation or the precipitation of the salt on low-temperature electrode.

Key words: *thermocell; thermoelectric converter; thin-layer cell.*

Introduction

The thermogalvanic cells, which are also called Thermocells or non-isothermal galvanic cells, are a kind of thermoelectric converter which consists of an electrolyte solution and two identical electrochemical electrodes placed at different temperatures¹⁻³. They are the electrochemical equivalent of thermoelectric devices and can directly convert thermal energy to electric one.

Conceptually and operationally, however, thermogalvanic cells are considerably more complex than ordinary metal or semi-conductor thermocouples, since ionic as well as electronic conduction is involved. During the operation, a charge-transfer reaction between ions and electrodes takes place, a compound is thus accumulated at one of the two electrodes. At another one, this same compound is consumed. These accumulated species must be recycled to the latter electrode in order to continuously produce electricity from the cell. It was shown that a thin-layer cell with a soluble redox couple is suitable to recycle⁴. The current at a

steady state in the thin-layer cell is, primarily, proportional to the speed of the diffusion determined by the concentration gradient induced by the flowing current. Natural convection induced by concentration difference and temperature one will also play an important role in this recycling.

In this paper some effects of the high concentration of the redox couple $[\text{Fe}(\text{CN})_6]^{4-/3-}$ and at great temperature difference between the electrodes, in which one of them is more than 100°C, are shown. In this system potential at the higher temperature side is negative, thus the redox reaction that occurs at the high temperature electrode (T_H) and at low temperature electrode (T_L) after connecting the two electrodes with a resistance is an oxidation one



and a reduction one, respectively/



Experimental

Cell

In the measurement, a cell made of stainless steel with two platinum electrodes as illustrated in Fig. 1 was used. The mixture solution in the same concentration of potassium ferrocyanide and potassium ferricyanide was put between the two platinum electrodes (10 mm in diameter and 1 mm thick) using teflon ring as a spacer (1 mm thick), which had a hole of 5 mm in diameter. The temperature of the electrodes were controlled by water circulating in one of the semi-cell and with an electric heater in another semi-cell. Temperatures were measured by thermocouples placed in the cells near the electrodes. The measurements were made with the cell placed horizontally and vertically.

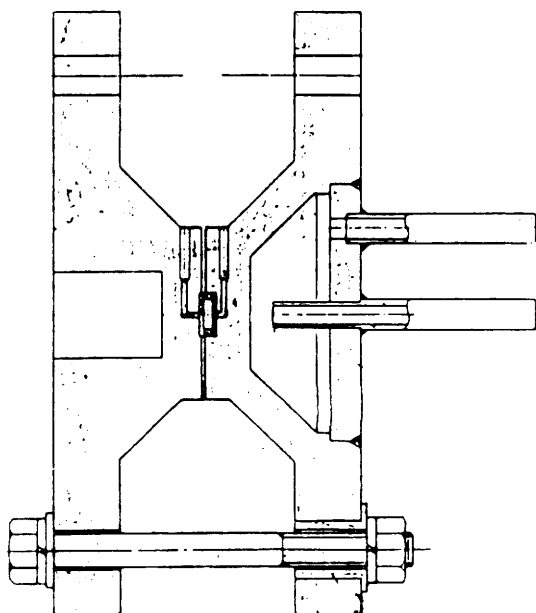


Figure 1. Schematic illustration of the stainless steel cell.

Equipments

A Solartron 1286 Electrochemical Interface was used as a potentiostat and to measure the potential difference. The thermostat used for the water circulating was Toyo Rikakikai NCB-211, which had the ability to control the temperature of water within ± 0.02 K. The electric heater was connected with a variable power supply to control the temperature within ± 3 K range. The voltage of the thermocouples were measured with a Hewlett-Packard HP-3457 A multimeter. The potentiostat and multimeter. The potentiostat and multimeter were connected to an HP-9000-310 personal computer.

Chemicals

Potassium ferrocyanide and potassium ferricyanide of guaranteed grade were used without further purification. Two types of aqueous electrolyte solutions were used: a) 0.4 m $[\text{Fe}(\text{CN})_6]^{4-/3-}$ solution, b) 0.8 m $[\text{Fe}(\text{CN})_6]^{4-/3-}$ solution of mixture of both salts.

Results and Discussion

Influence of Temperature on open-circuit potential difference

The open-circuit potential difference (ΔE) between two electrodes in the steady state is proportional to the tempera-

ture difference (ΔT) as shown in Fig. 2. The lower temperature (T_L) range was between 10-20°C. The linear relationship between $|\Delta E|$ and $|\Delta T|$ suggests thermodynamic entropies and transported ones, which primarily determine thermoelectric power, to be almost constant in this temperature range.

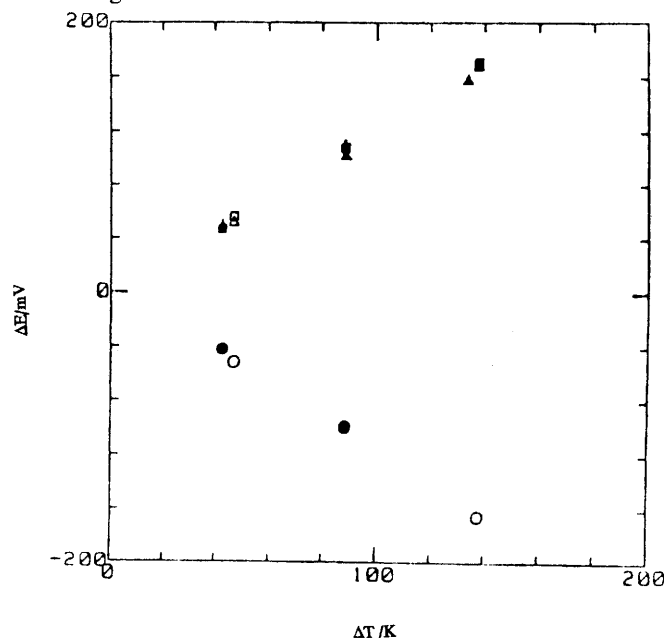


Figure 2. Open-circuit potential vs. temperature difference between the electrodes in (Δ)Horizontal position with the cold semi-cell in the upper, (\square)Vertical position and, (\circ)Horizontal position with the hot semi-cell in the upper. Empty marks are related with 0.4 m and full marks 0.8 m $[\text{Fe}(\text{CN})_6]^{4-/3-}$ solutions.

As is known, species in the thermogalvanic cell diffuse to the colder or hotter electrodes due to the temperature difference (called Soret diffusion or thermal diffusion). During the steady state, the Soret diffusion is in equilibrium with the diffusion due to a concentration difference built up by the Soret diffusion. This Soret equilibrium is disturbed by convection of the solution. Since the natural convection takes place due to the temperature difference in cases of the vertical electrodes and the horizontal electrodes with the cold plate in the upper side, the potential differences are slightly different from that with no convection in case of the horizontal electrodes with the cold plate in the lower side. The difference is corresponding to the potential difference due to the concentration polarization.

Influence of cell position on the current

When a small potential difference (± 10 mV) to the open-circuit potential was applied to cells, the current densities (j) through the cells decreased with time in different ways depending on the position of cells as shown in Fig. 3. The different values of current densities in the horizontal position with the cold plate in the upper side comparing with the inverse position, may be related with the natural convection of the electrolyte solution. For the onset of convection there are three causes: thermal expansion, the concentration change due to the Soret diffusion and the concentration change due to the electrolysis. When these causes for the convection were superimposed positively,

the biggest current flowed. In the horizontal position with the low temperature electrode in the upper position, a heavy species $K_4[Fe(CN)_6]$ is produced on the upper electrode by electrolysis. This species moves toward the lower electrode by gravitational effects.

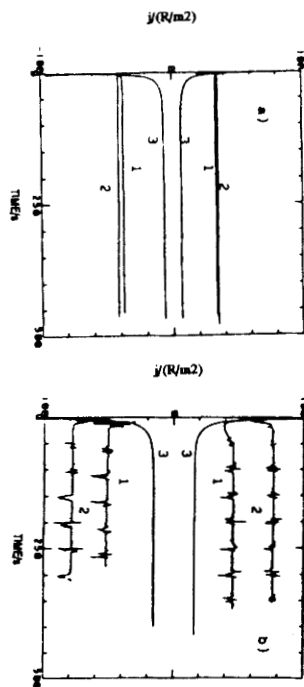


Figure 3. Current densities changes vs. time, recorded during ± 10 mV potential applied in different positions: a) 0.4 m $[Fe(CN)_6]^{4-/3-}$ solution with 138 K in temperature difference ($T_L=14^\circ C$) and b) 0.8 m $[Fe(CN)_6]^{4-/3-}$ solution with 47 K in temperature difference ($T_L=53^\circ C$). 1- Horizontal position with cold plate in the upper side; 2- vertical position and, 3- horizontal position with hot plate in the upper side.

Influence of Electrolyte Concentration

Relations between the applied potential difference and the steady state current at different electrolyte concentrations are shown in Fig. 4. The measurements were performed by applying the potential from the open-circuit potential difference to zero. Near the open-circuit potential, currents were linearly proportional to DE with different proportional ratios, i.e. different resistances, for the cell positions. At low concentration system, the resistance of the solution is lower in the vertical position. However, at high concentration, the vertical position show the lowest resistance.

All data related with the potential difference in the open-circuit (E_{open}), thermoelectric power (E) density (w) measured at $E_{open}/2$ and, the DC resistance (R) of the thermogalvanic cell with a 0.4 M $[Fe(CN)_6]^{4-/3-}$ solution are shown in Table 1.

The thermoelectric powers (E), of the cell, changes from -1.10 mV/K to -1.25 mV/K in the temperature range. The maximum value was observed in the vertical position at high temperature difference.

The power densities (w), increases with the temperature

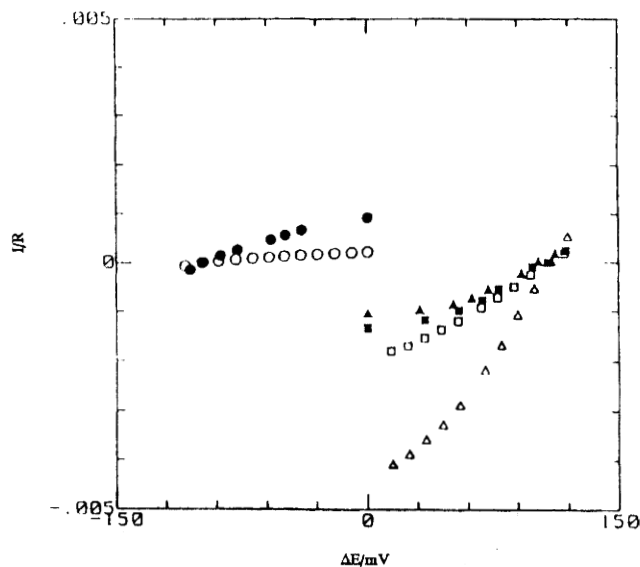


Figure 4. Steady state currents vs. applied potential with the cell in different positions at 89 K temperature difference ($T_L=10^\circ C$) in empty marks 0.4 m and full marks 0.8 m $[Fe(CN)_6]^{4-/3-}$ solutions. Δ , \square , and o , see caption of Fig. 2.

Table 1. Potential difference in the open-circuit (E_{open}), thermoelectric power (E), power density (w) measured at $E_{open}/2$, and the DC resistance (R) of the thermogalvanic cell with a 0.4M $[Fe(CN)_6]^{4-/3-}$ solutions in different temperatures and different positions.

	Horizontal position cold s.c. upper		Vertical position		Horizontal position hot s.c. upper				
$\Delta T/K$	46.9	89.5	136.7	47.1	88.2	137.5	46.6	87.6	139.3
$T_L/^\circ C$	7.60	10.4	14.8	7.20	9.90	14.0	7.50	9.40	12.1
E_{open}/mV	516	110	168	565	108	171	-515	-98.5	-165
$E/(mV/K)$	-1.10	-1.23	-1.23	-1.20	-1.22	-1.25	-1.10	-1.12	-1.18
$w/(W/m^2)$	0.590	8.12	20.1	6.86E-2	3.30	22.0	0.254	0.340	3.40
$R/(mWm^2)$	1.13	0.371	0.351	11.6	0.881	0.334	2.60	7.15	2.00

difference increases. The highest value observed, 22.0 W/m^2 , is the first one reported in the literature, with this system.

The DC resistance of the solutions (R), decreases with the temperature difference increases. The minimum value, $3.34E-4 \Omega m^2$, was observed in the vertical position at high temperature difference.

Even though the higher power density is expected at more concentrated solution, the values observed of these

data don't confirm this, as is shown in Table II for the cell with a 0.8 M $[\text{Fe}(\text{CN})_6]^{4/3-}$ solution. Higher values in the resistance of the 0.8 M solution may be related with: a) the formation of ionic pairs, that do not participate in the processes of ionic conductions, or b) the precipitations of the salts on the low temperature electrode (7 - 12°C), due to low solubility of the salts.

When the temperature of the low-temperature electrode is set at higher value (ca. 53°C), the power density of the cell increases and DC resistance of the solution decreases. This fact may be related with: a) the quantity of ionic pairs decreases or b) the solubility of the salts changes with the temperature increasing.

Table 2. Potential difference in the open-circuit (E_{open}), thermoelectric power (E), power density (w) measured at $E_{\text{open}}/2$, and DC resistance (R) of the thermogalvanic cell with a 0.8 m $[\text{Fe}(\text{CN})_6]^{4/3-}$ solutions in different temperatures and different positions.

	Horizontal position cold s.c. upper			Vertical position			Horizontal position hot s.c. upper		
$\Delta T/\text{K}$	42.4	88.6	46.6	42.4	88.9	46.9	42.7	88.4	46.3
$T_L/^\circ\text{C}$	7.77	11.3	53.6	7.61	11.1	53.3	7.58	11.4	53.6
$E_{\text{open}}/\text{mV}$	49.6	102	54.4	47.0	109	55.0	-41.7	-97.6	-49.6
$E/(\text{mV}/\text{K})$	-1.17	-1.15	-1.17	-1.11	-1.22	-1.17	-0.977	-1.10	-1.07
$w/(\text{W}/\text{m}^2)$	0.530	2.29	4.29	7.95E-2	2.75	5.84	3.51E-2	1.40	0.948
$R/(\text{m}\Omega\text{m}^2)$	1.16	1.14	1.73	6.98	1.09	0.130	12.4	1.70	0.647

Conclusion

The potential difference in thermogalvanic cells operating with $[\text{Fe}(\text{CN})_6]^{4/3-}$ concentrated solutions is proportional to the temperature difference between the two electrodes. The values of thermoelectric power, power density and resistance of the solutions, depends of the cell positions. Evidences of natural convection in the solution were well characterized when the electrochemical cell was positioned in the horizontal with the cold plate in the upper side and in the vertical position. All data confirms that a 0.4 M $[\text{Fe}(\text{CN})_6]^{4/3-}$ solution is better in this system that a 0.8 M one. Highest power density (22.0 W/m^2) was obtained in 0.4 M solutions of this redox couple with temperature difference at 137.5 K. At more concentrated solution, the processes of ionic-pair formation, or the precipitation of the salt on the low-temperature electrode can occur in the solutions.

Acknowledgment

One of us (RSG), acknowledges JICA (Japan International Cooperation Agency) for his fellowship, Universidade Federal de Santa Maria for a leave of absence and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico).

References

1. R. Haase, *Thermodynamic of Irreversible Processes*, Addison-Wesley (1962).
2. J. N. Agar, *Advances in Electrochemistry and Electrochemical Engineering*, ed. by P. Delahay, Wiley, Vol. 3, (1961).
3. T. Ikeshoji and F. N. B. de Nahui, *J. Electroanal. Chem.* **19**, 296 (1990).
4. T. Ikeshoji, *Bull. Chem. Soc. Jpn.* **60**, 1505(1987).