JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) · SHORT COMMUNICATION

SHORT COMMUNICATION

Thermogalvanic cells with aqueous redox couples and temperature differences larger than 100 K

T. IKESHOJI*

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

R. S. GONÇALVES

Departmento de Química, Universidade Federal de Santa Maria, Santa Maria, CEP 97119, Rio Grande do Sul, Brazil

Received 4 November 1991; revised 11 November 1992

1. Introduction

Thermogalvanic cells [1–3] may be used to generate electricity through direct conversion of thermal energy. Redox-type thermogalvanic cells with aqueous potassium ferrocyanide/potassium ferricyanide solution have been studied by many researchers [4–7]. The solution fills the space between two inert electrodes which are kept at different temperatures. Burrows [4] measured a power density (w) of about $0.9\,\mathrm{W\,m^{-2}}$ at a temperature difference (ΔT) of 50 K at steady state. Quickenden *et al.* [5] measured $w = 0.3\,\mathrm{W\,m^{-2}}$ at $\Delta T = 20\,\mathrm{K}$ during the initial stage immediately after loading the cell. In our laboratory, thin layer redox-type cells [6, 7] have been under research and development for several years. In two earlier papers, $w = 2.6\,\mathrm{W\,m^{-2}}$ at $\Delta T = 73\,\mathrm{K}$ [6] and $w = 3.2\,\mathrm{W\,m^{-2}}$ at $\Delta T = 50\,\mathrm{K}$ [7] were reported as steady-state power densities. The latter power density was obtained after optimizing values of the initial concentrations and cell positions [7]. In the work reported previously [4–7], temperature differences were less than 100 K, since aqueous electrolyte solutions were used in conditions open to the atmosphere [4, 5] or in cells with no antipressure mechanism [6, 7]. The purpose of the present work is to investigate the performance of the cells at temperatures above 373 K and subject to temperature differences larger than 100 K using a high pressure cell. The redox couples potassium ferrocyanide/potassium ferricyanide and ferrous chloride/ferric chloride were used. The former couple gives one of the highest thermoelectric powers except for some radio isotope species [8].

2. Experimental procedure

A schematic of the experimental cell is shown in Fig. 1. Two circular platinum electrodes (10 mm diameter and 1 mm thick) were mounted on two stainless steel support plates. The cell was operated at temperatures of up to 482 K (vapour pressure = 1.8 MPa). The electrodes were kept apart by a Teflon space (5 mm inner diameter and 1 mm thick). The space between the electrodes was filled with a 1 : 1 mixture of an aqueous solution of the redox couple. When an additional platinum electrode (0.5 mm thick) was placed between the original ones, the electrodes were separated by two Teflon spacers (0.5 mm thick). The temperature of the cold electrode was controlled by circulating water while the temperature of the hot electrode was regulated by an electric heater attached to its support plate. The temperature of each electrode was measured by thermocouples mounted near the electrodes. The temperature of the cold electrode (T_{low}) was 290 ± 10 K except for the cell with 0.8 M $[\mathrm{Fe(CN)_6}]^{4-/3-}$ solution, in which T_{low} was 323 K. Measurements were made for three cases; vertical electrodes, horizontal electrodes heated from below, and horizontal electrodes heated from above.

Aqueous solutions of potassium ferrocyanide and potassium ferricyanide of 0.40 + 0.40 mol (kg water)$^{-1}$ (0.4 M $[\mathrm{Fe(CN)_6}]^{4-/3-}$ solution) and 0.80 + 0.80 mol (kg water)$^{-1}$ (0.8 M $[\mathrm{Fe(CN)_6}]^{4-/3-}$ solution) were used. Solutions of ferric chloride and ferrous chloride of 0.82 + 0.82 M in 1 M hydrochloric acid (0.8 M $\mathrm{Fe^{2+/3+}}$ solution) and 1.6 + 1.6 M in 2 M hydrochloric acid (1.6 M $\mathrm{Fe^{2+/3+}}$ solution) were also used. With the exception of the 0.8 M $[\mathrm{Fe(CN)_6}]^{4-/3-}$ solution, which was prepared at about 320 K to avoid precipitation, all the solutions were prepared at room temperature.

3. Results and discussion

3.1. *Open circuit potential difference*

Figure 2 shows the measured values of open circuit potential difference ($\Delta\phi_{\mathrm{open}}$) at steady state against the imposed temperature difference (ΔT). For a 1 mm thick cell, it took about 10–20 min to reach steady state conditions [6, 9]. Measurements were carried out with the cell placed in three different positions. Only small differences were observed between the values of $\Delta\phi_{\mathrm{open}}$ in those positions. This indicates that the influence of natural convection on the measurements of $\Delta\phi_{\mathrm{open}}$ is negligible. The measured values of the thermoelectric power ($\varepsilon = \Delta\phi_{\mathrm{open}}/\Delta T$), for small ΔT, are given in Table 1.

In the experiments with the $[\mathrm{Fe(CN)_6}]^{4-/3-}$ redox couple, $|\Delta\phi_{\mathrm{open}}|$ increased monotonically from 0 V, under isothermal conditions, to 0.25 V for $\Delta T = 180\,\mathrm{K}$. This process was obviously irreversible, since when the same cell returned to isothermal conditions,

---

* To whom correspondence should be addressed at: National Institute for Advanced Interdisciplinary Research, Higashi 1-1-4, Tsukuba, Ibaraki 305, Japan.

0021-891X

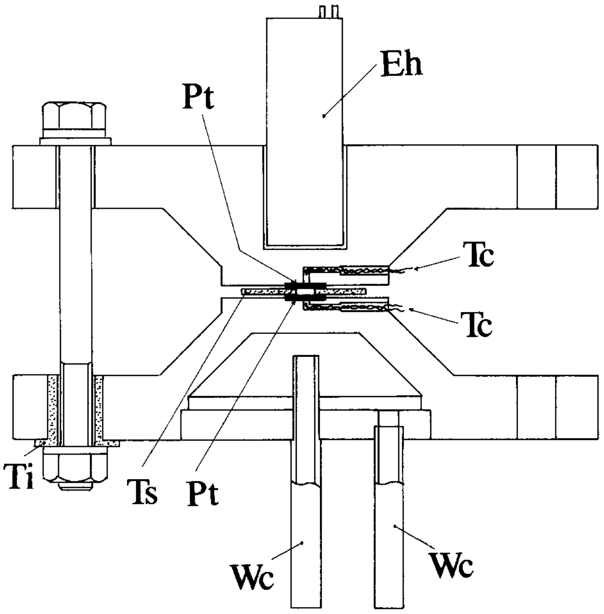

Fig. 1. Schematic illustration of the stainless steel cell. Eh, electric heater; Pt, platinum electrode; Tc, thermocouple; Ti, Teflon insulator; Ts, Teflon spacer; Wc, water circulation.

Table 1. Performance of thermogalvanic cells with redox couples

Redox couple	*Concentration /M*	*ε* /mV K⁻¹*	*w_{max}† /W m⁻²*	*ΔT /K*	
$[Fe(CN)_6]^{4-/3-}$	0.4	−1.18	3.4	138	△
		−1.24	20	137	▽
		−1.24	22	139	□
$Fe^{2+/3+}$	0.8	0.68	2.4	142	△
		0.68	6.6	142	▽
		0.67	7.9	142	□
$Fe^{2+/3+}$	1.6	0.49	1.5	133	△
		0.44	2.7	133	▽
		0.50	4.1	133	□
$Fe^{2+/3+}$	0.8	0.66	2.4	142	△‡
		0.65	2.6	142	▽‡
		0.66	4.5	150	□‡

* at small temperature difference.
† under steady state at temperature difference of ΔT
‡ with an inserted electrode.
(△) horizontal electrodes heated from above; (▽) horizontal electrodes heated from below; (□) vertical electrodes.

$\Delta\phi_{open}$ was not zero. This was probably due to decomposition of $[Fe(CN)_6]^{4-/3-}$ during the experiment [10].

In the cell with the $Fe^{2+/3+}$ redox couple, $\Delta\phi_{open}$ first increased with increasing ΔT up to a maximum value of 0.065 V for ΔT = 130 K, and decreased thereafter. This process proved to be reversible. It is possible to explain this nonlinear behaviour of $\Delta\phi_{open}$ in several ways. (i) Increasing ΔT may at some stage initiate a charge transfer reaction other than the $Fe^{2+/3+}$ redox

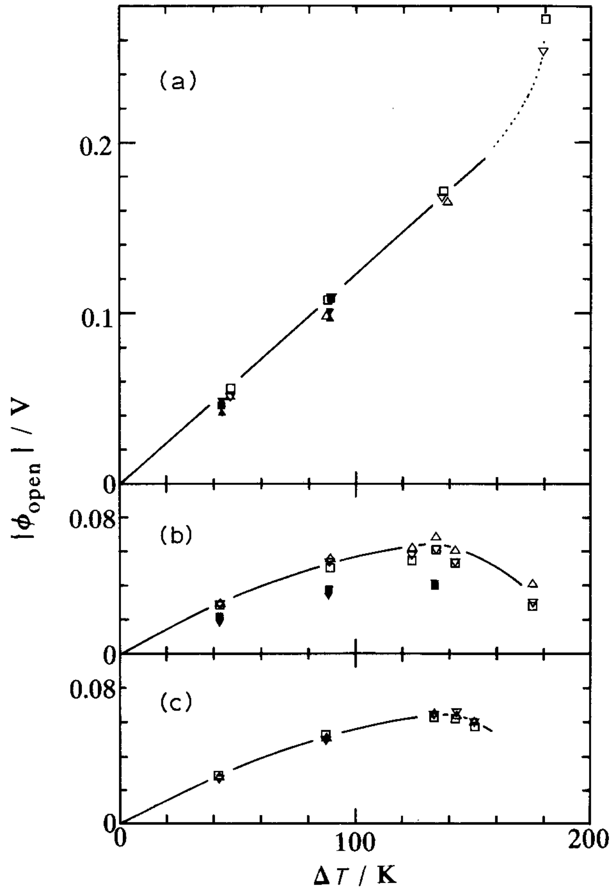

Fig. 2. Open circuit potential difference ($\Delta\phi_{open}$) as a function of temperature difference (ΔT). (a) Cells with $[Fe(CN)_6]^{4-/3-}$. Open symbols, 0.4 M (T_{low} = 290 ± 10 K); filled symbols, 0.8 M (T_{low} = 323 K). (b) Cells with $Fe^{2+/3+}$ solution (T_{low} = 290 ± 10 K). Open symbols, 0.8 M; filled symbols, 1.6 M. (c) cells with 0.8 M $Fe^{2+/3+}$ solution with an inserted electrode (T_{low} = 290 ± 10 K). (△) and (▲): horizontal electrodes heated from above; (▽) and (▼): horizontal electrodes heated from below; (□) and (■): vertical electrodes.

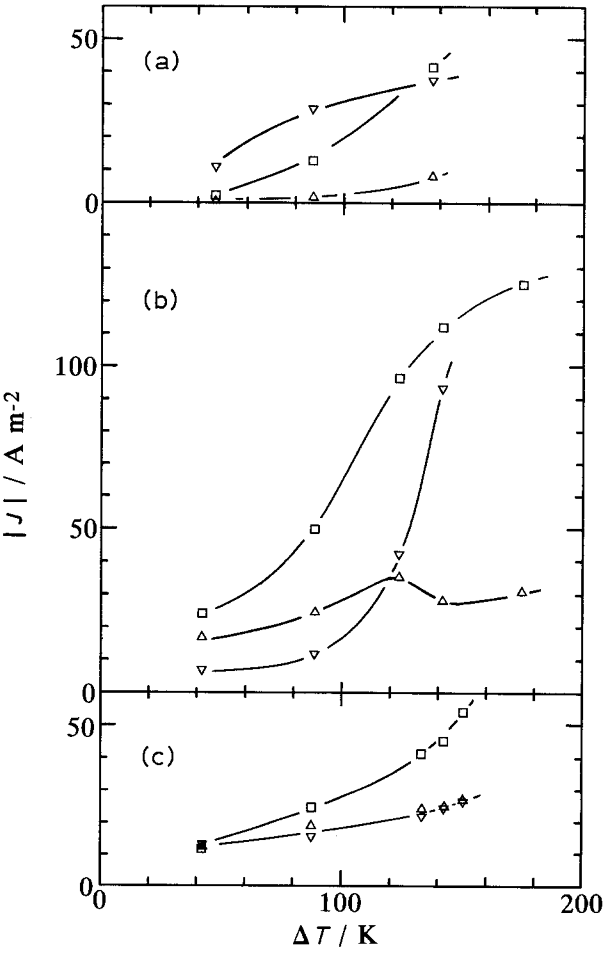

Fig. 3. Steady state current density (J) after applying $\Delta\phi_{open}$ − ($\Delta\phi_{open}/|\Delta\phi_{open}|$) × (10 mV) to the cells. (See also notes in Fig. 2).

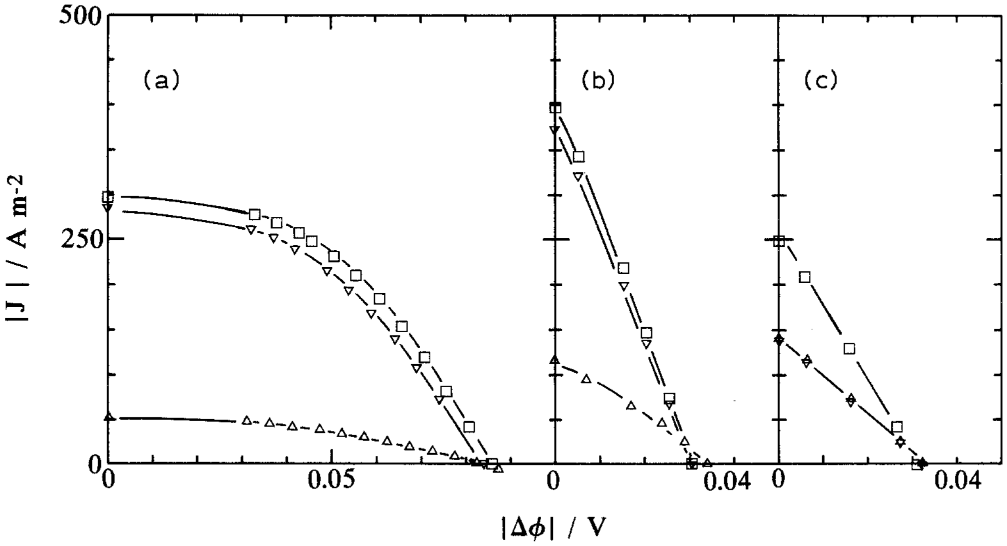

Fig. 4. Steady state current density (J) as a function of applied potential difference ($\Delta\phi$). (See also notes in Fig. 2.) (a) $\Delta T = 138\,K$; (b) $\Delta T = 134\,K$; (c) $\Delta T = 133\,K$.

reaction, or may change the complex form of Fe^{2+} or Fe^{3+}. Nonlinear behaviour due to the conformational change was observed and reported previously for the redox potential of cytochrome *c* [11]. (ii) Thermoelectric power is generally a linear function of the applied temperature difference, i.e. $\varepsilon = a + b\Delta T$, where a and b are constants. This would imply that $\Delta\phi_{open}$ is a parabolic function of the temperature difference and, for certain values of a and b, can have a maximum value within the domain of the applied values of ΔT [12].

The role of natural convection for the nonlinear behaviour of $\Delta\phi_{open}$ in the $Fe^{2+/3+}$ cell was investigated by inserting an additional electrode, which suppressed convection. The experimental results showed that the value of ΔT for which $\Delta\phi_{open}$ had a maximum was only slightly displaced ($\sim 20\,K$) compared to the cell with two electrodes, indicating that convection played only a minor role.

3.2. *Onset of convection*

In order to study the influence of natural convection on mass transfer, a potential difference of $\Delta\phi_{open} - (\Delta\phi_{open}/|\Delta\phi_{open}|) \times (10\,mV)$ was applied on the electrodes after the temperature difference had settled. The steady state current densities are plotted against ΔT in Fig. 3.

Experiments showed that, with the $[Fe(CN)_6]^{4-/3-}$ redox couple, convection occurs both when the cell is heated from below and when the cell is placed vertically. The current density measured for the latter case was larger than that for the former, Fig. 3(a).

With the $Fe^{2+/3+}$ redox couple, the current density for small values of ΔT was larger when the cell was heated from above than when heated from below, indicating that natural convection occurred in the former case, Fig. 3(b). This phenomenon, which does not take place in the purely thermal counterparts of this problem, can be attributed to Soret diffusion of species moving to hotter regions under the influence of a temperature gradient. For large values of ΔT ($> 120\,K$), the current density was larger for the cell heated from below than for the cell heated from above.

3.3. *E–I relations*

Due to concentration polarization, the electric current depended non-linearly on the applied potential for the three different cell placements, Fig. 4(a) and (b). The potential–current relationship, (*E–I*), became more linear after the insertion of an additional platinum electrode halfway between the first two, Fig. 4(c). The currents measured for the three-electrode cell were lower than those for the corresponding two-electrode cell. This is perhaps due to a reduction in convective transport.

3.4. *Electric power*

In previous work [6], the maximum power density (w_{max}) observed for a potential difference $\Delta\phi_{open}/2$ at ΔT was shown to exceed a simple prediction of $w_{max} \sim (\Delta T)^2$ with ε and electric conductivity (κ) constant. This was attributed to the increase in κ caused by a high average temperature in the cell. The increase in electric power in the present case was below that predicted by $w_{max} \sim (\Delta T)^2$. This is perhaps due to the non-linearity of the *E–I* relationship (Fig. 4) and, in the case of the $Fe^{2+/3+}$ redox couple, due to the decrease of ε with ΔT (Fig. 2(b) and (c)).

The vertically placed thermogalvanic cell, which contained 0.4 M $[Fe(CN)_6]^{4-/3-}$ solution, gave the largest electric power ($22\,W\,m^{-2}$) for $\Delta T = 139\,K$ (temperature of the hot electrode: 433 K), Table 1. This is seven times larger than the electric power generated in a similar cell [7] for $\Delta T = 50\,K$. For the $Fe^{2+/3+}$ solution, the electric power decreased for $\Delta T > 139\,K$ due to the large decrease in $|\Delta\phi_{open}|$. Solutions with high concentrations had lower power density for both the redox couples, probably due to the lower κ in the cell.

The low κ may arise from: (i) formation of ionic pairs which do not contribute to ionic conduction, and (ii) precipitation of salts on the low-temperature electrode due to saturation.

Acknowledgement

R.S.G. would like to acknowledge the Japan International Cooperation Agency (JICA) for his fellowship and the Santa Maria Federal University for authorizing his leave as well as recognizing the Conselho Nacional de Desenvolvimento Cientifico e Tecnologico (CNPq) for its support. The authors are indebted to Dr F. Alavyoon for reading the manuscript and providing discussion.

References

[1] J. N. Agar in P. Delahay (Ed.), 'Advances in Electrochemistry and Electrochemical Engineering', Vol. 3, J. Wiley & Sons, New York, (1961).

[2] R. Haase, 'Thermodynamics of Irreversible Processes', Addison-Wesley, (1962).

[3] S. K. Ratkje and T. Ikeshoji, *J. Electrochem. Soc.* **137** (1990) 2088.

[4] B. Burrows, *ibid.* **123** (1976) 154.

[5] T. I. Quickenden and C. F. Vernon, *Solar Energy* **36** (1986) 63.

[6] T. Ikeshoji, *Bull. Chem. Soc. Jpn.* **60** (1987) 1505.

[7] T. Ikeshoji, F. N. B. Nahui, S. Kimura and M. Yoneya, *J. Electroanal. Chem.* **312** (1991) 43.

[8] P. Blank and C. Madic, *Inorg. Chim. Acta* **95** (1984) 141.

[9] T. Ikeshoji, S. Kimura, F. N. B. Nahui and M. Yoneya, *J. Electroanal. Chem.* **307** (1991) 29.

[10] R. E. Kirk and D. F. Othmer (Ed.), 'Encyclopedia of Chemical Technology', Vol. 4, Interscience Encyclopedia and Maruzen, Tokyo (1949) p. 726 and p. 730.

[11] T. Ikeshoji, I. Taniguchi and F. M. Hawkledge, *J. Electroanal. Chem.* **270** (1989) 197.

[12] D. D. Macdonald, A. C. Scott and P. Wentrecek, *J. Electrochem.* **126** (1979) 1618.