

Influence of electrode materials on open-circuit voltage profiles with a temperature difference for a thermocell using a Br_2/Br^- -redox reaction

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Abstract

We investigated the dependence of open-circuit voltage (OCV) on temperature difference, δT , between hot and cold electrodes for a Br_2/Br^- -redox thermocell with carbon materials having a large specific surface area (Maxsorb) as electrodes and 3.36 M KBr aqueous electrolyte containing Br_2 and compared it with that for thermocells with Pt electrodes. The rate of change in OCV with δT largely changed at a certain value of δT (critical δT). We assumed that the OCV change with δT can be expressed by quadratic or linear equations of δT differently in the regions above and below critical δT . The influence of Br_2 concentration on thermoelectric power $|dE/dT|$ was smaller for Maxsorb electrode cells than for Pt electrode cells, and the $|dE/dT|$ for Maxsorb electrodes was smaller than that for Pt electrodes above the critical δT . This may be related to differences in the amount of Br_2 adsorption at the reaction sites on the electrode surface. We found hysteresis in the OCV change with δT for both electrode systems when δT was increased and decreased. The hysteresis appears to depend on cell configuration. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Temperature difference; Thermocell; Br_2/Br^- -redox reaction; Thermoelectric power; Open-circuit voltage; Hysteresis

1. Introduction

Environmental protection and effective use of energy resources are recognized globally as important issues. New energy systems that use natural energy resources like water, wind, solar, and geothermal power and hydrogen have been spreading or are being investigated extensively.

On the other hand, heat is often produced as residual energy in human activities and the amount is increasing year by year. Most of this heat is $<100^\circ\text{C}$ and is usually allowed to dissipate in the atmosphere. From the viewpoint of the effective use of energy, decreasing such wasted heat is important. The ultimate solution though would be to develop a way to reuse it. Galvanic thermocells are attractive as thermoenergy conversion systems because they would make it possible to transform useless thermal energy into useful energy directly.

We have investigated a thermocell that uses a Br_2/Br^- -redox reaction, and showed that electrodes made from a non-graphitized carbon (Maxsorb) sheet with a specific surface area of $1000\text{ m}^2/\text{g}$ or larger and a KBr electrolyte saturated

with Br_2 improved the characteristics of the thermocells [1]. In particular, the $|dE/dT|$ when the temperature difference δT between the hot and cold electrodes exceeded 40°C was $5.68\text{ mV}/^\circ\text{C}$, which is 2.5 times greater than that reported by Endo et al. [2]. However, the δT dependence of the open-circuit voltage (OCV) was not linear; the OCV changed very little when δT was below 40°C and sharply increased when it was about 40°C . In order to accomplish high power density and stable performance at temperatures $<100^\circ\text{C}$ for thermocells, the characteristic δT dependence of OCV should be investigated by increasing or decreasing δT for them.

We have investigated the characteristic δT dependence of OCV by increasing or decreasing δT for Maxsorb-electrode thermocells to clarify the influence of electrode materials on the characteristics of the thermocells. This paper shows how the electrode materials influence the change in $|dE/dT|$ at a critical δT and reports hysteresis in the OCV change with δT .

2. Experimental

2.1. Electrodes and electrolytes

Electrodes were prepared from a 1.5-mm-thick Maxsorb sheet with a specific surface area of $2480\text{ m}^2/\text{g}$ (The Kansai

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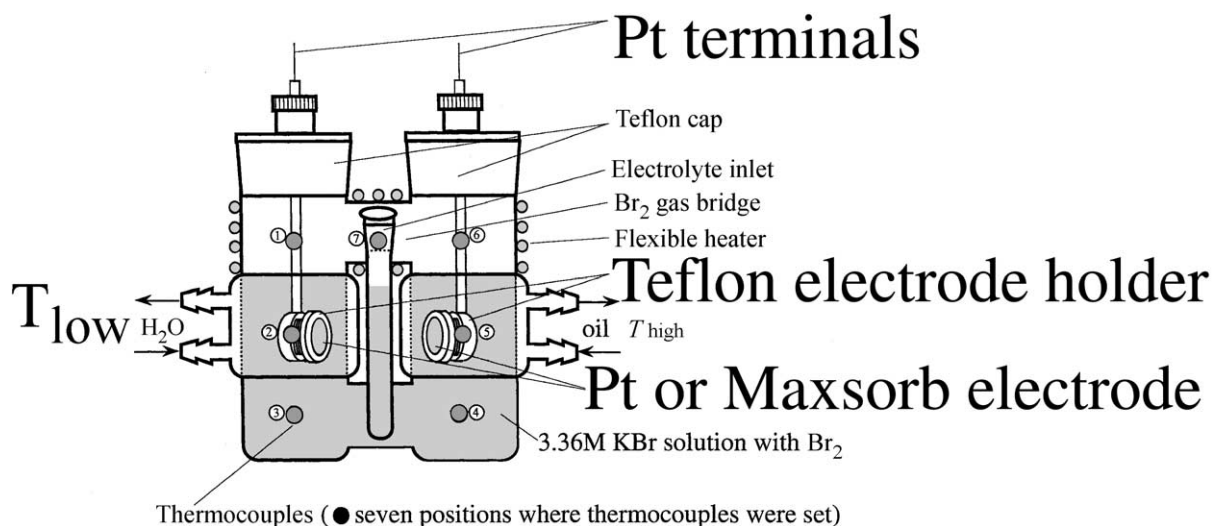


Fig. 1. Schematic diagram of the experimental cell.

Coke and Chemical Co.) and a 99.9% grade and a 0.1-mm-thick Pt sheet (Furuuchi Chemical Co.). The sheets were cut into 15-mm-diameter discs and the discs set in Teflon holders. The nominal area of the electrodes was 1.13 cm².

Solutions of 3.36 M KBr (Kishida Chemical Co.) containing 1 and 2 wt.% Br₂ or saturated with Br₂ (Wako Pure Chemical Industries Co.) were used as electrolytes.

2.2. Test cell configuration

A schematic diagram of the experimental cell is shown in Fig. 1. Temperatures of hot and cold electrodes were controlled by circulating silicon oil and water from thermostat baths. The gas bridge was kept at 80 °C by covering it with a heater jacket, so that the gaseous Br₂ would effectively be transferred through it. The temperature distribution in the experimental cell was monitored by thermocouples set at seven positions outside the cell (the thermocouples were set outside the cell because Br₂ would corrode them). The positions are indicated in the figure.

2.3. Electrochemical measurements

Electrochemical characteristics of the thermocells were measured by using charge and discharge control units (HJ-201B, Hokuto Denko Co.). In the measurements, the cold electrode was kept at 10 °C and the temperature of the hot electrode was changed in steps of 5 °C between 20 and 80 °C. The value of the OCV was recorded when the change in it became within ±0.1 mV/h.

3. Results and discussion

3.1. Dependence of OCV on temperature difference

Fig. 2(a) and (b) shows the δT dependence of OCV for cells with Pt electrodes and 3.36 M KBr containing 1 wt.%

Br₂ or saturated with Br₂. In the measurements, the temperature of the hot electrode was initially increased from room temperature to 80 °C and then decreased to 20 °C.

For the cells with the electrolyte saturated with Br₂ (Fig. 2b), OCV changed <0.5 mV/°C when δT was increased. On the other hand, OCV sharply increased at δT above 50 °C, reaching 204.9 mV at 55.8 °C. When δT was decreased, a

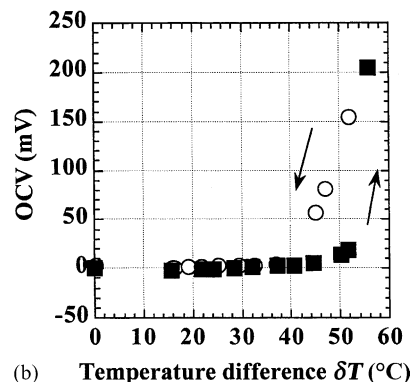
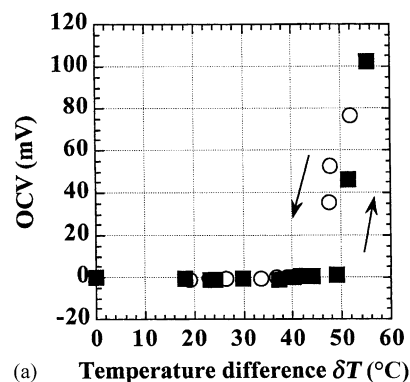


Fig. 2. Dependence of OCV on the temperature difference δT for Pt electrodes in 3.36 M KBr electrolyte (a) with 1 wt.% Br₂ and (b) saturated with Br₂: (■) OCV in the process for increasing δT ; (○) OCV in the process for decreasing δT .

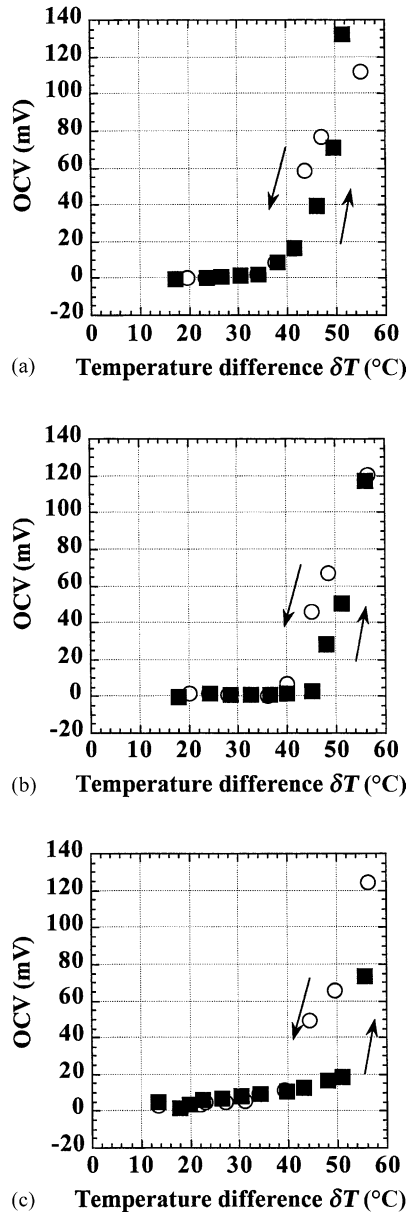


Fig. 3. Dependence of OCV on the temperature difference ΔT for Maxsorb electrodes in 3.36 M KBr electrolyte (a) with 1 wt.% Br_2 , (b) with 2 wt.% Br_2 , and (c) saturated with Br_2 : (■) OCV in the process for increasing ΔT ; (○) OCV in the process for decreasing ΔT .

region of large-OCV change and one of small-OCV change was also found. However, the rate of OCV change in the region of large-OCV change was smaller than that when ΔT was increased.

The OCV profiles for the electrolyte containing 1 wt.% Br_2 (Fig. 2(a)) are similar to those for Br_2 -saturated electrolyte. However, the critical point between large- and small-OCV-change regions is a little bit lower than that for the electrolyte saturated with Br_2 .

The OCV profiles for cells with Maxsorb electrodes and 3.36 M KBr containing 1 and 2 wt.% Br_2 or saturated with Br_2 are shown in Figs. 3(a)–(c). In these cases, the temperature of the hot electrode was set at 80 $^{\circ}\text{C}$, initially

Table 1

Critical ΔT where the rate of OCV changes with change in ΔT

Electrodes	Br_2 concentration	ΔT	Critical ΔT ($^{\circ}\text{C}$)
Pt	1 wt.%	Increasing	48.8
		Decreasing	39.7
	Saturated	Increasing	50.6
		Decreasing	41.2
Maxsorb	1 wt.%	Increasing	34.6
		Decreasing	34.4
	2 wt.%	Increasing	45.1
		Decreasing	38.7
	Saturated	Increasing	50.6
		Decreasing	38.6

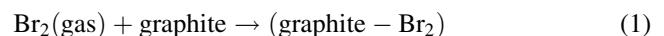
decreased to 20 $^{\circ}\text{C}$, and then increased to 80 $^{\circ}\text{C}$; the procedure was opposite than that for Pt electrodes. Again, we found the regions of large- and small-OCV changes with ΔT ; the same tendency was observed for Pt electrodes. However, the OCV change rate was smaller than for Pt electrodes in the large-OCV change region.

We estimated the critical ΔT between large- and small-OCV-change regions by obtaining the intersection points of the linear plots from the data for both regions by the least-squares method. Table 1 shows the critical ΔT for both electrodes. The critical ΔT was influenced by both types of electrode and the Br_2 concentration. It increased with increasing Br_2 concentration for both. It depended on Br_2 concentration for Maxsorb electrodes more strongly than for Pt electrodes. The difference in the critical ΔT for increasing and decreasing ΔT was smaller for Maxsorb electrodes than for Pt electrodes for the electrolyte containing 1 wt.% Br_2 . On the other hand, it was larger for Maxsorb electrodes than for Pt electrodes for the electrolyte saturated with Br_2 .

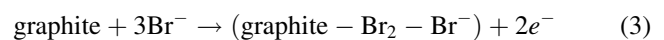
3.2. Thermoelectric power

Thermoelectric power $|dE/dT|$ is one of the most important factors for galvanic thermocells. It mainly controls the OCV of the cells and characterizes its ΔT dependence. The value of $|dE/dT|$ is usually estimated by differentiating between OCV and ΔT . However, it is not easy to characterize the $|dE/dT|$ for Br_2/Br^- -redox thermocells because the behavior of Br_2 and Br^- is complicated in the electrolyte [3–5]. Lalancette and Roussel [6] proposed the following thermocell reaction mechanism.

On a low-temperature electrode (cathode):



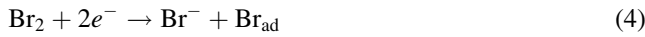
On a high-temperature electrode (anode):



These reactions are based on the intercalation and deintercalation of bromine into the graphite. On the other hand, Janssen and Hoogland [7] proposed a Br_2/Br^- -redox

reaction mechanism based on the adsorption and desorption of bromine on the surface of the graphite [8].

Cathodic reaction:



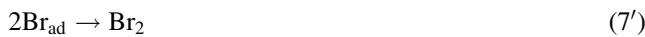
or



Anodic reaction:



or



Both reaction mechanisms are related to interactions between bromine and graphite, though the interactions are different. And, the reaction processes based on adsorption and desorption may essentially be the same for Maxsorb and Pt electrodes as for graphite.

From these viewpoints, bromine adsorption at reaction sites on the electrodes may affect $|dE/dT|$, which would mean that the type of electrode material can affect the $|dE/dT|$. This may be related to the difference in the OCV change with δT between Maxsorb and Pt electrodes. Maxsorb has a larger specific surface area than Pt and a surface condition different from Pt. This may be the reason for the weaker δT dependence of OCV for Maxsorb electrodes.

As shown in Fig. 4, the solubility of Br_2 in H_2O tends to first decrease gradually then increase slightly as temperature increases from 5.84 to 54.3 °C (boiling point of Br_2), and finally largely decrease above the boiling point [5]. This suggests that the solubility of Br_2 in the electrolyte can affect the δT dependence of OCV because the critical δT is very close to the boiling point. In order to estimate the δT

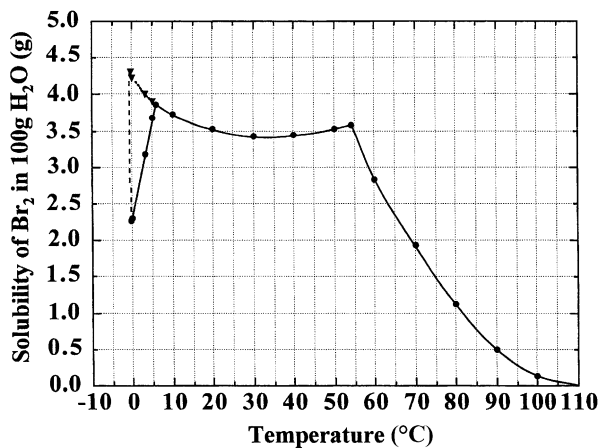


Fig. 4. Change in the solubility of bromine with temperature in aqueous solution [5].

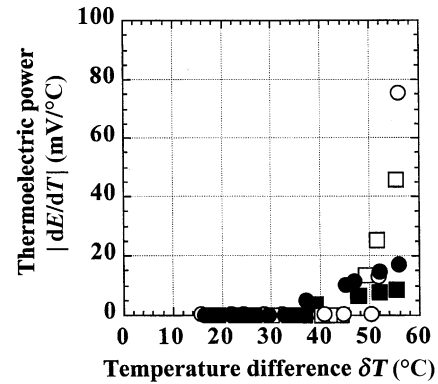


Fig. 5. Dependence of thermoelectric power $|dE/dT|$ on δT for Pt electrodes in 3.36 M KBr electrolyte with 1 wt.% Br_2 , (■) in the process for decreasing δT ; (□) in the process for increasing δT ; and saturated with Br_2 , (●) in the process for decreasing δT , (○) in the process for increasing δT .

dependence of $|dE/dT|$, we assumed OCV changed with δT as follows: we extrapolated the quadratic and linear equations to the δT dependence of OCV in the regions above and below critical δT and differentiated the equations to estimate the $|dE/dT|$. Therefore, the $|dE/dT|$ can be assumed to depend linearly on δT or be constant. The results are as shown in Fig. 5 for Pt electrodes and Fig. 6 for Maxsorb electrodes. The δT dependence of $|dE/dT|$ for Maxsorb electrodes is less influenced by Br_2 concentration than that for Pt electrodes. And the difference in $|dE/dT|$ between the δT -increasing and the δT -decreasing process for Maxsorb electrodes is smaller than that for Pt electrodes. Thermoelectric power $|dE/dT|$ in the region above critical δT for Pt electrode is larger than that for Maxsorb electrodes.

Our results on OCV change with δT show a large change in OCV at critical δT . This is different from Endo et al. [2] and Lalancette and Roussel [6], who found an almost linear change in OCV with δT . They used thermocells comprised of glass tubes filled with 1.0 g of graphite fibers

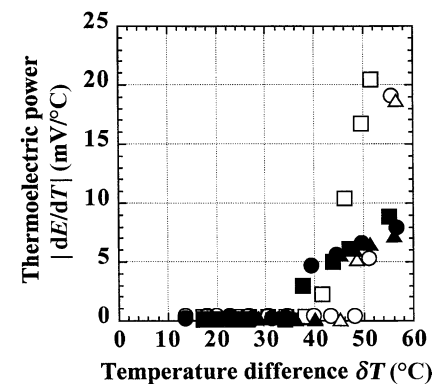


Fig. 6. Dependence of thermoelectric power $|dE/dT|$ on δT for Maxsorb electrodes in 3.36 M KBr electrolyte with 1 wt.% Br_2 , (■) in the process for decreasing δT , (□) in the process for increasing δT ; and 2 wt.% Br_2 , (▲) in the process for decreasing δT , (△) in the process for increasing δT ; and saturated with Br_2 , (●) in the process for decreasing δT , (○) in the process for increasing δT .

or powder-bromine intercalation compounds (Br-GIC) as electrode materials to estimate the δT dependence of OCV. Their Br-GIC electrodes contained Br_2 and possibly adsorbed Br^- , the anode reaction, (6), (7) or (7'), occurs mostly independent of the bromine concentration in the bulk of electrolyte, and the OCV linearly depended mainly on temperature difference δT . On the other hand, our cells had a Br_2 -free non-graphitized carbon (Maxsorb) sheet or a Pt plate as the electrode. Although Maxsorb has a specific surface area of $1000 \text{ m}^2/\text{g}$ or larger, which is larger than that of the Br-GIC, they used in their cells, it may have adsorbed and fixed Br_2 very weakly compared with their Br-GIC. The difference of electrode constitution suggests that our cells showed non-linear and specific OCV change with δT .

It is well known that two factors control thermoelectric powers of thermocells [9]. One is the initial thermoelectric power, which is defined under the condition of uniform concentration in the thermocell, i.e. just after the temperature is changed. The other is steady thermoelectric power, which is caused by Soret diffusion [10,11], and defined at a steady state with no convection, i.e. at time = ∞ . The rate of Soret diffusion can be evaluated by a characteristic time, τ , calculated as follows:

$$\tau = \frac{d^2}{\pi^2 D} \quad (8)$$

where d is the distance between electrodes, and D the diffusion coefficient of the species in the thermocell [9]. In our case, we estimated τ is more than 135 h from $D_{\text{Br}^-} = 2.08 \times 10^{-9} \text{ m}^2/\text{s}$ (25°C) and $d = 10 \text{ cm}$; that is, it takes a long time for our cells to reach a steady state. The values of $|dE/dT|$ for Maxsorb electrodes in the present measurements are different from those in our previous paper [1]. In particular, the difference between the previous and the present $|dE/dT|$'s for Maxsorb electrodes at δT below 40°C was large. This is because the measured OCV became stable within $\pm 0.1 \text{ mV/h}$, whereas, the OCV was recorded at 10 h intervals in the previous study [1].

3.3. Hysteresis of OCV

Our thermocells showed hysteresis in the OCV change as a result of increasing and decreasing δT . Such hysteresis has not been reported. We, therefore, address this point.

We set additional thermocouples at five positions, 1, 3, 4, 6 and 7, in cells as shown in Fig. 1, and the temperatures at these points were measured during the process for increasing and decreasing in the temperature at position 5 (on the hot electrode). The results are as shown in Figs. 7 and 8 for Pt and Maxsorb electrodes, respectively. Both the figures show that hysteresis appeared in the temperatures at positions beneath the hot and the cold electrodes. The temperature range of the hysteresis was about $15\text{--}30^\circ\text{C}$ in the δT range from 40 to 56°C . The area of the hysteresis for Maxsorb cells tended to be larger than that for Pt cells. We doubt that this hysteresis in the temperature is the major reason for the

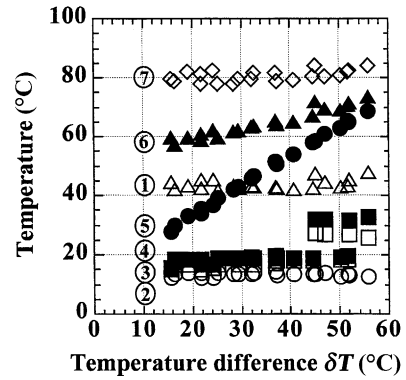


Fig. 7. Temperature difference δT dependence of the temperature at each position of the experimental cell for Pt electrodes in 3.36 M KBr saturated with Br_2 : (Δ) above cold electrode (at position ①); (\circ) on cold electrode (at position ②); (\square) below cold electrode (at position ③); (\blacksquare) below hot electrode (at position ④); (\bullet) on hot electrode (at position ⑤); (\blacktriangle) above hot electrode (at position ⑥); (\diamond) on the gas bridge (at position ⑦).

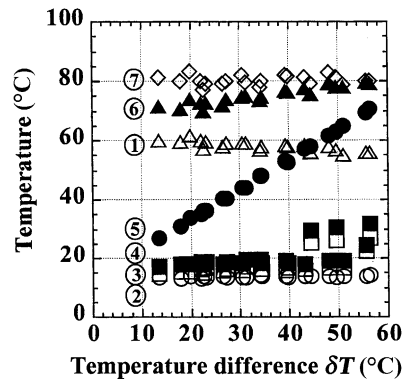


Fig. 8. Temperature difference δT dependence of temperature at each position of the experimental cell for Maxsorb electrodes in 3.36 M KBr saturated with Br_2 : (Δ) above cold electrode (at position ①); (\circ) on cold electrode (at position ②); (\square) below cold electrode (at position ③); (\blacksquare) below hot electrode (at position ④); (\bullet) on hot electrode (at position ⑤); (\blacktriangle) above hot electrode (at position ⑥); (\diamond) on the gas bridge (at position ⑦).

hysteresis in the OCV change with δT . If it is the reason though, an improvement of the thermocell configuration may be able to inhibit or prevent it. The hysteresis in the OCV change should depend on the cell configuration.

4. Conclusions

We investigated the dependence of the OCV on the temperature difference δT between the hot and cold electrodes for a Br_2/Br^- -redox thermocell with Maxsorb electrodes and Br_2 -dissolved 3.36 M KBr aqueous electrolyte and compared it with that for a thermocell with Pt electrodes. The OCV did not change linearly with δT , but the rate of OCV change with δT largely changed at a certain δT value (critical δT) for both cell systems. The change point is related to the boiling point of Br_2 ; the temperature of the hot electrode was close to it. We assumed that OCV change with δT can be expressed as quadratic or linear equations of

δT differently in the regions above and below critical δT ; that is, thermoelectric power $|dE/dT|$ linearly depends on δT or is constant. Maxsorb electrode cells showed less influence of Br_2 concentration on thermoelectric power $|dE/dT|$ than Pt electrode cells, and the $|dE/dT|$ for Maxsorb electrodes was smaller than that for Pt electrodes in the range of δT above critical δT . This may be related to differences in the amount of Br_2 adsorption at reaction sites on the electrode surface. Hysteresis appeared in the OCV change with δT for both electrodes when δT was increased and decreased. The hysteresis was larger for Maxsorb electrodes than for Pt electrodes. The hysteresis in temperatures at positions beneath the hot and cold electrodes suggests that the hysteresis in the OCV change depends on the cell configuration.

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