

Effect of non-graphitized carbon electrodes on the electrochemical characteristics of a thermocell with a Br_2/Br^- redox couple

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Received 5 May 1997; accepted 9 June 1997

Abstract

Electrodes made from a non-graphitized carbon (Maxsorb) sheet with a large specific surface area greatly improved the electrochemical characteristics of thermocells with a bromine/bromide-ion redox couple and a KBr aqueous electrolyte saturated with Br_2 . The Maxsorb electrodes provide a higher open-circuit voltage than graphite (Perma Foil) electrodes and the maximum discharge current density is 2.4 mA/cm^2 until the voltage reaches 0 V. The Maxsorb electrodes generate $5.68 \text{ mV/}^\circ\text{C}$ of thermoelectric power at a temperature difference greater than 40°C , which is 2.5 times the power reported previously. The Maxsorb electrodes also improve the cathodic polarization in the presence of a gas–liquid–solid interface in Br_2 -free electrolyte, while the graphite electrodes do not. Nevertheless, this improvement is insufficient to observe when the KBr electrolyte is saturated with Br_2 . An experimental cell with Maxsorb electrodes maintains a stable voltage up to 2.0 mA/cm^2 for over 450 h, even though the cell configuration has still to be optimized. © 1998 Elsevier Science S.A.

Keywords: Thermocell; Bromine/Bromide ion redox couple; Non-graphitized carbon; Saturation; Thermoelectric power; Gas–liquid–solid interface

1. Introduction

The effective use of energy resources continues to be an important issue, particularly to reduce the consumption of limited fossil fuels and to prevent the destruction of the global environment. In this respect, much effort has been focused on transforming thermal energy into other kinds of useful energy. This is because thermal energy is generally the final product of energy conversion and, most often, is wasted.

Thermoelectric generators with thermoelectric semiconductors, that are referred to as thermoenergy conversion systems, generally operate in the temperature range 200 to 600°C [1]. Unfortunately, however, most of the heat produced as residual energy in many human activities is below 100°C and is thus considered relatively useless. Therefore, this heat is usually allowed to escape into the atmosphere.

Galvanic thermocells with aqueous electrolytes are promising thermoenergy conversion systems because they can directly transform useless thermal energy (less than 100°C) into electrical energy [2]. Many cell systems have been proposed with different types of redox couples, namely Cu^{2+}/Cu [3], Zn^{2+}/Zn [3], and $\text{Fe}^{3+}/\text{Fe}^{2+}$ [4]. In particular, thermocells with a ferro-/ferricyanide ion ($[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$) redox couple have been investigated intensively [5–8] because of their relatively high thermoelectric power ($-1.4 \text{ mV/}^\circ\text{C}$) [8]. A thermochargeable cell has also been proposed that uses a $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ -redox couple [9,10].

These thermocells, however, have a very low voltage: their open-circuit voltage (OCV) is only 100 mV or less at a temperature difference of 30 to 40°C . This means that many cells need to be connected in series in order to obtain an OCV that is sufficiently high to be of practical use. To overcome this limitation, a redox couple with thermoelectric power higher than that of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ -redox couple is required.

Thermocells with a bromine/bromide ion (Br_2/Br^-) redox couple that have a thermoelectric power of $2.3 \text{ mV/}^\circ\text{C}$ have been reported [11]. In this cell system, the

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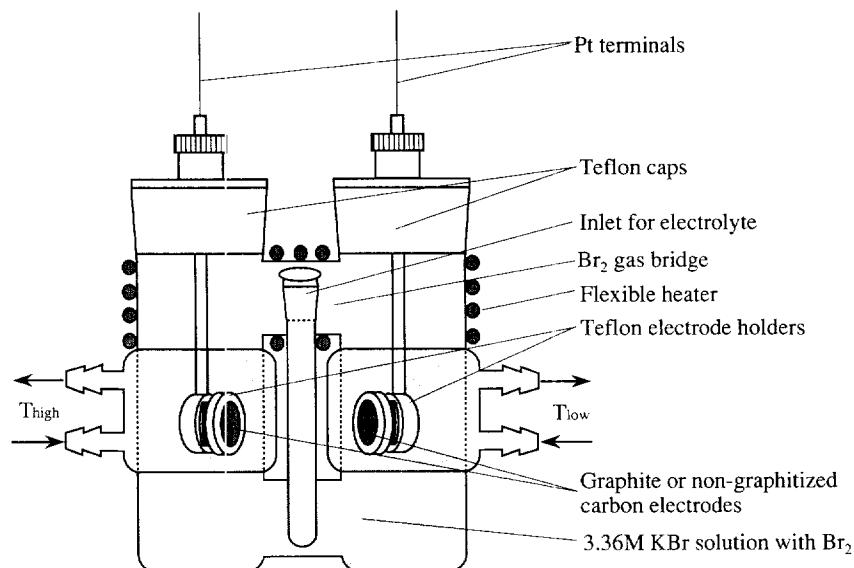


Fig. 1. Schematic diagram of experimental cell.

oxidation of the Br^- to Br_2 occurs on the hot electrode, and the reduction of the Br_2 to Br^- occurs on the cold one [12]. The power might be improved further by using suitable electrode materials and by optimizing the cell configuration [13]. The employment of bromine–graphite–intercalation compounds (Br–GIC) has been proposed, but so far the performance has only been measured experimentally using glass cells with electrodes prepared by stacking the powder or the fiber. The performance with sheet electrodes still has to be investigated.

The study presented here examines the use of both graphite and non-graphitized carbon sheets as electrodes in galvanic thermocells in order to develop a practical cell system. In particular, an evaluation is made of the effect of these materials on the thermocell characteristics, viz., the

thermoelectric power, the voltage dependence on the discharge rate, the voltage stability.

2. Experimental

2.1. Electrode materials

Graphite electrodes were prepared from a 0.76 mm-thick Perma Foil sheet (Toyo Tanso) that was free from binder. A brominated electrode was also fabricated by immersing the graphite in liquid Br_2 for 24 h at room temperature. The excess Br_2 in the electrode was evaporated under a vacuum of about 0.133 Pa for 3 h. The brominated graphite was estimated to form C_{70}Br based on the increase in

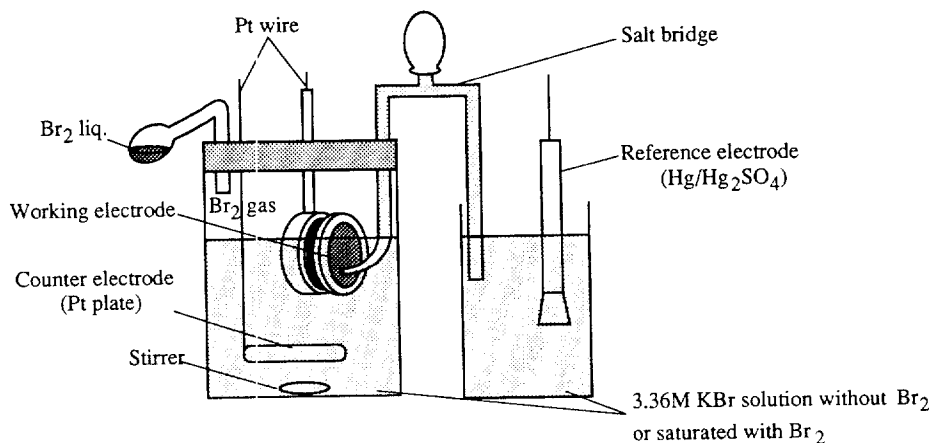


Fig. 2. Schematic diagram of measurement system.

weight, although significant structure differences were not observed from XRD analysis

Non-graphitized-carbon electrodes, which had a large surface area, were prepared from a 1.5 mm-thick Maxsorb sheet (The Kansai Coke and Chemical).

A platinum electrode was prepared from a Pt sheet of thickness 0.1 mm.

All the electrodes were disc with a 15 mm diameter, and were set in teflon holders. The apparent electrode area was 1.13 cm².

2.2. Electrolyte

Cell performance was evaluated by using an electrolyte solution of 3.36 M KBr saturated with Br₂. An investigation was made of the effect of the electrolyte on the electrochemical characteristics for solutions containing 1, 2, and 3 wt.% Br₂, or saturated with Br₂.

2.3. Cell configuration

A schematic diagram of the experimental cell is shown in Fig. 1. The temperature between the hot and cold electrodes was controlled by circulating silicon oil and water from thermostat baths. The gas bridge was kept at a constant temperature of 80°C by covering it with a heater jacket.

A schematic diagram of the measurement system used to evaluate the effect of a gas–liquid–solid (GLS) interface on cell performance is shown in Fig. 2. The Br₂ gas was vaporized from liquid Br₂ and stored in a pot. The working electrode was either fully dipped into the electrolyte or dipped only 80% (partially dipped) to produce a GLS interface.

2.4. Electrochemical measurement

The polarization of the electrodes and the electrochemical characteristics of the thermocells were measured for both systems by using a galvanostat and a potentiometer (HJ-201B and HA-501, respectively, Hokuto Denko). An Hg/Hg₂SO₄ electrode was used as a reference electrode. The polarization was measured galvanostatically by increasing the current density stepwise.

2.5. Electrode wettability estimation

The contact angle of the 3.36 M KBr solution was determined for the three samples (Pt, Perma Foil, and Maxsorb) with a contact-angle meter (FACE CA-A, Kyowa Interface Science). Each sample was measured three times and the results were averaged.

3. Results and discussion

3.1. Dependence of OCV on temperature difference

An important factor in thermocell performance is obtaining a high OCV for a given thermal condition. Therefore, the thermoelectric power ($|dE/dT|$) has been intensively investigated [5,10,14,15] because it controls the OCV.

The dependence of OCV on the temperature difference (δT) for the cells with Maxsorb and Perma Foil electrodes is shown in Fig. 3. The temperature at the hot electrode was decreased in steps of about 10°C from 70 to 30°C, and the temperature at the cold electrode was kept constant at 10°C.

The OCV dependence on the temperature difference was about the same, and roughly parabolic, for both types of electrodes, although the OCV for the Perma Foil electrode was slightly lower than that for the Maxsorb electrode at each temperature difference. These changes in the OCV differ from the linear relationship reported by Endo et al. [11]. The reason for this difference is not clear at the present time. It may be related either to the electrode materials or to the cell configuration, especially the distance between the hot and cold electrodes, as postulated by Endo et al. [13]. This behavior is being investigated further.

The values of $|dE/dT|$ in the δT ranges below and above 40°C were calculated by assuming that $|dE/dT|$ depends linearly on δT . The approximate value of $|dE/dT|$ at temperature differences above 40°C was 5.68 mV/°C, which is about 2.5 times larger than that reported by Endo et al. [11].

3.2. Comparison of current–voltage characteristics between graphite and non-graphitized carbon electrodes

The current–voltage (i – V) characteristics for the Maxsorb and Perma Foil electrodes are shown in Fig. 4. The

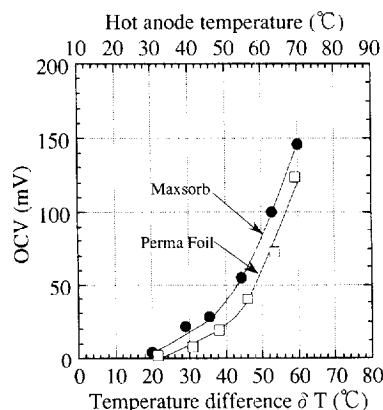


Fig. 3. Dependence of OCV on temperature difference for cells with Maxsorb and Perma Foil electrodes and an electrolyte solution of 3.36 M KBr with Br₂.

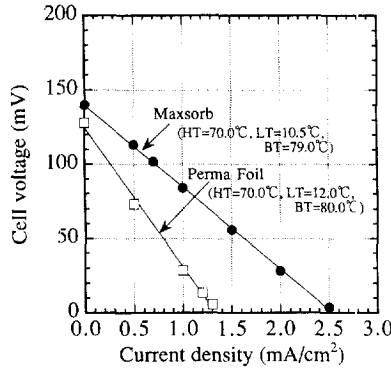


Fig. 4. Cell voltage as a function of current density for cells with Maxsorb and Perma Foil electrodes and an electrolyte solution of 3.36 M KBr with Br₂ (HT: hot electrode temperature; LT: cold electrode temperature; BT: gas bridge temperature).

Maxsorb electrodes display a higher OCV and a higher limiting current density than the Perma Foil electrodes. The term ‘limiting current density’ refers to the maximum current density that is drawn until the voltage reaches 0 V. The limiting current density of 2.4 mA/cm² for the Maxsorb electrodes is 1.7 times higher than that for the Perma Foil counterparts. The current density corresponds to 37.7 mA/g, which is about four times higher than that previously reported [11], viz., 10 mA/g. Both cell systems exhibit linear dependence of the OCV on the current density. This ohmic dependence is in line with that reported for other redox couples [16].

The polarization of the electrodes was measured in order to determine the effect of the electrode materials on the cell characteristics. The anodic polarization was determined at 90°C, and the cathodic polarization at 25°C. The polarization of brominated Perma Foil (Br-GIC) was undertaken to evaluate the effect of bromination. As shown in Fig. 5(a) and (b), there is almost no difference in either the open-circuit potential (OCP) or the anodic polarization of the three electrodes. There is, however, a clear difference in the cathodic polarization between the Maxsorb and the other two electrodes: the Maxsorb electrode experiences a smaller polarization.

Brominated electrodes have been reported to show excellent electrochemical characteristics [11,13]. Nevertheless, bromination did not improve the electrochemical characteristics in this work, possibly because the bromination was insufficient to enhance the activity of the electrochemical reaction.

3.3. Effect of Br₂ concentration on electrochemical characteristics

The effect of the Br₂ concentration in the electrolyte on the *i*-*V* characteristics and on the value of $|dE/dT|$ was evaluated. As shown in Fig. 4, the cell voltage depends linearly on the current density. Therefore, the thermoelec-

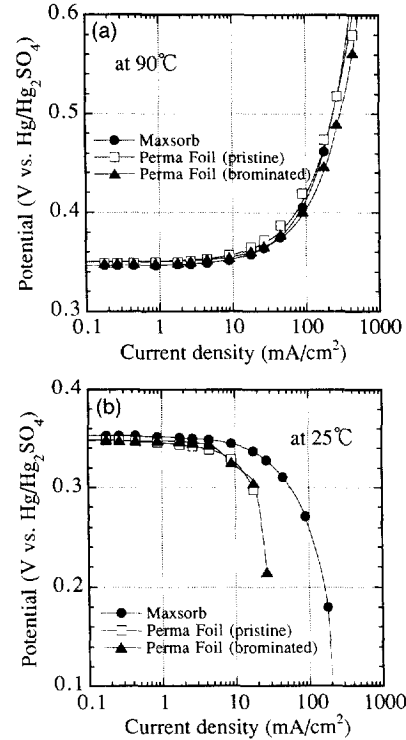


Fig. 5. Polarization curves for three types of electrodes in 3.36 M KBr solution saturated with Br₂: (a) anodic polarization at 90°C; (b) cathodic polarization at 25°C.

tric power $|dE/dT|$ can be evaluated as two values in the δT ranges below and above 40°C by assuming that it depends linearly on δT .

The *i*-*V* characteristics are estimated from the slope dV/di in the relationship with the Br₂ concentration. The results are shown in Fig. 6, along with the limiting current density *i*_{max}. The negative value of dV/di decreases and the limiting current density increases with increase in the Br₂ concentration. Compared with the Perma Foil electrode, the Maxsorb electrode displays a smaller rate of change in dV/di and a larger *i*_{max}.

Table 1 shows the dependence of the thermoelectric power (dE/dT) on the Br₂ concentration for the Maxsorb electrode. The power increases with increasing Br₂ con-

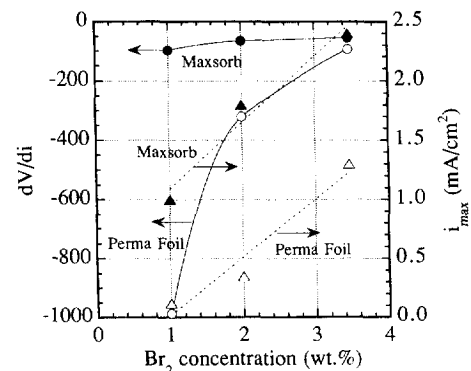


Fig. 6. Dependence of dV/di and limiting current density on Br₂ concentration in the electrolyte.

Table 1
Dependence of thermoelectric power on Br₂ concentration

Br ₂ concentration	$S_{<40}$ (mV/°C)	$S_{>40}$ (mV/°C)
1 wt. %	0.69	3.90
2 wt. %	1.19	4.87
Saturated	1.55	5.68

$S_{<40}$: thermoelectric power at temperature difference less than 40°C.

$S_{>40}$: thermoelectric power at temperature more than 40°C.

centration at temperature differences both below and above 40°C.

These results indicate that thermocell characteristics depend on the Br₂ concentration in the electrolyte and that electrolyte saturated with Br₂ obviously gives the greater improvement in performance.

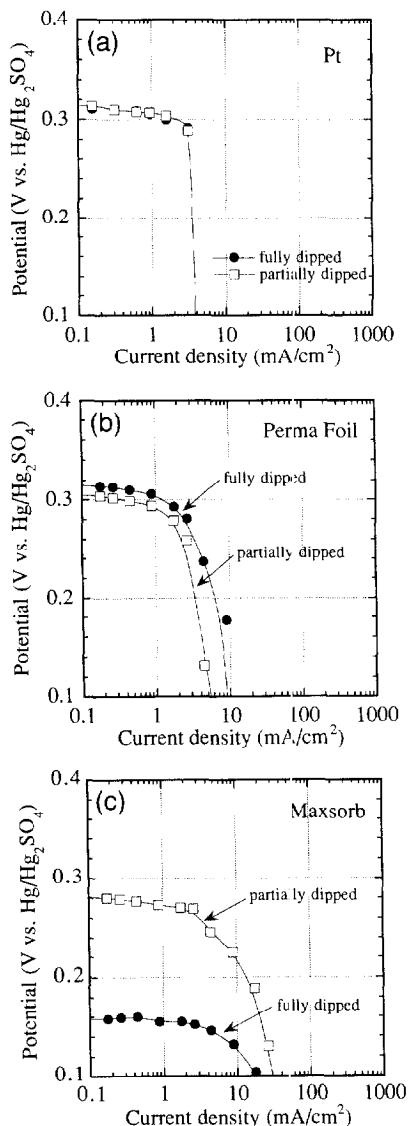


Fig. 7. Cathodic polarization for partially and fully dipped electrodes in electrolyte without Br₂ at 25°C: (a) Pt; (b) pristine Perma Foil; (c) Maxsorb.

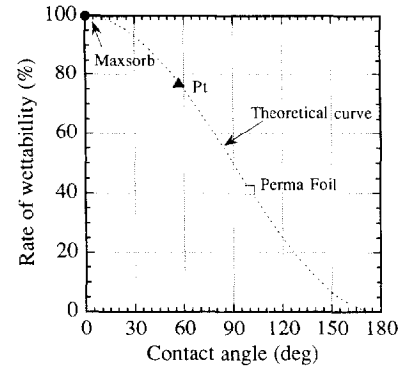


Fig. 8. Rate of wettability as a function of contact angle.

3.4. Effect of a gas–liquid–solid (GLS) interface

The boiling point of Br₂ is 54.3°C [17]. Thus, it is possible that gaseous Br₂ affects the cell reaction. If so, a direct gaseous Br₂ reduction at the GLS interface on the cold electrode can improve the cell characteristics. Accordingly, a study was made of the effect of a GLS interface on the cathodic polarization.

Fig. 7(a)–(c) shows the cathodic polarization curves for fully and partially-dipped Pt, pristine Perma Foil electrodes, and Maxsorb electrodes, respectively. The characteristics were measured at 25°C for an electrolyte without Br₂. The polarizations for the fully and partially-dipped Pt and Perma Foil electrodes are almost the same. The GLS interface has no apparent effect on the polarization of either electrode type. By contrast, the polarization is changed greatly by dipping the Maxsorb electrode. This suggests that the GLS interface promotes Br₂ gas reduction at the Maxsorb electrode.

The wettability (W) of the electrode could be an important factor in reduction of the Br₂ gas. Fig. 8 shows the rate of wettability as a function of the contact angle. The theoretical curve is derived from the function: $W(\%) = [(1 + \cos \theta)/2] \times 100$. The Maxsorb electrode obviously exhibits the fastest rate of wettability. In fact, the electrolyte

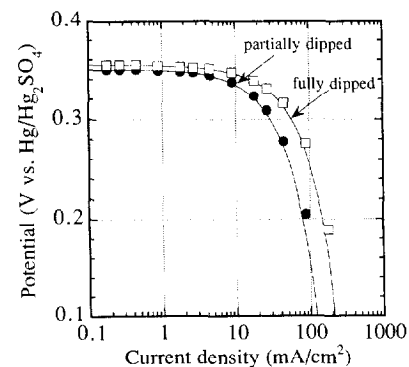


Fig. 9. Cathodic polarization for partially and fully dipped Maxsorb electrodes in electrolyte saturated with Br₂ at 25°C.

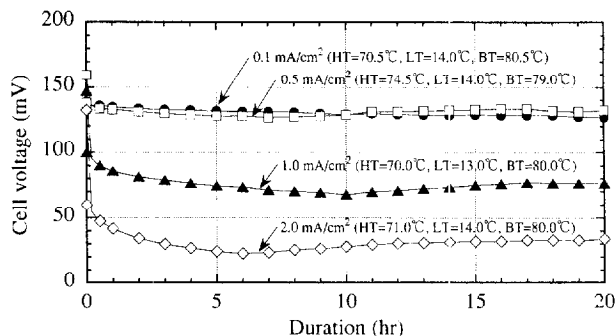


Fig. 10. Voltage change with time at discharge current densities of 0.1, 0.5, 1.0 and 2.0 mA/cm² for cells with Maxsorb electrodes and an electrolyte solution of 3.36 M KBr saturated with Br₂ (HT: hot electrode temperature; LT: cold electrode temperature; BT: gas bridge temperature).

soaked through the Maxsorb sheet too fast to measure the contact angle. This good wettability possibly produces a large GLS interface on the Maxsorb electrode.

The cathodic polarization of Maxsorb electrodes both fully and partially dipped in electrolyte saturated with Br₂ is given in Fig. 9. It can be seen that the effect of the GLS interface disappears. Thus, the cathodic polarization characteristics are improved by Br₂ saturation to such an extent that the improvement due to the GLS interface is hidden, even if the interface is effective.

Consequently, a cell system consisting of Maxsorb electrodes and electrolyte saturated with Br₂ does not require a GLS interface.

3.5. Stability of cell performance

Fig. 10 shows the voltage change with time at several discharge current densities for cells with Maxsorb electrodes and an electrolyte solution of 3.36 M KBr saturated with Br₂. The voltages declined rapidly during discharge, and then remained nearly constant at each current density

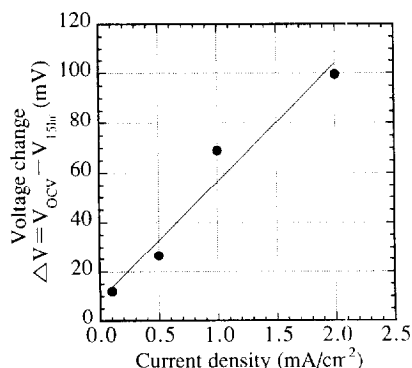


Fig. 11. Dependence of voltage difference ΔV on current density for cell with Maxsorb electrodes and an electrolyte solution of 3.36 M KBr saturated with Br₂ ($\Delta V: V_{ocv} - V_{15h}$).

for over 450 h. This demonstrated the good long-term electrochemical stability of the system.

Fig. 11 shows the dependence of the difference, ΔV , between the OCV and the discharge voltage at 15 h on the current density. The difference increased linearly with current density and, thereby, indicated that the voltage difference may be due to an IR drop caused by the solution resistance. This suggests that optimizing the electrode distance and the cell geometry will improve cell performance.

4. Conclusions

The electrochemical characteristics of thermocells with a bromine/bromide-ion (Br₂/Br⁻) redox couple have been investigated. In particular, an examination has been made of the effect of the electrode material, the bromination of graphite electrodes, a gas–liquid–solid (GLS) interface on the cold electrode, and the Br₂ concentration in the electrolyte.

The findings show that electrodes made from a non-graphitized carbon (Maxsorb) sheet with a large specific surface area and an electrolyte solution of 3.36 M KBr saturated with Br₂ improve the characteristics of the thermocells.

The Maxsorb electrodes generate thermoelectric power of 5.68 mV/°C at a temperature difference above 40°C. This value is 2.5 times greater than that reported previously. The electrodes also improve the cathodic polarization in the presence of a GLS interface in Br₂-free electrolyte.

Bromine saturation in the electrolyte improves significantly the *i*-*V* characteristics and the thermoelectric power of the cells. The improvement is sufficiently effective to hide the effect of a GLS interface.

It has not been possible to determine the effect of bromination of graphite electrodes on the cell characteristics. Nevertheless, because of the difficulty of bromination, it is not considered that bromination is an effective way to improve the cell characteristics. The use of a Maxsorb sheet for the electrodes is an easier and more effective way to enhance the characteristics.

The thermoelectric power of the experimental cells depends on the temperature difference between the hot and cold electrodes in a way that is different from that previously reported. This may be caused by the cell configuration, especially the distance between the hot and cold electrodes.

Cells with Maxsorb electrodes exhibit good stability for over 450 h. The difference in the open-circuit voltage and the voltage after 15 h depends linearly on the current density. This means that the *i*-*V* characteristics are related mainly to the ohmic drop. Consequently, optimizing the cell configuration should improve cell performance.

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