THEORY OF NEW ELECTROCHEMICAL HEAT PUMP
AND ITS EXPERIMENTAL STUDY

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ABSTRACT

A new electrochemical heat pump which absorbs heat under electrolysis at lower temperature and releases heat under thermochemical reaction at higher temperature is proposed. The coefficient of performance of this electrochemical heat pump would reach the value of inverse Carnot factor, the maximum under a given condition.

The reduction of CO₂ to CO, which is the key reaction of our electrochemical heat pumping system, was mainly investigated. The overpotential of the electrolytic reduction of CO₂ to CO on Au was estimated to be about 0.2V at 0.1 mA/cm². When the roughness factor of the Au electrode exceeds 100 times larger than that of the present case, fixing $T_H$ and $T_L$ at 1023K and 973K, respectively, the electrochemical heat pump can release the heat, 0.2kW/m².

INTRODUCTION

The efficient use of energy and energy savings should be promoted in order to establish a novel environmentally friendly system. From thermodynamic analysis, it is possible to reduce the energy consumption in various industrial processes(1). To increase the energy efficiency, the development of new technologies for the recovery of waste thermal energy is of practical importance. In particular, having the following merits, chemical heat pumps have been developed actively(2,3). 1. Materials are easy to store and to transport, 2. High density of heat storage. The conventional chemical heat pumps, however, have some problems. For example, the system is complicated due to the coupling of two or more reactions and it is not easy to use the industrial high temperature waste heat. Then we proposed, retaining the above merits, the application
of electrical energy in order to simplify the conventional chemical heat pump system. In case of supplying electrical energy, there may be many possibilities to set up the heat pump system.

THEORY OF A NEW ELECTROCHEMICAL HEAT PUMP

A new electrochemical heat pump utilizing simple redox reaction was proposed. Electrical work input enables the endothermic reaction to proceed at lower temperature. While, at higher temperature the reverse exothermic reaction occurs thermochemically. Then, the total system consumes electrical work and transports heat from lower temperature to higher temperature, as shown in Fig. 1.

Kreysa et al. also proposed an electrochemical heat pump consisted of two identical electrochemical cells operating at different temperatures in opposite directions(4,5). The difference between these two electrochemical heat pumps is the way of heat release at higher temperature. Our electrochemical heat pump releases heat due to changes in enthalpy by using thermochemical reaction, whereas Kreysa’s does due to changes in entropy by operating galvanic cell.

When molten salts are used as electrolyte for the electrochemical heat pump, high temperature industrial waste heat can be utilized. Due to the high operating temperature, the overpotential of the electrochemical reaction is expected to be low.

Thermodynamic Consideration of a New Electrochemical Heat Pump

The chemical reactions included in the electrochemical heat pump must satisfy the following conditions: (1) The reaction should be the redox one. (2) The reaction should be highly reactive in both directions. In this sense, the water gas shift reaction [1] is expected to satisfy above two conditions and it was applied to the proposed electrochemical heat pump.

\[
\text{CO(g) + H}_2\text{O(g) }\rightleftharpoons \text{CO}_2\text{(g) + H}_2\text{(g)} \tag{1}
\]

The forward reaction [1] is exothermic and takes place spontaneously. In turn, the back reaction does not proceed unless work is added. If the back reaction is performed by electrolysis in molten carbonates, it may be divided to the following two electrode reactions,
In electrolysis, electrical work input enables the reactions [2] and [3] to proceed to the right with heat absorption. In the electrochemical heat pump using shift reaction, the reduction of CO₂ to CO is the key reaction, since the overpotential of H₂ to H₂O in molten carbonate has been reported to be small(6,7).

Each electrolysis process and thermochemical reaction process is treated as a closed system. The initial state of the closed system is assumed to be the state existing CO(g) 1mol and H₂O(g) 1mol. The extent of reaction, \( \xi \), is introduced. The number of total molecules in the closed system is 2. When the above gases are assumed to behave ideally, the thermodynamic properties such as Gibbs energy, enthalpy, and entropy of the closed system can be calculated from the thermodynamic relations.

Figure 2 shows the relationship between \( G, H, \) and \( T \cdot S \) and \( \xi \) obtained from thermal data(8) for the water gas shift reaction at different temperatures, i.e., upper one is at \( T_h=1200K \) and the lower one is at \( T_L=1100K \), with adjustment of each X axis. All irreversible processes occurring at constant T and P must proceed in such a direction as to decrease the Gibbs energy of the system. The extent of reaction corresponding to the equilibrium at high temperature is expressed as \( \xi_e \). The change of the extent of reaction due to electrolysis at \( T_L \) is depicted as \( \Delta \xi \) and \( \xi_e - \Delta \xi \) is expressed as \( \xi_1 \), and \( \Delta \xi \) is also equal to the change due to thermochemical reaction at \( T_h \). Here, the subscripts H and L designate higher and at lower temperatures, respectively.

In the electrochemical heat pump, the water gas shift reaction [1] proceeds from right to left by the electrolysis. Electrolytic cell takes up heat, \(( T_L \cdot S_{iL} - T_L \cdot S_{eL} )\), reversibly from the lower temperature heat reservoir with input of electrical work, i.e., \( G_{iL} - G_{eL} \). When the reaction system is removed to higher temperature, remaining the gas composition represented by \( \xi_1 \), the reaction proceeds spontaneously until \( \xi_e \) at which the state is in the equilibrium with heat release, \(( H_{iH} - H_{eH} )\).

The coefficient of performance (COP) of a heat pump is defined as the ratio of the heat output at \( T_H \) to the electrical work input at \( T_L \). In the case of the new electrochemical heat pump, COP is expressed as

\[
\begin{align*}
2\text{CO}_2(g) + 2e^- &\rightarrow \text{CO}(g) + \text{CO}_2^2(l) & [2] \\
\text{H}_2(g) + \text{CO}_2^2(l) &\rightarrow \text{H}_2\text{O}(g) + \text{CO}_2(g) + 2e^- & [3]
\end{align*}
\]
COP is a function of $\Delta \xi$, $T_h$, and $T_L$. Figure 3 represents the variation between COP and $\Delta \xi$ under several $T_L$ conditions, fixing $T_h$ at 1200K. COP decreases rapidly with increasing $\Delta \xi$ and finally gets to unity.

To obtain the high COP value, the reactions included in the electrochemical heat pump should proceed reversibly. It is possible to transport the reaction substances continuously. The case that the amount of the whole reaction substances is much larger than that treated by electrolysis is considered. The products of the electrolysis, CO and $H_2O$, are removed continuously to the higher temperature reactor and allowed to react thermochemically with heat release until the reaction gets to the equilibrium. Then, the products, CO$_2$ and $H_2$, are returned again to the electrolytic cell at lower temperature. As a whole the heat pump system is operated in the closed system, therefore it is possible to transport reaction substances back and forth continuously between $T_L$ and $T_H$. A large amount of reaction substances makes $\Delta \xi$ infinitesimal. Due to continuous transportation of substances, the heat pump reactions can be operated at near $\xi_s$ at any time. For the case of $\Delta \xi \rightarrow 0$, Equation [4] results in the reciprocal Carnot factor.

Under real conditions, energy losses due to internal irreversibility such as the overpotential in the electrolysis must be taken into account. The irreversibility caused by the overpotential is changed to heat (Joule heat). Considering the overpotential $\eta$, COP is expressed as

$$\text{COP} = \frac{T_h}{(T_h - T_L)} - \frac{T_h}{(T_h - T_L)} \times \frac{\eta}{(\eta + U_h)}$$

where $U_h$ is theoretical electrolytic voltage. When $T_h$ and $T_L$ are fixed at 1023K and 973K, respectively, the dependence of COP on $\eta$ can be calculated as shown in Fig.4. Since COP is generally required to be above 3, $\eta$ must be lower than about 50mV under this condition.

It is necessary to investigate the overpotential of CO$_2$ to CO. Figure 5 shows that the relationship between the equilibrium electrode potential and the equilibrium partial gas pressure. According to the calculation, CO$_2$ could be reduced to CO below -0.9V vs. SOE. The electrochemical deposition of carbon from CO$_2$ reduction also proceeds under cathodic condition as well as CO formation at below -1.048V.
\[ 3\text{CO}_2(\text{g})+4\text{e}^{-}\rightarrow\text{C(s)}+2\text{CO}_3^2(\text{l}) \]  

[6]

EXPERIMENTAL

The eutectic carbonate mixture Li/K (62/38mol\%) was utilized as the electrolyte. Pure CO\(_2\) gas (p\(_{\text{CO}_2}\)=1atm) was bubbled continuously into the melt. The product gases were analyzed by gas chromatography. A Au wire (diameter:1mm, length:20cm) was used as a working electrode. The reference electrode was a Au wire placed in the same atmosphere. The potential was corrected by the standard oxygen electrode (S.O.E.) scale. All measurements were taken at 973K.

RESULTS AND DISCUSSION

Figure 6 shows the dependence of the volume percent of formed CO on the electrode potential. CO concentration increased with decreasing the electrode potential. CO formation was observed experimentally at \(-1.1\text{V}\), where the overpotential of CO\(_2\) reduction to CO was estimated to be about 0.2V at 0.1 mA/cm\(^2\). Deposition of carbon was also observed on the electrode when the potential was lowered than \(-1.3\text{V}\). Since carbon is possible to deposit at \(-1.048\text{V}\), the overpotential of carbon deposition was estimated to be about 0.25V. It is possible to reduce CO\(_2\) to CO without carbon deposition by controlling the electrode potential, because the overpotential of carbon deposition is large.

Tafel plot of CO formation is shown in Fig. 7. According to the Tafel plot, the overpotential may be reduced to about 50mV by increasing the roughness factor of working electrode. In the case of Au, it was found that the roughness factor must be 100 times larger than that of this experimental condition. Then, the electrochemical heat pump can produce the efficient thermal energy, 0.2kW/m\(^2\). Other materials having good effective catalysis of CO formation should be also developed.

CONCLUSIONS

1. A new electrochemical heat pump which absorbs heat under electrolysis at lower temperature and releases heat under thermochemical reaction at higher temperature is proposed.

2. From thermodynamic consideration, when \(T_H\) and \(T_L\) were 1023K and 973K,
respectively, the overpotential must be lowered than about 50mV in order to obtain the COP value above 3.

3. The overpotential of the electrolytic reduction of CO$_2$ to CO on Au was estimated to be about 0.2V at 0.1 mA/cm$^2$.

4. When the roughness factor of the Au electrode exceeds 100 times larger than that of the present case, fixing $T_H$ and $T_L$ at 1023K and 973K, respectively, the electrochemical heat pump can release the heat, 0.2kW/m$^2$.

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REFERENCES

1. Kam W. Li “Applied Thermodynamics: Availability Method and Energy Conversion”, Chap.1, Taylor & Francis (1996).
2. H. Kameyama, M. Yamashita and Y. Saito, Catalyst, 31, 285 (1989).
3. H. Kameyama, Refrigeration, 71, 476 (1996).
4. G. Kreysa and G.F. Darbyshire, Electrochim. Acta, 35, 1283 (1990).
5. L. Dittman, K. Juttner and G. Kreysa, “Electrochemical Engineering and Energy”, Plenum Press, pp.57-65 (1994).
6. P.G.P. Ang and A.F. Sammells, J. Electrochem. Soc., 127, 1287 (1980).
7. T. Nishina, M. Takahashi and I. Uchida, J. Electrochem. Soc., 137, 1112 (1990).
8. Ihsan Barin, “Thermochemical Data of Pure Substances, 3rd ed. Vol. I”, VCH (1995).
**Figure 1** Principle of a new electrochemical heat pump.

**Figure 2** Behavior of a new electrochemical heat pump.

**Figure 3** Variation between COP and $\Delta \xi$. $T_H=1200K$

**Figure 4** Dependence of COP on $\eta$. $T_H=1023K$, $T_L=973K$
\[ 2\text{CO}_2(g) + 2e^- = \text{CO}(g) + \text{CO}_3^{2-} (\text{I}) \]
\[ 3\text{CO}_2(g) + 4e^- = \text{C}(s) + 2\text{CO}_3^{2-} (\text{I}) \]

Figure 5 Relationship between equilibrium electrode potential and partial equilibrium gas pressure. $\text{P}_{\text{CO}} + \text{P}_{\text{CO}_2} = 1\text{atm}, T=973\text{K}$

Figure 6 Relationship between vol\% of formed CO and the electrode potential.

Figure 7 Tafel plot of the reduction of CO\textsubscript{2} to CO.