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# *Single electrode heat of molten NaCl electrolysis: measurement by electrolytic calorimeter and heat flux transducer (HFT)*

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An electrolytic calorimeter employing a heat flux transducer (HFT) has been developed. By means of this apparatus the single electrode Peltier heat for the anodic chlorine evolution reaction in the electrolysis of molten NaCl–ZnCl$_2$ using a $\beta$-alumina diaphragm was measured. The value of the single electrode Peltier heat obtained by such a method was 0.697 J C$^{-1}$ at 377° C, which is very close to the value 0.614 J C$^{-1}$ previously determined by a thermoelectric power measurement. The coincidence between the two methods indicates that a thermoelectric power measurement is quite valid for determining the single electrode Peltier heat.

## 1. Introduction

In our previous paper [1], single electrode heats of the electrolysis of molten NaCl–ZnCl$_2$ by the use of a $\beta$-alumina diaphragm were estimated by measuring thermoelectric power of the thermogalvanic cells:

$$(T)\ \mathrm{Na}/\beta\text{-alumina}/\mathrm{NaCl–ZnCl_2}/\beta\text{-alumina}/\mathrm{Na}\ (T + \mathrm{d}T)$$

and

$$(T)\ \mathrm{C,Cl_2/NaCl–ZnCl_2/Cl_2,C}\ (T + \mathrm{d}T)$$

and single electrode Peltier heats for sodium deposition and chlorine evolution at 377° C were estimated to be $-0.026$ and $+0.614$ J C$^{-1}$, respectively.

But the question still remains as to whether these values actually indicate single electrode heats, because in our experiment [1], measured e.m.f.s of thermogalvanic cells were regarded as *initial* e.m.f. only from several indirect inferences, without any actual proof.

This paper intends to prove that these values were actually the single electrode heats, by comparing them to the values measured directly by means of the electrolytic calorimeter.

## 2. Principle of the electrolytic calorimeter

Ito *et al.* [2] derived a differential equation, Equation 1, for the temperature distribution in the electrolyte, assuming a one-dimensional steady state energy flow, in which an approach by Førland and Ratkje [3] was chosen since it is thermodynamically rigorous and more suitable for engineering application.

$$k\frac{\mathrm{d}^2T}{\mathrm{d}x^2} + \rho i^2 - \chi i\frac{\mathrm{d}T}{\mathrm{d}x} + \frac{\mathrm{d}k}{\mathrm{d}T}\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^2 = 0 \quad (1)$$

In Equation 1, $i$, $\rho$, $k$, and $\chi$ are the current density, resistivity, thermal conductivity and Thomson coefficient, respectively and $x$ is the distance from the centre of the electrolyte.

Generally, $k$ is almost constant and $\chi$ is nearly zero over a wide temperature range [1], and $\rho$ changes linearly with temperature, thus,

$$\frac{\mathrm{d}k}{\mathrm{d}T} = 0, \quad \chi = 0 \tag{2}$$

and

$$\rho = \rho_0 - a(T - T_0) \tag{3}$$

where $\rho$ and $\rho_0$ are the resistivity at temperature $T$ and $T_0$ respectively, and $a$ is the positive temperature coefficient. The assumption $\chi = 0$ is reasonable since the transported entropy of the electrolyte is almost constant over a wide temperature range [1].

From Equation 1–3, Equation 4 is obtained.

$$k\frac{\mathrm{d}^2T}{\mathrm{d}x^2} + \left[\rho_0 - a(T - T_0)\right] i^2 = 0 \tag{4}$$

Equation 4 is solved with the boundary conditions:

$$T = T_0 \text{ at } x = \pm \ell \tag{5}$$

to give

$$\frac{\mathrm{d}T}{\mathrm{d}x} = -\left\{\frac{\rho_0 (a/k)^{\frac{1}{2}} i}{a \cosh\,[(a/k)^{\frac{1}{2}} \ell i]}\right\} \sinh\,[(a/k)^{\frac{1}{2}} x i] \tag{6}$$

and

$$T = T_0 + \frac{\rho_0}{a}\left\{1 - \frac{\cosh\,[(a/k)^{\frac{1}{2}} x i]}{\cosh\,[(a/k)^{\frac{1}{2}} \ell i]}\right\} \tag{7}$$

Fig. 1 shows the scheme of temperature profile and potential profile in the electrolyte during steady state electrolysis. Referring to Fig. 1, heat $X_{\mathrm{A}}^{\swarrow}$ and $X_{\mathrm{C}}^{\swarrow}$, to be supplied to the anode part and cathode part, respectively, are expressed as follows:

$$X_{\mathrm{A}}^{\swarrow} = \pi_{\mathrm{A}}^{\swarrow} i - \eta_{\mathrm{A}} i - k\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_{-\ell} \tag{8}$$

$$X_{\mathrm{C}}^{\swarrow} = \pi_{\mathrm{C}}^{\swarrow} i - |\eta_{\mathrm{C}}| i + k\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_{+\ell} \tag{9}$$

where the first term on the right corresponds to the single electrode Peltier heat, and the second corresponds to the heat due to overvoltage. The third term on the right is a function of heat conductivity and resistivity (cf. Equation 6).

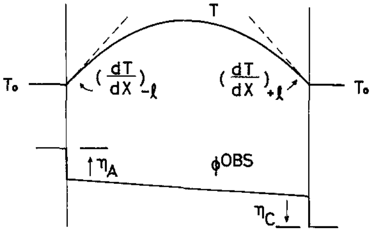

Fig. 1. Scheme of temperature and potential profiles.

From Equations 6, 8 and 9, the single electrode heat to be supplied is expressed as:

$$X^{\swarrow} = \pi^{\swarrow} i - |\eta| i - \rho_0 (k/a)^{\frac{1}{2}} i \tanh\,[(a/k)^{\frac{1}{2}} \ell i] \tag{10}$$

In Equation 10, the second and third terms on the right converge to zero rapidly when the current density approaches zero (parabolically), though the first term does so slowly (linearly).

Thus,

$$\lim_{i \to 0}\left(\frac{X^{\swarrow}}{i}\right) = \pi^{\swarrow} \tag{11}$$

Therefore, if the heat evolved or absorbed at the single electrode is measured at several steady state electrolytic current densities, the single electrode Peltier heat can be obtained by an extrapolation according to Equation 11.

## 3. Experimental details

Fig. 2 is a schematic diagram of the electrolytic calorimeter. An H-type cell containing molten NaCl–ZnCl$_2$ (40–60 mol%) is set in the electric furnace. To ensure accurate temperature control, the upper part of the cell is surrounded by an aluminium tube and the lower part is fitted in the aluminium block. The whole furnace is covered by ceramic fibres. The anode compartment and the cathode compartment are thermally insulated.

The heat flux transducer (HFT: Thermonetics

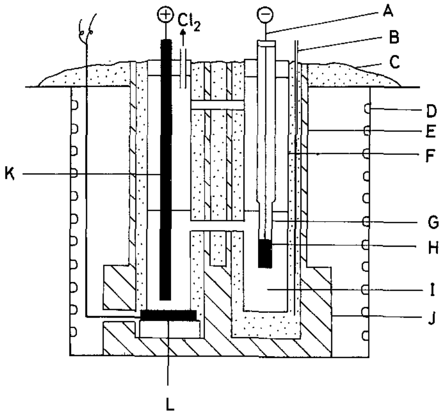

Fig. 2. Schematic diagram of electrolytic calorimeter.
A: Mo wire, B: thermocouple, C: ceramic fibre, D: heater, E: aluminium tube, F: pyrex cell, G: $\beta$-alumina, H: sodium, I: molten NaCl–ZnCl$_2$, J: aluminium block, K: graphite rod, L: heat flux transducer (HFT).

Corporation H-21-100-10 MC) is set beneath the anode compartment where chlorine evolution occurs. The HFT consists of a sensitive thermopile, composed of many fine-gauge thermocouples connected in series on opposite sides of the flat core whose thermal resistance is known and stable. When heat flows normally through the flat matrix a transient or steady state temperature difference is established across the core. In practical systems the difference is usually rather small but it is increased approximately 100 to 1000 times due to the multijunction sensor. Steady state heat flux through the HFT is uniquely related to the voltage generated across the thermopile, an output signal that can be measured by a potentiometer.

A graphite rod (10 mm, diameter) was used as anode. A $\beta$-alumina/Na electrode was used as cathode, in which argon gas was flowing in order to inhibit the oxidation of sodium. Measurement was carried out at 377° C.

Heat is absorbed at the anode compartment, by electrolysis, which causes a slight temperature difference across the bottom wall of the anode compartment. This temperature difference is directly related to the heat flux to be measured by the HFT.

In order to estimate the collection efficiency of the HFT, which denotes the ratio of heat caught by the HFT to total heat evolved at the anode compartment, the calibration curve for this system was constructed as follows: A micro heater whose output power can be controlled by an external power source, was immersed into the anode compartment in place of the anode. Then, the relationship between the output voltage of HFT and the heater output power was measured at different conditions.

## 4. Results and discussions

Fig. 3 shows the relation between HFT output voltage and the output power of the compensation heater. A linear relation was obtained and from the slope of this line, the calibration rate of the HFT was determined to be 820 W V$^{-1}$. With the use of this calibration rate, the single electrode heat of anodic reaction was measured from the output voltage of the HFT. Fig. 4 shows the single electrode heat measured at several electrolytic current densities. By extrapolation of this curve to $i = 0$, according to Equation 11, the single electrode Peltier heat was estimated to be 0.697 J C$^{-1}$. This value is very close to the value 0.614 J C$^{-1}$ obtained by the authors from thermoelectric power measurements [1]. Coincidence between these results suggests that these two methods and experiments were both appropriate.

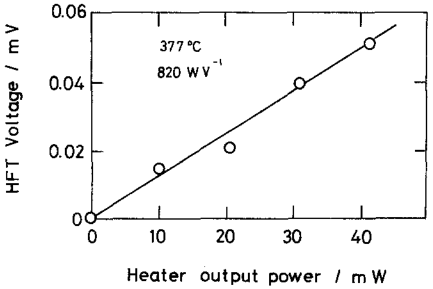

Fig. 3. Calibration line for heat flux transducer (HFT)

The appropriateness of these two experiments can also be seen by comparing the above two values to the values calculated from thermodynamic data. The partial molar entropies of $Cl_2$, Na and NaCl (in $ZnCl_2$) are 250.85, 81.82 and 111.46 J K$^{-1}$, respectively at 377° C [4, 5]. From these data, the sum of the single electrode Peltier heat is calculated to be:

$$\overset{\swarrow}{\pi}_{Cl_2} + \overset{\swarrow}{\pi}_{Na} = 0.645\,\mathrm{J\,C^{-1}}\ (377°\mathrm{C}) \qquad (12)$$

From our thermoelectric power experiment [1], the single electrode Peltier heat for Na deposition was estimated to be $-0.026$ J C$^{-1}$, which is very small compared to the value 0.614 J C$^{-1}$, though, unfortunately, the single electrode Peltier heat for Na deposition could not be measured by an electrolytic calorimeter due to its very low value. This very low value is also acceptable when we compare the closeness of the values 0.614 and 0.645.

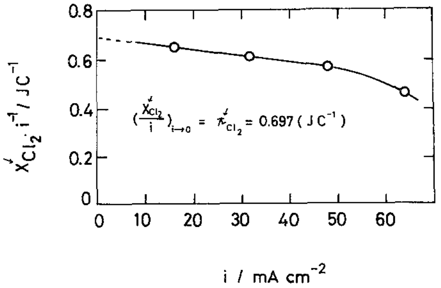

Fig. 4. Single electrode heat at various current densities.

## 5. Conclusions

The single electrode Peltier heat was measured by means of an electrolytic calorimeter for the anodic chlorine evolution reaction of the electrolysis of molten $NaCl–ZnCl_2$ using a $\beta$-alumina diaphragm.

The measured single electrode Peltier heat was $0.697\ J\ C^{-1}$ at 377° C which is very close to the value $0.614\ J\ C^{-1}$ previously obtained by a thermoelectric power measurement. Coincidence between the values suggests that the two methods and experiments were both appropriate, though they could still be improved to ensure more accurate results.

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