Electrode heat balances of electrochemical cells: application to NaCl electrolysis

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Received 6 June 1984

This paper deals with a method of estimating single electrode heat balances during the electrolysis of molten $NaCl-ZnCl_2$ in a cell using a β-alumina diaphragm.

By measuring the thermoelectric power of the thermogalvanic cells:

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

and

$$(T) \ C, Cl_2/NaCl-ZnCl_2/Cl_2, C \ (T + dT)$$
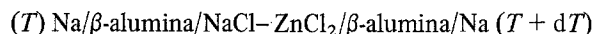
the single electrode Peltier heat for sodium deposition and for chlorine evolution at 370° C were estimated to be $-0.026 \pm 0.001 \ J \, C^{-1}$ and $+0.614 \pm 0.096 \ J \, C^{-1}$, respectively.

1. Introduction

This paper concerns the estimation of single electrode heat balances for the electrolysis of molten $NaCl-ZnCl_2$ using a β-alumina diaphragm [1, 2]. A scheme of the process is shown in Fig. 1. The anolyte consists of a molten mixture of sodium chloride and zinc chloride; the cathode compartment is filled with liquid sodium metal. During the electrolysis, chlorine is evolved at the anode and liquid metal deposits at the cathode as sodium ions move from the anolyte to the cathode compartment through the β-alumina solid electrolyte.

The operating temperature in this case is about 370° C. The total heat balance of this electrolytic cell is estimated from a knowledge of the enthalpy change, which has been determined previously [3].

But, in a high temperature molten salt system, especially when the electrolytic cell is divided into a cathode part and an anode part through the use of a diaphragm, as in the present case, it is further necessary to know the single electrode heat balance at the cathode and anode, respectively, in order to improve the energy conversion efficiency or to ensure adequate temperature control. If heat is not supplied to those parts of the electrodes where endothermic processes take place, there will be a drop in temperature that can lead to an increase in terminal voltage or even freezing of the electrolyte.

Conversely, if heat is not eliminated from those parts of the electrodes where exothermic processes take place, there will be a rise in temperature that can lead to a breakdown of the cell, especially the diaphragm, or electrolyte boiling. From these

Anode $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$

Cathode $Na^+ + e \longrightarrow Na$

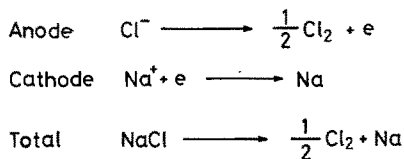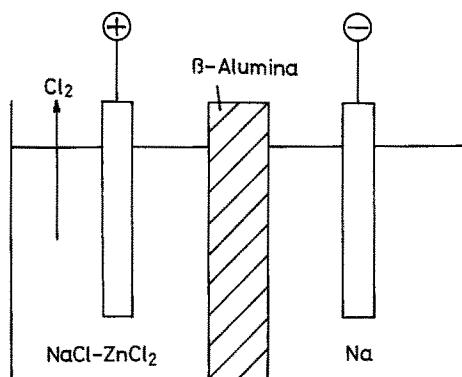Total $NaCl \longrightarrow \frac{1}{2}Cl_2 + Na$

Fig. 1. Scheme of electrolytic cell.

aspects, a theoretical and experimental procedure to estimate the single electrode heat from the measurement of the electromotive force of a thermogalvanic cell has been presented [4], in which nonequilibrium thermodynamics developed by Førland and Ratkje [5] was applied. This approach is most suitable for engineering applications and is thermodynamically rigorous. But, in the previous work [4], only a one-component electrolyte system was considered, and further extension to a multi-component system, as in the present case, will be necessary.

The procedure described below can be further applied to the electrolysis in general of multi-component electrolyte systems.

2. Relations between single electrode heat (Peltier heat) and thermoelectric power

According to Førland and Ratkje [5] and Ratkje [6], the entropy production θ per unit time and unit volume at any point in the electrochemical system can be written as

$$\theta = \nabla \frac{1}{T} J_{q'} - \frac{1}{T} \sum_{i=1}^{k} \nabla\mu_{iT} J_i - \frac{1}{T} \nabla\phi^{obs} I$$

(1)

where $J_{q'}$ is the measurable heat flux, J_i denotes the component fluxes of the k independent

components and I is the electric current. The chemical potential gradient $\nabla\mu_{iT}$ contains only pressure and composition dependent terms. The symbol $\nabla\phi^{obs}$ denotes the differential emf, measured with defined identical electrodes across the volume element. T is the absolute temperature. By integration across all volume elements the emf of the system is obtained. The standpoint for deriving Equation 1 is in contrast to the conventional one [7], which describes emf by local electric potential differences due to charge separation. The other main features of the approach of Førland and Ratkje are:

(a) The avoidance of single ion activities or electrochemical potentials. This is because energy changes are only defined and measurable with respect to electroneutral processes.

(b) The components of the system obey the phase rule. Components involved in electrode reactions are included. This ensures independent mass variables.

(c) The electric current is an independent flux of the system since this can be controlled externally.

(d) The frame of reference is the wall of the cell container.

To apply Equation 1 to our thermodynamic consideration, let the k independent components in the system be divided into the following three categories:

(a) components involved in the electrode reactions and belonging to a different phase from the electrolyte phase: $i = (n + 1) \sim k$ (Na or Cl_2 in the present case)

(b) components involved in the electrode reactions and contained in the electrolyte phase: $i = (m + 1) \sim n$ (NaCl in the present case)

(c) components in the electrolyte which are not involved in the electrode reactions: $i = 1 \sim m$ ($ZnCl_2$ in the present case)

Coupling of the fluxes of these components to the electric current can be written as:

$$J_i = x_i I \ (i = n + 1 \sim k) \ \text{(complete coupling)}$$

(2)

$$J_i = t_i I + J_i' \ (i = m + 1 \sim n) \tag{3}$$

$$J_i = t_i' I + J_i' \ (i = 1 \sim m) \tag{4}$$

where x_i is the number of moles of component i produced (negative sign) or consumed (positive sign) at the electrode by the anodic charge transfer of 1 C, and t_i and t_i' are the transference numbers of component i [8]. The transference number here is defined as the number of moles of the neutral component i transferred in the electrolyte by a charge transfer of 1 C when no temperature gradient and chemical potential gradient exist.

J_i' is the flux of component i due to a temperature and chemical potential gradient.

Taking into account Equations 2–4, Equation 4 can be rewritten as:

$$\theta = \nabla\left(\frac{1}{T}\right)J_{q'} - \frac{1}{T}\sum_{i=1}^{n}\nabla\mu_{iT}J_i - \frac{1}{T}\nabla\phi I \tag{5}$$

where

$$\nabla\phi = \nabla\phi^{\text{obs}} + \sum_{j=n+1}^{k}x_j\nabla\mu_{jT} \tag{6}$$

The expression of Equation 5 for the entropy production can be used to define independent fluxes. This will be done in the following for the special case at hand.

Apart from sodium metal or chlorine gas, there are two additional components in this system, i.e. NaCl and $ZnCl_2$.

Using the general expression for the fluxes and forces of the system:

$$J_{q'} = y_{q'q'}\nabla\left(\frac{1}{T}\right) - y_{q'1}\frac{1}{T}\nabla\mu_{1T}$$

$$- y_{q'2}\frac{1}{T}\nabla\mu_{2T} - y_{q'Q}\frac{1}{T}\nabla\phi \tag{7}$$

$$J_1 = y_{1q'}\nabla\left(\frac{1}{T}\right) - y_{11}\frac{1}{T}\nabla\mu_{1T}$$

$$- y_{12}\frac{1}{T}\nabla\mu_{2T} - y_{1Q}\frac{1}{T}\nabla\phi \tag{8}$$

$$J_2 = y_{2q'}\nabla\left(\frac{1}{T}\right) - y_{21}\frac{1}{T}\nabla\mu_{1T}$$

$$- y_{22}\frac{1}{T}\nabla\mu_{2T} - y_{2Q}\frac{1}{T}\nabla\phi \tag{9}$$

$$I = y_{Qq'}\nabla\left(\frac{1}{T}\right) - y_{Q1}\frac{1}{T}\nabla\mu_{1T}$$

$$- y_{Q2}\frac{1}{T}\nabla\mu_{2T} - y_{QQ}\frac{1}{T}\nabla\phi \tag{10}$$

where y represents the Onsager coefficients and subscripts 1 and 2 represent NaCl and $ZnCl_2$, respectively.

In the following, Equations 7–10 will be used to derive the relation between *initial* thermoelectric power and single electrode Peltier heat.

Initial thermoelectric power is the thermoelectric power obtained when the electrolyte composition is homogeneous; $\nabla\mu_{iT}$ is always zero for NaCl and $ZnCl_2$ and $\nabla\mu_{iT}$ for Na or Cl_2 is also zero, so Equations 7 and 10 can be simplified as follows:

$$J_{q'} = y_{q'q'}\nabla\left(\frac{1}{T}\right) - y_{q'Q}\frac{1}{T}\nabla\phi^{\text{obs}} \tag{11}$$

$$I = y_{Qq'}\nabla\left(\frac{1}{T}\right) - y_{QQ}\frac{1}{T}\nabla\phi^{\text{obs}} \tag{12}$$

Taking into account the condition $I = 0$, the expression for the initial thermoelectric power can be obtained as:

$$\epsilon_{\text{in}} = \frac{d\phi^{\text{obs}}}{dT} = -\frac{y_{Qq'}}{y_{QQ}}\frac{1}{T} \tag{13}$$

On the other hand, by eliminating $\nabla\phi^{\text{obs}}$ from Equations 11 and 12, Equation 14 is obtained:

$$J_{q'} = \left(y_{q'q'} - \frac{y_{q'Q}y_{Qq'}}{y_{QQ}}\right)\nabla\left(\frac{1}{T}\right) + \frac{y_{q'Q}}{y_{QQ}}I \tag{14}$$

The total heat transferred ($\Delta q'$) and the charge transferred (ΔQ) during a short time interval, Δt, are $J_{q'}\Delta t$ and $I\Delta t$, respectively. Thus

$$\Delta q' = \left(y_{q'q'} - \frac{y_{q'Q}y_{Qq'}}{y_{QQ}}\right)\nabla\left(\frac{1}{T}\right)\Delta t + \frac{y_{q'Q}}{y_{QQ}}\Delta Q \tag{15}$$

This equation shows that the transferred heat consists of one time-dependent term which is the first term on the right hand side, and one charge dependent term [4]. The latter is time-independent, its sign is reversed by reversing the sign of ΔQ. This part of the heat transfer is reversible. The heat balance is

$$\Delta q' = \Delta q'(t) + \Delta q'(Q) \qquad (16)$$

The entropy absorbed from the external heat reservoir by the reversible charge transfer of 1 C is,

$$S'(Q) = \frac{\Delta q'(Q)}{T\Delta Q} \qquad (17)$$

The heat $\Delta q'(Q)$ will contain the heat associated with the electrode reactions, but $\Delta q'(Q)$ will also contain contributions from the reversible transport processes through the electrolyte and metal leads. This means that the coefficient ratio $y_{q'Q}/y_{QQ}$ is also determined by the mechanism of transport. Combining Equations 15–17 gives Equation 18:

$$Y_{q'Q}/y_{QQ} = TS'(Q) \qquad (18)$$

Taking into account the Onsager reciprocal relation $y_{Qq'} = y_{q'Q}$, Equation 19 is obtained from Equations 13 and 18:

$$\epsilon_{in} = -S'(Q) \qquad (19)$$

$S'(Q)$ is the entropy absorbed from the external heat reservoir by the reversible charge transfer of 1 C, which is the sum of the transported entropy $\bar{\bar{S}}$ which flows out from the anode region into the electrolyte and the partial entropy change Δs in the electrode region with respect to the electrode reaction by the reversible charge transfer of 1 C:

$$S'(Q) = \bar{\bar{S}} + \Delta s \qquad (20)$$

3. Details of $S'(Q)$ by the electrolysis

In the electrolysis of molten NaCl–ZnCl$_2$ using a β-alumina diaphragm, $1/2F$ mol of chlorine gas is evolved at the anode and $1/F$ mol metallic sodium deposits at the cathode by a current passage of 1 C (F is the Faraday constant). If this electrolysis is carried out reversibly, the mass balance of the cell is as given in Fig. 2 and the entropy balance is as given in Fig. 3. Then, the details of $S'(Q)$ and Δs can be summarized to give Table 1.

4. Experimental details

From Equation 19 derived above, the single electrode Peltier heat can be obtained from the thermoelectric power measurements of the thermogalvanic cells:
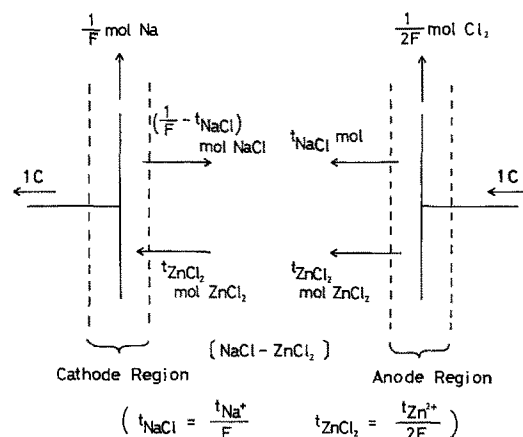

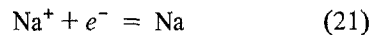
Fig. 2. Mass balance of the cell.

$$(T)\ \text{Na}/\beta\text{-alumina}/\text{NaCl–ZnCl}_2/\beta\text{-alumina}/\text{Na}$$
$$(T + \mathrm{d}T) \qquad (A)$$

and

$$(T)\ \text{Cl}_2/\text{NaCl–ZnCl}_2/\text{Cl}_2\ (T + \mathrm{d}T) \qquad (B)$$

for the reactions

$$\text{Na}^+ + e^- = \text{Na} \qquad (21)$$

and

$$\text{Cl}^- = \tfrac{1}{2}\text{Cl}_2 + e^- \qquad (22)$$
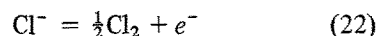
respectively.

An experimental cell, shown in Fig. 4, was thus constructed to measure the emf of the thermogalvanic cells (A) and (B). With respect to thermogalvanic cell (A), two sodium electrodes enveloped by β-alumina tubes were immersed in the separate vessels at different temperatures. The left hand side of the H-type cell was set
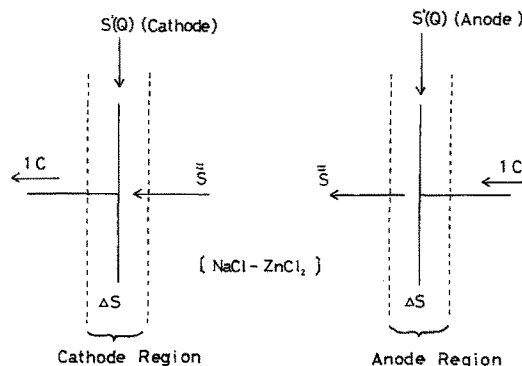

Fig. 3. Entropy balance of the cell.

Table 1. Details of entropy balance

Quantity	Anode region	Cathode region
Transported entropy	$\bar{\bar{S}}$	$-\bar{\bar{S}}$
Entropy change	$\Delta s = s_{Cl_2} - t_{NaCl}Fs_{NaCl} - 2t_{ZnCl_2}Fs_{ZnCl_2}$	$\Delta s = s_{Na} - F\left(\dfrac{1}{F} - t_{NaCl}\right)s_{NaCl} + 2t_{ZnCl_2}Fs_{ZnCl_2}$
$S'(Q)$ (Electrode)	$s_{Cl_2} - t_{NaCl}Fs_{NaCl} - 2t_{ZnCl_2}Fs_{ZnCl_2} + \bar{\bar{S}}$	$s_{Na} - F\left(\dfrac{1}{F} - t_{NaCl}\right)s_{NaCl} + 2t_{ZnCl_2}Fs_{ZnCl_2} - \bar{\bar{S}}$

at a constant temperature of (T_1) and the temperature of the right hand side (T_2) was varied, and the electromotive force between the two electrodes was measured.

With respect to thermogalvanic cell (B), it is also possible to measure the emf of a thermogalvanic cell composed of two gas diffusion type chlorine gas electrodes, but from preliminary experiments, it was found rather difficult to obtain reversible chlorine electrode potentials, so that a pulse-electrolysis technique was adopted. That is, by the use of the H-type cell shown in Fig. 4, pulse-electrolysis was carried out between a glassy carbon anode and a sodium/β-alumina cathode in the right hand cell, and the electromotive force was measured between this glassy carbon electrode on which chlorine was evolving and the sodium/β-alumina reference electrode in the left hand cell. Temperature control was maintained as described above. The conditions of the pulse-electrolysis were as follows:

Current density: $500\,\text{mA cm}^{-2}$; Duty ratio: 0.2;

Pulse width: $100\,\text{msec}$

5. Results and Discussion

Fig. 5. shows the electromotive force of thermogalvanic cell (A) when NaCl (39 mol %)–$ZnCl_2$ (61 mol%) was used as the electrolyte. The thermoelectric power of this cell is $-0.042\,\pm$
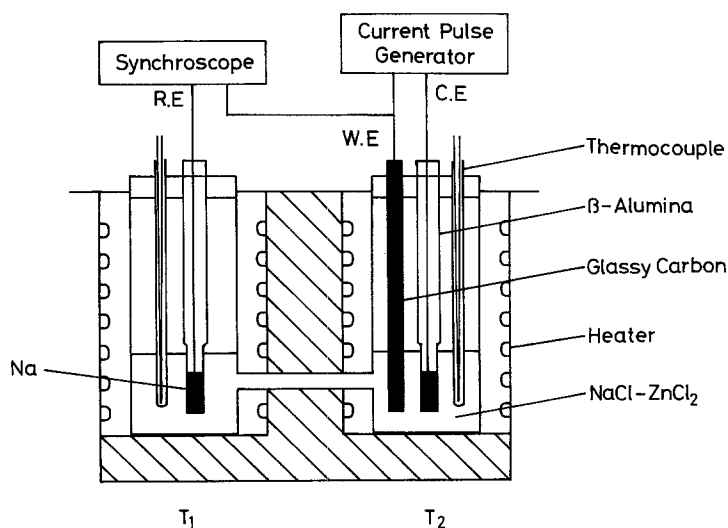

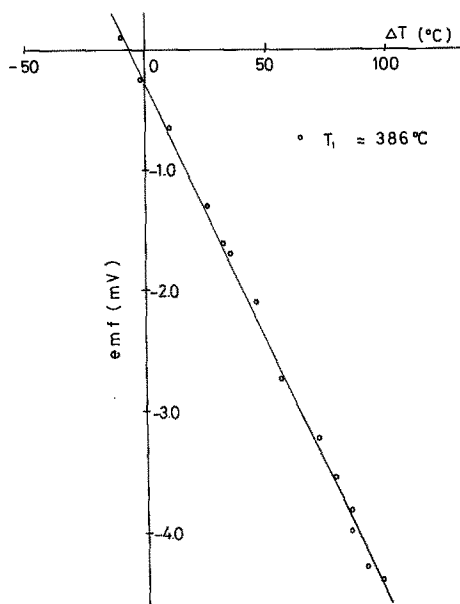Fig. 4. Experimental cell to measure thermogalvanic emf.

Fig. 5. The emf of thermogalvanic cell:
(T) Na/β-alumina/NaCl–ZnCl$_2$/β-alumina/Na $(T + dT)$.

Fig. 6. The emf of thermogalvanic cell:
(T) C, Cl$_2$/NaCl–ZnCl$_2$/Cl$_2$, C $(T + dT)$.

0.001 mV K^{-1}. That means, from Equation 19[*],
the single electrode Peltier heat at 370° C for
Reaction 21 is $-$ 0.026 $\pm$ 0.001 J C^{-1}. That is,
when sodium metal deposits at the cathode,
0.026 J is *evolved* with the current passage of 1 C.

Fig. 6 shows the electromotive force of thermo-
galvanic cell (B) when NaCl (39 mol%)–ZnCl$_2$
(61 mol%) was used as the electrolyte. Thermo-
electric power of this cell is $-$ 0.96 $\pm$ 0.15 mV
K^{-1}. Thus, from Equation 19, the single electrode
Peltier heat at 370° C for Reaction 22 is 0.614 $\pm$
0.096 J C^{-1}. That is, when chlorine is evolved
at the anode, 0.614 J is *absorbed* with the current
passage of 1 C.

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[*] As is well known, the initial thermoelectric power
ϵ_{in} differs from the steady state thermoelectric power
(Soret equilibrium) ϵ_{steady} [8] by:

$$\epsilon_{steady} - \epsilon_{in} = \frac{1}{TD} \sum_{l=1}^{n} t_l \Lambda_l \qquad (F1)$$

The physical meanings of the symbols appearing in the
right hand term have been given in a previous paper [8].

But, for reasons given in the previous paper [8], the
measured value can be regarded rather as an *initial*
thermoelectric power, which corresponds to the condition
of constant electrolyte composition. This has also been
proved by separate experiment [9], in which the calcu-
lated value from emf measurements was very close to the
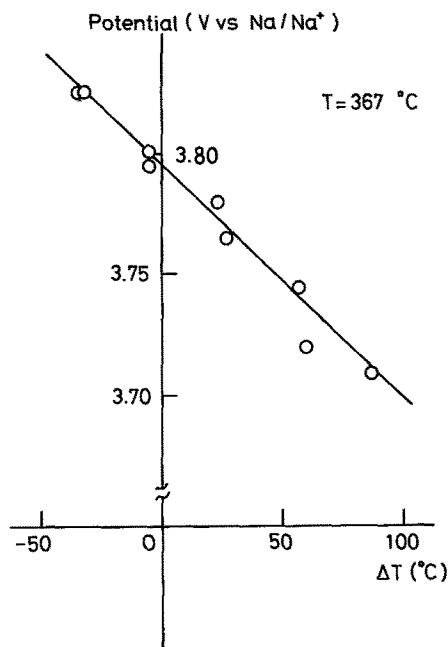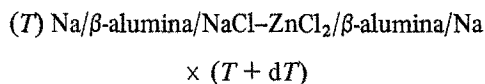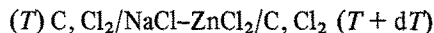value measured directly with the use of an electrolytic
calorimeter.

6. Conclusions

The single electrode heat balances for the elec-
trolysis of molten NaCl–ZnCl$_2$ in a cell using a
β-alumina diphragm were analysed by measuring
the thermoelectric power of the thermogalvanic
cells:

$$(T) \text{ Na}/\beta\text{-alumina/NaCl–ZnCl}_2/\beta\text{-alumina/Na}$$

$$\times (T + dT)$$

and

$$(T) \text{ C, Cl}_2/\text{NaCl–ZnCl}_2/\text{C, Cl}_2 \ (T + dT)$$

The approach of Førland and Ratkje was
successful in deriving the relation between the
single electrode Peltier heat and the initial
thermoelectric power of the above thermogalvanic
cells.

The single electrode Peltier heat for sodium
deposition and chlorine evolution were thus calcu-
lated, from the thermoelectric power of each
thermogalvanic cell, to be $-$ 0.026 $\pm$ 0.001 J C^{-1}
and 0.614 $\pm$ 0.096 J C^{-1}, respectively. That is,
when 1 C is passed through the electrolytic cell,
0.026 J is *evolved* at the cathode and 0.645 J is
absorbed at the anode.

Acknowledgement

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