

Reversible and irreversible heat effects in ZEBRA cells

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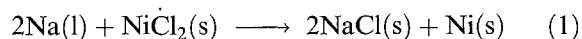
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When a sodium–nickel chloride cell is discharged reversibly, heat is liberated. The amount of heat involved has been found from measured values of the open circuit voltage of the cell over a range of temperatures. The thermal capacity of a 40 A h cell has also been measured, at various states of discharge, and is found to be a linear function of the temperature and of the degree of discharge. The information has been combined to find the temperature changes which occur when a fully charged cell undergoes a reversible discharge–charge cycle. Complete discharge of the cell involves a temperature rise of some 30–35 K, depending on the starting temperature; the effect is reversed on charge. The techniques employed in these calculations could be applied to other cells in which all reactants and products of the cell reaction are pure phases, such as the sodium–sulphur cell or ZEBRA cells involving transition metals other than nickel.

1. Introduction

The acronym ZEBRA (zeolite batteries for research in Africa) is used to describe a family of secondary cells in which one electrode is liquid sodium, the electrolyte is β'' -alumina (superceding the zeolite used in earlier versions) and the other electrode is a transition metal chloride suspended in molten sodium tetrachloraluminate, NaAlCl_4 [1–4]. Upon discharge of the cell, the sodium is oxidized to Na^+ and the transition metal chloride is reduced to the metal. The NaAlCl_4 takes no direct part in the cell reaction, but allows transport of sodium ions between the β'' -alumina and the site of the reduction reaction.

In the nickel version of the ZEBRA cell, the discharge reaction is



All reactants and products are pure solids or liquids, and are in the standard state at the temperature of cell operation.

If ΔG° , ΔH° and ΔS° are the standard Gibbs energy, enthalpy and entropy changes for the reaction, these parameters are related to the open circuit voltage (o.c.v.), E° , and its temperature coefficient, $(\partial E^\circ/\partial T)_p$, by the expressions

$$\Delta G^\circ = -zE^\circ F \quad (2)$$

$$\Delta S^\circ = -(\partial \Delta G^\circ/\partial T)_p = zF(\partial E^\circ/\partial T)_p \quad (3)$$

$$\Delta H^\circ = -zE^\circ F - zFT(\partial E^\circ/\partial T)_p \quad (4)$$

If Reaction 1 were carried out by direct mixing of sodium and nickel chloride, the heat released in the exothermic reaction would be $-\Delta H^\circ$. If, on the other hand, the cell were discharged through an external resistor, and if the electrodes were perfectly reversible and the cell had zero internal resistance, the heat liberated in the external circuit would be $-\Delta G^\circ$. The heat liberated in the cell under these conditions would be $-T\Delta S^\circ$, since the total heat liberated must be the same in both experiments and

$$-\Delta H^\circ = -\Delta G^\circ - T\Delta S^\circ \quad (5)$$

In the following, $-T\Delta S^\circ$ will be referred to as the ‘reversible heat’ for the discharge reaction; it transpires that ΔS° is negative for Reaction 1, so a positive amount of heat is released on reversible discharge. Upon recharging the cell under the ideal conditions specified, the heat $-T\Delta S^\circ$ would be reabsorbed. If the cell were thermally insulated, there would be a temperature rise on discharge, and this would be exactly reversed on recharge. The measurement of the reversible heat for the ZEBRA cell is described in Section 2.

The reversible heat is not generated uniformly in all parts of the cell; a detailed study [5] has shown that, on discharge, about 80% of the total reversible heat is generated in the sodium electrode and the remaining 20% in the nickel chloride electrode. This partition of the total heat into anodic and cathodic contributions requires measurement of the Seebeck coefficient for each electrode and derivation of the respective Peltier heats.

The thermal capacity of the standard SL/08 cell [6] has been measured, as a function of temperature and state of charge. Using these results, it is now possible

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to calculate the temperature changes undergone by a cell on discharge-charge cycling, for a given starting temperature. These calculations are presented in Section 3.

In addition to the reversible heat, there is additional heat generation arising from the finite electrical resistance, R , of the cell (Joule heat). The Joule heat evolved by passage of a current i for time t is i^2Rt , or iRx , where x is the charge passed ($x = it$). The Joule heat is directly proportional to the current for a given charge passed; it falls to zero in the limit of small current. In practice, R includes the effect of overpotentials at the electrodes, and is defined by the expression

$$E^{\circ} - E = iR \quad (6)$$

where E° is the open circuit potential and E is the potential when current i is flowing. R is a function of temperature, current and state of charge of the cell.

The Joule heat generated by these mechanisms may be termed 'dissipative', as it occurs at the expense of the maximum energy available externally ($-\Delta G^{\circ}$). Unlike the reversible heat, it does not change sign on current reversal. It must be regarded as a tax on the efficiency of the cell as an energy storage device. The magnitudes involved are discussed in Section 3.

2. Evaluation of the reversible heat

A specially-constructed ZEBRA cell was supplied, having the same external dimensions as the production cells [2, 3, 6] but containing only the essential constituents needed to correspond to Reaction 1. The sodium chloride content was 1.49 moles, corresponding to a theoretical charge capacity of 1.49 faradays (~ 40 A h).

The cell was mounted vertically in a furnace. Chromel-alumel thermocouples were secured to the outside of the cell case, with their respective junctions near the top and bottom of the case. The thermocouples

Table 1. Variation of o.c.v. with temperature for the ZEBRA cell. The temperatures are accurate to ± 0.5 K, and the o.c.v. values to ± 0.3 mV

Temperature /°C	E /V
303.5	2.5847
274.0	2.5908
244.0	2.5973
214.5	2.6032
185.5	2.6094
198.0	2.6077
226.5	2.6018
256.5	2.5950
286.0	2.5888
319.0	2.5813
342.5	2.5770
378.5	2.5691
409.5	2.5626
395.5	2.5655
363.5	2.5718
335.0	2.5781

were connected to direct-reading display units, which indicated that the temperature difference between the ends of the cell was never more than 1 K.

The cell was heated to 300 °C, and was charged to half capacity (20 A h) at a current of 1 A. It was left overnight to equilibrate, after which the temperature was cycled 300 \rightarrow 400 \rightarrow 200 \rightarrow 300 °C. Open circuit voltage readings were taken at a series of temperatures during this operation, the temperature being held constant for at least 30 min before each reading was recorded. The results are listed in Table 1 and are displayed in Fig. 1, which shows a plot of E° against temperature. The points lie on a straight line, of slope -0.211 mV K $^{-1}$. The o.c.v. at temperature T is given (with a standard deviation of ± 0.0003 V) by

$$E^{\circ}/V = 2.6490 - 0.000211(T/K - 273) \quad (7)$$

At 300 °C ($T = 573$ K), $E^{\circ} = 2.5857$ V. Using this result, the following values are obtained for the standard

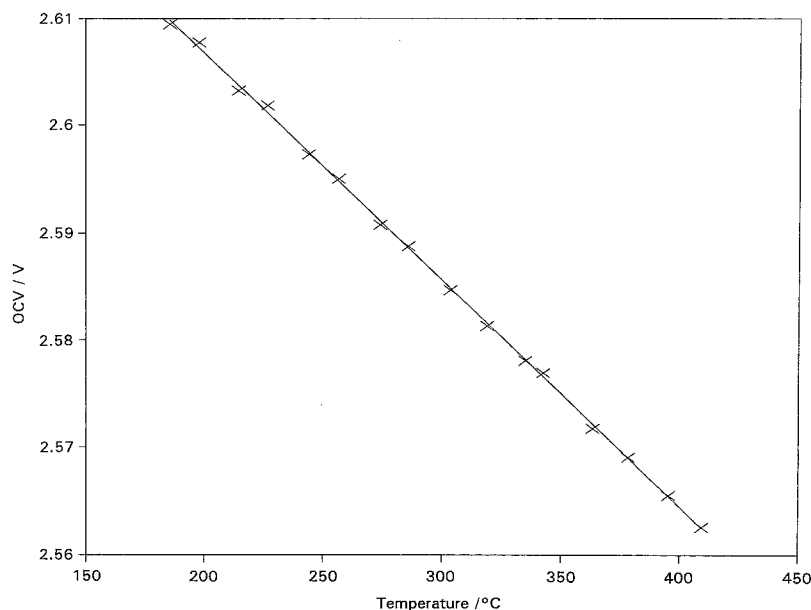


Fig. 1. Variation of o.c.v. with temperature for the sodium-nickel chloride cell.

thermodynamic parameters for the discharge Reaction 1 (per two faradays of charge) at this temperature:

$$\Delta G^{\circ} = -499.0 \pm 0.2 \text{ kJ mol}^{-1}$$

$$\Delta H^{\circ} = -522.3 \pm 0.2 \text{ kJ mol}^{-1}$$

$$T\Delta S^{\circ} = -23.3 \pm 0.2 \text{ kJ mol}^{-1}$$

(The uncertainty ranges quoted correspond to 95% confidence). Thus, the reversible heat evolved in the ZEBRA cell on discharge at 300 °C is 23.3 kJ (per two faradays).

3. Temperature changes during reversible discharge-charge cycling

The thermal capacity of the standard SL/08 cell has been measured, as a function of temperature and degree of discharge, using a method based on Newton's law of cooling. Cooling rates were measured at 250, 275 and 300 °C, and at degrees of discharge of 0, 10, 20, 30 and 40 A h, and these were compared with cooling rates of dummy cells filled with metal powder of known thermal capacity. The thermal capacity of the cell increases with temperature (for a given state of charge), and increases with discharge (for a given temperature). The results are adequately represented by the equation

$$\text{heat capacity} = A + BT + Cx \quad (8)$$

where x is the discharge capacity in A h (i.e., $x = 0$ corresponds to a fully charged cell and $x = 40$ to a fully discharged cell) and T is the cell temperature in kelvin. The experimental heat capacity data were fitted to this equation, and the values of the constants were:

$$A = 136.2 \text{ J K}^{-1} \quad (9a)$$

$$B = 0.600 \text{ J K}^{-2} \quad (9b)$$

$$C = 2.146 \text{ J K}^{-1} (\text{A h})^{-1} \quad (9c)$$

Using the information embodied in Equations 8 and 9, together with the value of the reversible heat presented in Section 2, it is possible to calculate the temperature changes arising from the reversible heat effect for any charge/discharge sequence, given the starting conditions (temperature and state of charge). Two methods will be described. The first, or differential, method involves a notional passage of charge in small increments, and calculation of the resulting temperature increments using a thermal capacity which is assumed constant over a small range. The process is repeated many times, and the thermal capacity is updated for each new temperature and state of charge. This approximate method becomes exact as the charge increments are reduced in size. The second method, the 'integral method', involves a mathematical solution of the differential equation on which the first method is based. By integrating the equation, an explicit expression is obtained for the final temperature in terms of the initial temperature and degree

of discharge and the final degree of discharge. This, more elegant, method gives the same results as the first method, but the final expression is surprisingly complex since it contains a term involving a nonintegral power of the starting temperature.

3.1. Differential method

Suppose the initial cell temperature and discharge capacity are T and x , respectively, and that an additional incremental discharge dx is carried out. The resulting temperature rise, dT , is required.

A discharge dx (A h) corresponds to $dx/26.80$ faradays. From Section 2, $T\Delta S^{\circ}$ is -23300 J for two faradays at 573 K. ΔS° for one faraday is then $-20.36 \text{ J K}^{-1} \text{ mol}^{-1}$, and may be taken to be independent of temperature over the small ranges involved. The heat, q , evolved when the discharge dx occurs is

$$q/\text{J} = (T \times 20.36 \times dx)/26.80 = 0.7597 T dx$$

The thermal capacity of the cell is $A + BT + Cx$ (with values of A , B and C as given in Equation 9). Dividing q by the thermal capacity, the temperature rise dT is given by

$$dT = \frac{0.7597 T dx}{A + BT + Cx} \quad (10)$$

Inserting the values of A , B and C from Equations 9,

$$dT = \frac{T dx}{179.28 + 0.7897 T + 2.824 x} \quad (11)$$

For given starting conditions (T , x), this expression is used to find dT when charge dx is withdrawn from the cell. The temperature is updated to $(T + dT)$, and the calculation is repeated for a further increment of discharge dx . The cycle of calculations is repeated until the required final conditions have been reached.

A charge increment, dx , of 2 A h was found to be satisfactory, and the calculations were performed for a range of starting temperatures for a fully charged cell ($x = 0$ initially). The results are plotted in Fig. 2, which shows that the cell temperature would rise by some 30–35 K (depending on the starting temperature) for complete discharge. Reversal of the charge would restore the temperature to its initial value.

3.2. Integral method

Equation 11 may be rewritten as

$$T \frac{dx}{dT} = A' + B'T + C'x \quad (12)$$

where $A' = 179.28 \text{ A h}$, $B' = 0.7897 \text{ A h K}^{-1}$ and $C' = 2.824$. It is required to integrate Equation 12 to give T as a function of x , with the starting values of T and x as boundary conditions.

Let $T = e^y$; then $dT = e^y dy = T dy$, and $T dx/dT = dx/dy$. Making this substitution in Equation 12 and rearranging,

$$\frac{dx}{dy} - C'x = A' + B'e^y \quad (13)$$

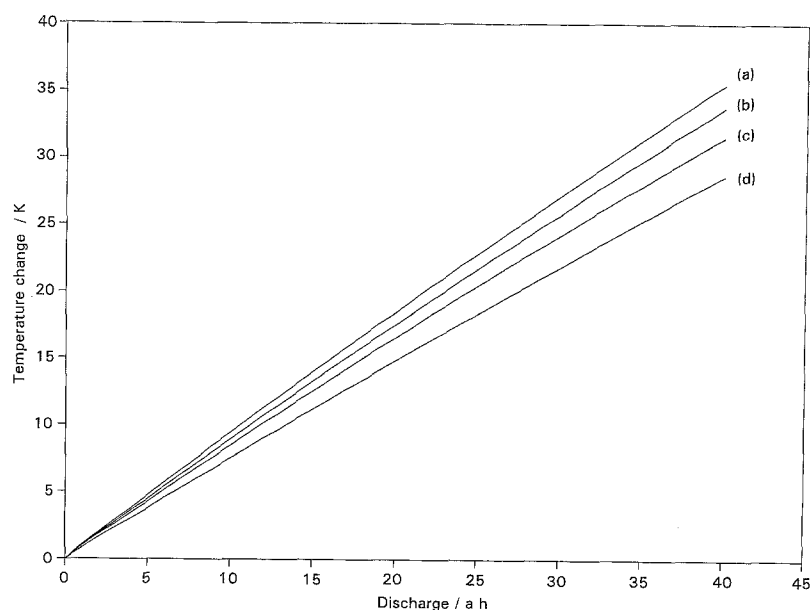


Fig. 2. Temperature change due to reversible heating on discharge, for different starting temperatures: (a), 400 °C; (b) 300 °C; (c) 200 °C; (d) 100 °C.

Multiplying by an integration factor $e^{-C'y}$, Equation 13 becomes

$$\frac{dx}{dy} e^{-C'y} - C' x e^{-C'y} = A' e^{-C'y} + B' e^{y(1-C')} \quad (14)$$

Integrating

$$x e^{-C'y} = \int A' e^{-C'y} dy + B' \int e^{y(1-C')} dy + K' \quad (15)$$

where K' is an integration constant. Evaluating the integrals, multiplying throughout by $e^{C'y}$ and replacing e^y by T ,

$$x = -\frac{A'}{C'} + \frac{B'T}{1-C'} + K'T^{C'} \quad (16)$$

where $A' = 179.28 \text{ A h}$, $B' = 0.7897 \text{ A h K}^{-1}$ and $C' = 2.824$. This is the required relationship between x and T . The constant K' is evaluated by inserting the boundary condition: $T = T_0$ when $x = x_0$. The result is

$$K' = \frac{x_0}{T_0^{C'}} + \frac{A'}{C'T_0^{C'}} - \frac{B'T_0^{(1-C')}}{1-C'} \quad (17)$$

Equation 16, with this value of K' , can now be used to find T as a function of x for given values of T_0 and x_0 , using a simple BASIC computer program. It is not possible to rearrange Equation 16 to give T explicitly as a function of x , because the constant C' is non-integral. An iterative method is used in the computer program. The results from the two methods are in excellent agreement; the maximum difference is less than 0.1 K, which is the temperature increment specified in the iteration loop of the integral program.

3.3. Joule heating

The calculations detailed above are based on an idealized cell in which the only heat effects are those due to the reversible chemical reaction. Under adiabatic conditions, the cell would heat up on discharge, and cool

Table 2. Joule heat per two faradays of charge, for representative values of current and resistance. For comparison, the reversible heat per two faradays is 23.3 kJ, and the maximum energy available externally is 499 kJ

Current /A	Joule heat per 2 faraday/kJ	
	$R = 10 \text{ m}\Omega$	$R = 20 \text{ m}\Omega$
1	1.9	3.9
2	3.9	7.7
5	9.7	19.3
10	19.3	38.6
20	38.6	77.2
40	77.2	154.4

again on charge, and would return to the same temperature at the same state of charge. The effect of Joule heating must be superimposed on this picture. For current i flowing for time t through a resistance R , the Joule heat is $i^2 R t$, or $i R q$ where q is the charge. The cell resistance varies with temperature and state of charge, so it is not practicable to present exact calculations of Joule heat. However, it is useful to give a range of illustrative figures to cover conditions of typical use. This is done in Table 2, in which the Joule heat is listed for two faradays of charge, for a range of currents and for $R = 10 \text{ m}\Omega$ and $R = 20 \text{ m}\Omega$.

Inspection of the data in Table 2 shows that the Joule heat becomes comparable to the reversible heat at currents in the region of 5–10 A (depending on the resistance). Athermal charging could be achieved if the Joule heat balanced the reversible heat, which would be the case if the cell were charged at a potential equal to $-\Delta H^\circ/2F$.

Acknowledgements

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- [6] This cell is manufactured by Beta Research & Development, 50 Goodsmoor Road, Sinfyn, Derby DE24 9GN, Great Britain. It has a maximum capacity of 40 A h.