HEAT RELEASE AND EMF OF NONISOTHERMAL MOLTEN SALT FUEL CELLS

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ABSTRACT

Expressions based on nonequilibrium thermodynamics are presented for the emf and local heat production of a nonisothermal fuel cell operating in steady state. Using these expressions, contributions to the local heat release rate can be attributed to: separate electrode Peltier heats, electrode overpotentials, Joule heating, electrolyte diffusion and thermal diffusion potentials, and bulk electrolyte Peltier and Thomson heats. The sizes of these terms and of the various terms contributing to the emf have been estimated for molten carbonate fuel cells.

1. INTRODUCTION

In an operating fuel cell, the amount of heat produced or absorbed at any point varies with location in the cell. This is so not only because fuel and oxidant gas utilization causes the cell operating conditions to be nonuniform across the electrode faces, but also because there are many different physical and chemical mechanisms responsible for the heat release. As a result, the cell is likely to operate in a nonisothermal mode. Knowledge of the strengths and locations of the various heat sinks and sources is required in order to fully assess the importance of nonisothermal effects on cell performance.

Using linear irreversible thermodynamics, we have recently completed an analysis of a nonisothermal fuel cell that enables us to identify all of the heat release mechanisms and their loci of operation within the cell. We have also obtained an expression for the emf of such a cell. In this presentation we use these results to estimate the sizes of the various effects contributing to the heat release and emf of a molten carbonate fuel cell at an average temperature of 923 K operating at a current density of 160 mA/cm².
Our analysis was limited to a cell satisfying the following set of conditions and limitations: 1) The cell is in a nonisothermal steady state under load. 2) The cell half reactions involve dissolved gas species and electrolyte anions. 3) The electrolyte may be a mixture, but only a single anionic species is permitted. 4) Gas-electrolyte interfaces are in close proximity to the electrodes. 5) Uniform conditions pertain at each electrode and gas-electrolyte interface. 6) The metal used for the reference leads differs from that used for both electrodes. 7) Gas phase transport is neglected. 8) Constant pressure conditions prevail.

A schematic diagram of the cell is depicted in Fig. 1. For future use we note that the subscripts A and C refer to anode and cathode, subscript i denotes electrolyte ions with N being reserved for the anionic species CO$_3^-$, subscript e is used for electrons, and the letters h, w, o, d, c, m will designate the following gaseous species: H$_2$, H$_2$O, O$_2$, CO$_2$, CO, CH$_4$. As usual, F will stand for the Faraday. For this presentation we specialize a bit further and consider only monovalent cations, e.g. Li$^+$, Na$^+$, K$^+$. The specific half-reactions at the cathode and anode are, as usual,

\[
\frac{1}{2}O_2 + CO_2 + 2e^- = CO_3^-(1)
\]

\[
H_2 + CO_3^- = H_2O + CO_2 + 2e^- . \quad (2)
\]

The effects of CO and CH$_4$ reactivity will be included only indirectly by assuming gas phase equilibrium for anode fuel mixtures.

A detailed derivation and additional discussion of the general results presented here will appear elsewhere. 1

2. NONISOTHERMAL CELL EMF

2.1 General Expression

Using the procedures presented by Haase$^2$, we were able to obtain the following expression for the potential difference $\Delta \phi$ between points 1 and 2 of the reference leads. (Refer to Fig. 1.)
\[ \Delta \phi = \phi_2 - \phi_1 = E(T_A) - IR - \eta_A(T_A) - \eta_C(T_C) \]

\[ - (2F)^{-1} \sum_{i \neq N}^C t_i \left[ (\nu_{i1N})_T \cdot F + (Q_{i1N}/T) \cdot \tau_T \right] \cdot d\tau \]

\[ + (2F)^{-1} \sum_{i \neq N}^C S_{N1N} \cdot \tau_T - (2F)^{-1} \int_{T_A}^{T_C} (\xi_s - 2S_e) \cdot dT \]

The terms in this equation will be interpreted and evaluated in the following sections.

2.2 Nernst Potential

The Nernst open circuit potential \( E(T_A) \) of the cell is calculated at the anode temperature for the prevailing gas conditions. For the molten carbonate cell \( E \) is typically about 1 volt.

2.3 Ohmic Loss

The \( IR \) term is the familiar ohmic potential loss attributable to the finite conductivities of the electrolyte and electrodes. (In practical cells, electrode contact resistances might also be important.) Considering only the ohmic loss in the electrolyte we may rewrite the product of cell current \( I \) and resistance \( R \) in terms of cell current density \( j \), specific conductivity \( \kappa \) and electrode separation \( \ell \):

\[ IR = j\kappa^{-1} \ell \]

For molten carbonate/lithium aluminate tiles \(^3 \kappa \approx 1 \text{ ohm}^{-1} \text{ cm}^{-1} \), then for \( j = 160 \text{ mA/cm}^2 \) and \( \ell = 2 \text{ mm} \), we find

\[ IR = 32 \text{ mV} \]

2.4 Overpotentials

At 160 mA/cm\(^2\) the sum of the anode and cathode overpotentials, \( \eta_A + \eta_C \), is about 100 - 150 mV. We note that the total measureable electrode overpotential does not include the "concentration overpotential" arising from changes in the activity (chemical potential) of the anion from its open circuit value in the vicinity of each electrode. These thermodynamically indeterminable potential changes have been
combined with the diffusion and thermal diffusion potentials resulting in the measurable quantities discussed next.

2.5 Measurable Diffusion Potential

The next term,

\[-\Delta \varphi_D = (2F)^{-1} \sum_{i \neq N} \int_{A}^{C} t_i \left( \mu_{iN} \right) \nabla T \cdot dL \]

is formally the emf of a concentration cell with transference. It can also be interpreted as the measurable part of a diffusion potential resulting from composition gradients that may be established when current is passing through the cell. In the above expression \( t_i \) is the Hittorf (internal) transference number of cation \( i \) relative to \( CO_3^2^- \), \( \mu_{iN} \) is the chemical potential of the \( i \)th electrolyte component,

\[ \mu_{iN} = z_i \mu_i + \mu_N \]

and the integral is to be evaluated along a path from the anode to the cathode. The possible occurrence, consequences and size of \( \Delta \varphi_D \) in molten carbonate cells have been the subject of several recent reports.\(^4\)\(^-\)\(^7\) A likely upper limit for \( \Delta \varphi_D \) is given\(^4\) by \( \Delta \varphi_D = RT/2F \approx 40 \text{ mV} \), at 923 K, but more refined calculations\(^5\)\(^,\)\(^6\)\(^,\)\(^7\) give values that are usually less than 10 mV.

2.6 Measurable Thermal Diffusion Potential

We choose to call the next term,

\[-\Delta \varphi_{TD} = (2F)^{-1} \sum_{i \neq N} t_i \left( *Q_{iN}/T \right) \nabla T \cdot dL \]

the measurable part of the thermal diffusion potential. This nomenclature is somewhat arbitrary, but it does reflect the origin\(^2\) of the term. The \( *Q_{iN} \) are the heats of transport of the electrolyte components,

\[ *Q_{iN} = z_i *Q_i + *Q_N \]

They can be determined from measurements made in Soret (currentless) steady states for which we find
\[ (\nabla_{iN})_{P} + (Q_{iN}/T) \nabla T = 0 \]  

(3)

The \( Q_{iN} \) can also be related to thermocell measurements:

\[ (2F)^{-1} \sum_{i \neq N} t_i Q_{iN}/T = \varepsilon_{\infty} - \varepsilon_0 \]  

(4)

Here, \( \varepsilon_0 \) and \( \varepsilon_{\infty} \) are the initial and steady state thermoelectric powers of a thermocell consisting of a mixed electrolyte and of electrodes reversible to the anion\(^2\). Data for \( Q_{iN} \) in molten carbonate mixtures are apparently lacking, making it difficult to estimate the size of \( \Delta \varphi_{TD} \). If we use results for \( \varepsilon_0 \) and \( \varepsilon_{\infty} \) for molten nitrate systems\(^8\), we may get a crude idea of the magnitudes involved. (Although their net charges are different, \( NO_3^- \) and \( CO_3^- \) are iso electronic and have similar geometries.) At the highest temperature studied, 340°C, the largest difference reported for the \( LiNO_3/AgNO_3 \) system was

\[ \varepsilon_{\infty} - \varepsilon_0 = 58 \mu V/K \]

A considerable overestimate of \( \Delta \varphi_{TD} \) should be afforded by putting \( Q = TS \) where \( S \) is the molar entropy of a molten alkali carbonate, \( S \approx 200 \text{ JK}^{-1}\text{mol}^{-1} \). Then

\[ \frac{\Delta \varphi_{TD}}{\Delta T} \approx \frac{Q}{2FT} \approx 1 \text{ mV K}^{-1} \]

2.7 Transported Anionic Entropy

The next term

\[ \frac{1}{2F} \int_{A}^{C} \frac{S_{N}}{T} \cdot d\ell \]

arises when the change in chemical potential of the anions caused by a temperature gradient in the electrolyte is combined with the contribution of \( Q_{iN} \) to the thermal diffusion potential not already included in the preceding term. Using an extension of the Third Law, conventional values of the transported entropy \( S_{N} \) can be obtained from the thermocell measurements as discussed by Haase\(^2\). We defer the size estimate to Section 2.9.
2.8 Other Entropic Corrections

In the last term, $S^{(g)}$ represents the combination of partial molar entropies

$$S^{(g)} = S_d + \frac{1}{2} S_o$$

which arise when the cathode half-cell potential is referenced to the anode temperature. The nearly negligible transported entropy of electrons in the reference leads, $S_e, r$ appears because of the contact potentials between reference leads and electrodes and the thermal diffusion potentials in the reference leads.

2.9 Thermocell Measurements

The measurements on thermocells mentioned in Section II.6 have been made by Jacobsen and Broers (JB)\(^9\) for molten carbonate mixtures. Apparently, JB measured the initial thermoelectric power $\varepsilon_0$, given by

$$2F\varepsilon_0 = S_N - 2S_e, r - S^{(g)} - \sum_{i \neq N}^{t} \frac{Q_i N}{T}$$

and their results can be used to estimate the size of the sum of terms discussed in Sections 2.6, 7 and 8. JB\(^9\) also estimated that $\Sigma_j Q_j N / T$ was a small term, hence we also have

$$\varepsilon_0 \approx \varepsilon_\infty$$

where

$$2F\varepsilon_\infty = S_N - 2S_e, r - S^{(g)}$$

The value

$$\varepsilon_0 \approx 1 \text{ mV/K}$$

found by JB indicates that comparatively small potential drops will occur in cells with electrode temperatures differing by only a few degrees.
3. HEAT RELEASE

3.1 General Expression

The local heat release rate $\dot{Q}$ (watts/cm$^3$) for the cell described in the introduction is given by the following expression:

$$\dot{Q} = j^2 \gamma^{-1} + (2F)^{-1} j \cdot \sum_{i \neq N} \left[ (\nabla_{iN})_{T,P} + \left( \frac{\partial Q_{iN}}{\partial T} \right) \nabla T \right]$$

$$+ (2F)^{-1} j \cdot \left[ T \left( \frac{\nabla S}{\partial T} \right)_{T,P} + T \left( \frac{\partial S}{\partial T} \right) X \right]_{T,P}$$

As in the case of the cell potential, we identify each term and provide an estimate of its size in the following sections.

3.2 Joule Heating

The Joule heating term $j^2 \gamma^{-1}$ is easy to identify. For our earlier choices of $\gamma = 1$ ohm$^{-1}$ cm$^{-1}$, $j = 160$ mA/cm$^2$ we find

$$j^2 \gamma^{-1} \approx 26 \text{ mW/cm}^3.$$

The heat evolved per unit area of electrode surface can be estimated for a cell with electrode separation $L = 2$ mm as

$$j^2 \gamma^{-1} L \approx 5 \text{ mW/cm}^2.$$

3.3 Measurable Diffusion and Thermal Diffusion Potentials

The next two terms

$$(2F)^{-1} j \cdot \sum_{i \neq N} \left[ (\nabla_{iN})_{T,P} + \left( \frac{\partial Q_{iN}}{\partial T} \right) \nabla T \right]$$

represent the energy dissipated (or absorbed, depending on sign) by the passage of current through what we termed earlier the measurable part of the diffusion and thermal diffusion potentials. Probably, these two terms will be of opposite sign. (As can be seen from Eq. (3), they cancel in the Soret steady state.) We also anticipate
only small temperature differences between electrodes. An overestimate of the size of these two terms should therefore be obtained by using the earlier estimated value of 40 mV for just the diffusion potential, Δφ_D. For the 2 mm cell, we thus find

\[ j \left| \frac{\Delta \varphi_D}{l} \right| \leq 30 \text{ mW/cm}^3 , \]

and per unit electrode area we have

\[ j \Delta \varphi_D \leq 6 \text{ mW/cm}^2 . \]

3.4 Bulk Peltier and Thomson Effects

The next two terms are very interesting from a conceptual point of view. By analogy with the formal expressions occurring in the theory of metallic thermoelectric effects, it is reasonable to identify Tj • (∇*S_N)_T as the heat evolved or absorbed with passage of current because of a bulk electrolyte Peltier effect. In the steady state under discussion, the effect arises because of the possible composition dependence of the transported entropy of the anions. Likewise, the other term Tj • (b^*S_N/bT)_x y T is a formal representation of a bulk electrolyte Thomson heat that arises from the possible temperature dependence of *S_N.

Information regarding the temperature and composition dependence of *S_N is lacking. For the sake of making an estimate, let us attribute half of the standard deviation reported by JB^9 in their measurements of \( \varepsilon_Q \) (Eq. (5)), to a variation in *S_N. Then after noting the simplification

\[ \bar{\nu} * S_N = \left( (\nu * S_N)_T, P + \left( b^*S_N / bT \right) x , P \right) \]

we find (for l=2 mm)

\[ jT \left| \frac{\Delta * S_N}{l} \right| \approx 7 \text{ mW/cm}^3 , \]

and per unit electrode area
3.5 Electrode Heat Release

Because of our assumption of close proximity of gas/electrolyte interfaces and electrodes, the following contributions may be included as part of the heat release/absorption rates at the anode, $Q_A$, and the cathode, $Q_C$: 1) the enthalpy change of gas dissolving or evaporating, 2) the transported enthalpy flux of dissolved gas species, and 3) the changes in electrochemical enthalpy and heats of transport for all species involved in the half reactions. The ponderous expression that results will be presented and discussed elsewhere. It is far more instructive here to integrate $Q_A$ and $Q_C$ over the volumes $V_A$, $V_C$ enclosing the electrode and gas/electrolyte interfaces and divide by the electrode areas $A_A$, $A_C$:

$$\dot{q}_{A,C} = A_{A,C}^{-1} \int \dot{Q}_{A,C} \, dV_{A,C}$$

We then find for the individual cathode and anode heat release/absorption rates (in mW/cm$^2$) the expressions

$$2F \dot{q}_C = j \left( \Delta H_C^\circ + ^\circ Q_N - 2^\circ Q_e \right)$$  \hspace{1cm} (8)

$$2F \dot{q}_A = j \left( \Delta H_A^\circ + 2^\circ Q_e - ^\circ Q_N \right)$$  \hspace{1cm} (9)

where the half cell enthalpy change, $\Delta H^\circ$, is the appropriate linear combination of gas phase partial molar enthalpies for neutral species and of electrochemical enthalpies for charged species partaking in the half reactions, Eqs. (1) and (2). Equations (8) and (9) can be readily manipulated into the form

$$\dot{q} = j \left( \frac{T \Delta S^P}{2F} - \eta \right)$$  \hspace{1cm} (10)

where $\eta$ is the absolute value of the electrode overpotential and $\Delta S^P$ is the steady state Peltier entropy of the electrode half reaction. For the estimates of Section 2.4, we find

$$jT \Delta S_N \approx 1 \text{ mW/cm}^2$$
\[ j(\eta_A + \eta_C) = 16 \text{ to } 24 \, \text{mW/cm}^2. \]

The size and behavior of \( \Delta S^P \) will be considered in detail in the next section.

4. ELECTRODE PELTIER HEAT RELEASE

4.1 General Considerations

Aspects of this problem have been treated previously. See in particular the work of Agar\(^{10}\), and Jacobsen and Broers\(^{11}\) in which the Peltier entropy for a half reaction taking place on an electrode immersed in an electrolyte of uniform composition has been formulated. Our results, as indicated, apply to the steady state in which any possible composition gradients have been fully established. The difference between the Peltier entropies in these two extremes is slight, and is given by the term \( \Sigma t_j Q_{2N}/T \) which we have seen to be small. Needless to say, in the case of a pure molten salt \( Q_{2N} = 0 \) and the two Peltier entropies become identical. In the remainder of this section, we intend to consider the gas pressure and composition dependence of the molten carbonate steady state Peltier entropies. Initially, we treat only the hydrogen half reaction at the anode. We will shortly consider the complications introduced by the shift and methanation equilibria. Using the classical thermodynamic expressions for ideal gas entropies, we can write

\[ \Delta S^P_C = \Delta S^\theta_C + R \ln \left( X_o^{1/2} X_d \right) + \frac{3}{2} R \ln P \] (11)

and for the \( H_2(h) \) half reaction at the anode

\[ \Delta S^P_{A, h} = \Delta S^\theta_{A, h} - R \ln \left( X_w X_d / X_h \right) - R \ln P \] (12)

For \( \Delta S^\theta \) we have the following combinations of gaseous standard state entropies \( S^\theta \) and transported entropies \( *S \) of charged species:

\[ \Delta S^\theta_C = *S_N - 2 *S_e - S_d^\theta - \frac{1}{2} S_o^\theta \]

\[ \Delta S^\theta_{A, h} = S_w^\theta + S_d^\theta - S_h^\theta + 2 *S_e - *S_N \]

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These two quantities depend primarily on $T$, and, through $^*S_N$ and $^*S_e$, on electrolyte composition and electrode material. This last dependence is unimportant because $^*S_e$ is negligibly small, usually on the order of 1 J/K-mol. Furthermore, Jacobsen and Broers$^9$ found no indication of any appreciable composition dependence or temperature dependence for $\Delta S^\theta$. This last point must mean that the individual temperature variations of the $S^0$'s and $^*S_N$ very nearly cancel. From the JB$^9$ work and Eqs. (6) and (7), we find for various molten carbonate mixtures in the temperature range 800 - 1150 K, the average values

$$\Delta S^\theta_C = -217 \text{ JK}^{-1} \text{ mol}^{-1},$$

and

$$\Delta S^\theta_A = 162 \text{ JK}^{-1} \text{ mol}^{-1}.$$

Using Third Law entropies for the gaseous species we also obtain at 923 K, $^*S_N \approx 170 \text{ JK}^{-1} \text{ mol}^{-1}$, an appreciable quantity.

Because $\Delta S^\theta$ is the largest term in either Eq. (11) or Eq. (12), we see that the cathode is highly exothermic and the anode is nearly as endothermic. The power densities that correspond to these Peltier entropies can be computed using Eq. (10). At 160 mA/cm$^2$, we find

$$q^C = -166 \text{ mW/cm}^2$$

and

$$q^A = 124 \text{ mW/cm}^2.$$

Thus to maintain a thermal steady state, besides removing net heat from the cell, approximately 120 mW/cm$^2$ must be transferred from the cathode to the anode. This value is comparable to the electrical power density output, $jV = (160 \text{ mA/cm}^2) (0.8V) = 128 \text{ mW/cm}^2$, but the temperature gradient needed to effect this transfer directly through the electrolyte is small. We find

$$\frac{\Delta T}{x} = \frac{1}{k_T} (120 \text{ mW/cm}^2) \approx 1.3 \text{ K/mm},$$

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where we have conservatively taken the thermal conductivity \( k_T \) of a molten carbonate/lithium aluminate tile to be one-half of the value estimated for a carbonate melt\(^{12} \). On this basis we can expect that only small temperature differences will exist between electrodes across the cell. Inclusion of the remaining terms of Eq. (11) and (12), which are discussed below, will not alter the general conclusions reached above, although the precise numbers may change somewhat.

4.2 Pressure Dependence

The predominant pressure dependence of \( \Delta S^P \) arises from the gas phase species and is given by the \( \ln P \) terms in Eqs. (11) and (12). In Fig. 2 we present the pressure dependence of the heat release rates that can be obtained from Eqs. (10), (11) and (12):

\[
[\dot{q}_C]_P = j(3RT/4F) \ln P
\]

\[
[\dot{q}_A]_P = - j(RT/2F) \ln P
\]

It is easy to see that a constant current density cathode exothermity, anode endothermity and overall cell exothermity decrease with increasing \( P \). It is also clear that pressure variations would have to be quite extreme in order to effect substantial changes in overall cell exothermicity.

4.3 Cathode Composition Dependence

The composition dependence of the cathode heat release rate is easily obtained from Eqs. (10) and (11) as

\[
[\dot{q}_C]_X = j(RT/2F) \ln(X_0^{1/2} X_d)
\]

In Fig. 3, a plot of \([\dot{q}_C]_X \) versus \( X_d \) for air/\( CO_2 \) mixtures is presented. The noble mixture (2/3 \( CO_2 \), 1/3 air) is the least exothermic, but changes in \( \dot{q} \) with composition are small.

4.4 Anode Heat Release for Fuel Mixtures

The anode heat release can be considered as arising from the electro-oxidation of \( H_2 \), with possible additional contributions from the electrochemical reaction of \( CO \) and \( CH_4 \) as well as from the water gas shift reaction.
\[ \text{H}_2 + \text{CO}_2 = \text{H}_2\text{O} + \text{CO} \]  

(13)

and the methanation reaction

\[ 4\text{H}_2 + \text{CO}_2 = \text{CH}_4 + 2\text{H}_2\text{O} \]  

(14)

Provided the latter two reactions always remain in equilibrium, the question of the electrochemical reactivity of CO and \( \text{CH}_4 \) need not be addressed, and a complete mathematical description of the heat release can be given as follows.

Aside from the heat of transport of the charged species which can be added in later, the amount of heat released, \( \text{dH} \), by small \( \text{dn} \) changes in the numbers of moles of the involved species is

\[ \text{dH} = \sum_{\alpha} H_{\alpha} \text{dn}_{\alpha} + \sum_{\alpha} H_{\alpha} \text{dn}_{\alpha} + \sum_{\alpha} H_{\alpha} \text{dn}_{\alpha} \]  

(15)

where the sum on \( \alpha \) extends over \( h, w, d, c \) and \( m \). Here, \( H_{\alpha} \) is the usual partial molar enthalpy of gaseous substance \( i \) and \( H_{j} \) is the electrochemical enthalpy of charged substance \( j \):

\[ \tilde{H}_{j} = H_{j} + z_{j} \Phi_{j} \]

where \( z_{j} \) is the charge, and \( \Phi_{j} \) is the electrical potential of the phase in which species \( j \) is found.

The changes in the \( \text{dn} \) in Eq. (15) are not arbitrary, but are constrained by the requirement of maintaining equilibrium, at constant \( T \) and \( P \), before and after the shift and methanation reactions have proceeded a small extent:

\[ K_{s} = \frac{w_{c}}{h_{d}} = \frac{(w + \text{dn}_{w})(c + \text{dn}_{c})}{(h + \text{dn}_{h})(d + \text{dn}_{d})} \]  

(16)

\[ K_{m} = \frac{m_{w}n_{i}^{2}}{h_{d}^{4}d_{w}^{2}} = \frac{(m + \text{dn}_{m})(w + \text{dn}_{w})^{2}n_{f}^{2}}{(h + \text{dn}_{h})^{4}(d + \text{dn}_{d})P^{2}} \]

(17)

For simplicity of notation we have also used the letters \( m, c, d, h \) and \( w \) to denote the number of moles of each gaseous substance. The initial \( n_{i} \) and final \( n_{f} \) numbers of moles present are

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\[ n_i = m + c + d + h + w \]

\[ n_f + n_i + \sum_{\alpha} \Delta n_{\alpha} \cdot \]

We also need the equation
\[ -d\xi = dn_N = dn_c + dn_h + 4 dn_m \quad (18) \]

to define the variable \( \xi \) which measures the extent to which the electrochemical reaction of \( H_2 \) has proceeded. We next expand Eqs. (16) and (17) and retain only terms linear in \( dn \). We then combine the resulting expressions with Eq. (18) and with the stoichiometric relations that arise from the conservation of \( C, H \) and \( O \) atoms and of charge in order to obtain from Eq. (15) the expression
\[ \Delta H_A = \frac{dH}{d\xi} = \Delta H_{A, h} - \Delta H_{A, s} + \frac{\beta \mu + \gamma \nu}{\alpha \beta - \gamma^2} \Delta H_s + \frac{\mu \lambda + \alpha \nu}{\alpha \beta - \gamma^2} \Delta H_m \quad (19) \]

where \( \Delta H_{A, h} \) is the electrochemical enthalpy change for the anodic \( H_2 \) half reaction and \( \Delta H_s \) and \( \Delta H_m \) are the enthalpy changes for the water gas shift and methanation reactions:
\[ \Delta H_{A, h} = H_w + H_d + 2 \tilde{H}_e - \tilde{H}_N - H_h \]
\[ \Delta H_s = H_c + H_w - H_d - H_h \]
\[ \Delta H_m = H_m + 2H_w - 4H_h - H_d \]

The other quantities appearing in Eq. (19) are defined as
\[ \alpha = \frac{1}{h} + \frac{1}{c} + \frac{1}{w} + \frac{1}{d} \]
\[ \beta = \frac{1}{m} + \frac{4}{w} + \frac{16}{h} + \frac{1}{d} - \frac{4}{n_i} \]
\[ \gamma = \frac{2}{w} + \frac{4}{h} + \frac{1}{d} \]
\[ \mu = \frac{1}{h} + \frac{1}{w} - \frac{1}{d} \]
\[ \nu = \frac{1}{d} - \frac{4}{h} - \frac{2}{w} - \frac{2}{n_i} \].

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For the mixed reaction system under consideration, Eq. (17) is appropriate for use in Eq. (9). The terms in \( \Delta H_s \) and \( \Delta H_m \) obviously account for heat released or absorbed as the water gas shift and methanation reactions take place in order to maintain the equilibrium disturbed by the electro-oxidation of \( H_2 \).

Using a different starting point, Jacobsen and Broers\(^{11}\) have also treated the problem of heat release from a mixed reaction system at the anode. Aside from the difference noted in Section IV. 1., Eqs. (9) and (19) can be shown to be identical with their results.

For cells running on low BTU gasifier output mixtures, the effects of the \( \Delta H_s \) and \( \Delta H_m \) terms are not too large. At 923 K, \( \Delta H_s = 35.6 \text{ KJ mol}^{-1} \) and \( \Delta H_m = -189.1 \text{ KJ mol}^{-1} \), but for the fuel mixture consisting of 17.7 mole\% \( H_2 \), 16.6\% \( CO \), 4.7\% \( H_2O \), 0.74\% \( CH_4 \), and 51.1\% \( N_2 \), we find \((\mu + \alpha\nu)/(\alpha\beta + \gamma\nu)\ \Delta H_s = 3.3 \text{ KJ mol}^{-1} \) and \((\nu\beta + \alpha\nu)/(\alpha\beta - \nu^2)\ \Delta H_m = 28.9 \text{ KJ mol}^{-1} \). The contribution of the \( \Delta H_s \) term is quite small compared to \( T\Delta S_{A,h}^g \) which equals 150 \text{ KJ mol}^{-1} at 923 K. The \( \Delta H_m \) term is somewhat larger, but is still only 20\% of \( T\Delta S_{A,h}^g \) at this low \( CH_4 \) concentration. Under full equilibrium conditions, the \( CH_4 \) content would decrease with fuel utilization in a working cell. Then, because \( \beta \to \infty \) as \( m \to 0 \), the \( \Delta H_m \) term will become even less important. If, on the other hand, \( CH_4 \) does not remain in equilibrium because of slow reaction kinetics, Eq. (19) is inappropriate. In the limit of complete unreactivity of \( CH_4 \), we have

\[
\Delta H_A^T = \Delta H_{A,h}^T - (\mu/\alpha) \Delta H_s
\]

but intermediate cases require further consideration.

4.5 Anode Composition Dependence

For simplicity we consider \( CH_4 \) to be unreactive, but we do include the effects of shift equilibrium, Eq. (13). Then in view of the smallness of the \( \Delta H_s \) term, the anode heat release composition dependence will be adequately described by the equation

\[
[A]_X = -j(RT/2F) \ln(X_w X_d/X_h)
\]

which follows from Eqs. (10) and (11).

We first consider the variation of endo- or exothermicity of fuel gas mixtures lying on the carbon deposition boundary (CDB). This will
be of interest because such mixtures typify inlet conditions at the anode. The present calculations were performed for fuel mixtures lying just on the CDB at $T = 923$ K, $P=1$ and 10 atm and with no methane present. The composition along the CDB is readily calculated using the analytical methods of Broers and Treijtel. The results are presented in Fig. 4. The most notable feature of the results is the drastic increase in endothermicity with increasing $H_2/CO$ ratio.

Also of interest is the variation of the heat release with composition changes arising from utilization of fuel. In Fig. 5, results of a representative calculation are plotted. For an initial fuel mixture we took 17.9% CO, 19.1% H$_2$, 8.6% CO$_2$, 4.4% H$_2$O and 50.0% N$_2$ at a temperature of 923 K and a pressure of 1 atm. This is a typical output of a low BTU, air blown gasifier, allowed to equilibrate with added H$_2$O to prevent carbon deposition. To give an indication of the composition of the mixture we plotted power density (mW/cm$^2$) at 160 mA/cm$^2$ versus the sum of the H$_2$ and CO mole fractions divided by the initial value of the quantity. Throughout the calculation $X_C \approx X_H$. The arrows (†) on the figure mark points at which the indicated % of fuel (CO + H$_2$) has been expended. The results show a steady decline in endothermicity with increasing utilization. The range of variation in the anode heat release is also large compared to that found in the cathode (Fig. 3).

V. SUMMARY

The most important contributions to the cell heat release rate are the large, exothermic cathode Peltier heat and the somewhat smaller, but endothermic, anode Peltier heat. These individual electrode heat release rates have variations from changes in gas pressure and composition that are comparable in size to the additional exothermic heat release derived from the ohmic drop in the electrolyte and from the electrode overpotentials.

Other smaller, but conceptually interesting contributions to the heat release rate arise when current is passed through an electrolyte containing composition and temperature gradients. These contributions are caused by potential drops that we termed "measurable parts of the diffusion and thermal diffusion potentials" and by bulk electrolyte Peltier and Thomson heats.

It was also interesting to find that the cathode-to-anode heat flux required to maintain a nearly isothermal steady state is comparable in size to the electrical power density output of the cell. The
small temperature gradient (1 - 2 K/mm) needed to sustain this heat flux through the electrolyte/tile, implies that the temperature difference between electrodes should be small at any point in the cell. As a result, only small voltage losses (1 mV/K) should occur because of temperature differences between electrodes. Effects of temperature variations in the plane of an operating cell are beyond the scope of this investigation.

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REFERENCES

1. G. Wilemski, J. Chem. Phys. 72, 369 (1980).

2. R. Haase, "Thermodynamics of Irreversible Processes", (Addison-Wesley, Reading Ma, 1969).

3. Institute of Gas Technology, "Fuel Cell Research on Second Generation Molten-Carbonate Systems, Project 8984 Quarterly Report, October-December 1976", pp. 61-63.

4. J. Braunstein and C. E. Vallet, "Migrational Polarization in High-Current Density Molten Salt Electrochemical Devices", Proc. Symp. on Electrode Materials and Processes for Energy Conversion and Storage, Vol. 77-6, (The Electrochemical Society, Princeton, N. J., 1977), pp. 559-571.

5. J. Braunstein, H. R. Bronstein, J. I. Padova and C. E. Vallet, "Molten Carbonate Fuel Cell Program Progress Report for Periods October 1 - December 31, 1977, January 1 - March 31, 1978", ORNL Report ORNL/TM-6168/V3.

6. J. Braunstein, H. R. Bronstein, S. Cantor and J. I. Padova, "Molten Carbonate Fuel Cell Program Progress Report for Period April 1 - June 30, 1978", ORNL Report ORNL/TM-6168/V4.
7. H. R. Bronstein, J. I. Padova and J. Braunstein, "EMF Relaxation in Electrolyzed Molten Carbonate Fuel Cell Tiles", These Proceedings.

8. R. Haase, U. Pruser and J. Richter, Ber. Bunsenges. Phys. Chem. 81, 577 (1977).

9. T. Jacobsen and G. H. J. Broers, J. Electrochem. Soc. 124, 207 (1977).

10. J. N. Agar, "Thermogalvanic Cells", in "Advances in Electrochemistry and Electrochemical Engineering", Vol. 3, ed. by P. Delahay (Interscience, N. Y., 1963).

11. T. Jacobsen and G. H. J. Broers, J. Electrochem. Soc. 124, 210 (1977).

12. Institute of Gas Technology, "Fuel Cell Research on Second Generation Molten-Carbonate Systems, Project 8984 Quarterly Report, Vol. II, Characteristics of Carbonate Melts, July-September 1976", p. 154.

13. G. H. J. Broers and B. W. Treijtel, Advan. Energy Convers. 5, 365 (1965).
Fig. 1 Schematic cell diagram. Electrode Temperatures, $T_A$, $T_C$. Reference points 1 and 2 at temperature $T$.

![Schematic cell diagram]

| $[q]_P$ (mW/cm$^2$) | $T = 923$ K | $j = 160$ mA/cm$^2$ |
|---------------------|-------------|---------------------|
|                     | 0           | 0                   |
|                     | -40         | -40                 |

Fig. 2 Pressure dependence of electrode Peltier heat release rate.

![Pressure dependence of electrode Peltier heat release rate]

$[q]_{X_c}$ (mW/cm$^2$)

| $T = 923$ K | $j = 150$ mA/cm$^2$ |
|-------------|---------------------|
|             | -20                 |
|             | -18                 |
|             | -16                 |
|             | -14                 |
|             | -12                 |

Fig. 3 Gas composition dependence of cathode Peltier heat release rate for CO$_2$/air mixtures.
Fig. 4 Gas composition dependence of anode Peltier heat release rate along methane free carbon deposition boundaries.

Fig. 5 Gas composition dependence of anode Peltier heat release rate as a function of % fuel utilization (↑).