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Nonequilibrium thermodynamics of fuel cells: Heat release mechanisms and voltage^{a)}

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Nonequilibrium thermodynamics is used to analyze the spatial distribution of heat release mechanisms occurring in fuel cells operating under load in nonisothermal steady states. Novel contributions to heat release in the bulk electrolyte are found which are analogous to Peltier and Thomson effects in metallic conductors. Expressions for the heat release at individual electrodes are presented. An equation for the voltage of these cells is also derived.

I. INTRODUCTION

Heat is not produced or absorbed uniformly within an operating electrochemical cell. Different physical/chemical mechanisms govern the strength and sign of the heat released in the bulk electrolyte, in the electrode regions, and in the external circuit. In this article, we use nonequilibrium thermodynamics¹⁻³ to analyze the spatial distribution of heat release mechanisms occurring in a particular class of fuel cells. We also derive an expression for the voltage of such cells.

Theoretical treatments of special aspects of these problems and of related questions that have appeared in the literature were helpful in guiding our thinking in the present analysis. Particularly useful to us were the following: Haase's¹ general formulation of the heat conduction equation and his treatment of thermocells and of thermoelectric effects in metals; Vetter's⁴ discussion of electrode kinetics, overpotentials, and energy changes in electrode reactions; the work of Jacobsen and Broers⁵ on heat release at individual electrodes; Agar's⁶ reviews on thermocells and thermal diffusion; and the analysis of Vallet and Braunstein⁷ of composition profiles in molten salt electrolyte mixtures.

In the remainder of this section, we outline the paper and discuss assumptions and limitations that apply to the work presented. In Sec. II, we carefully derive an expression for the voltage of a fuel cell operating nonisothermally under load. Although we believe the result is new, our primary intent is to introduce notation and definitions of quantities for later use. In Sec. III, the spatial distribution of heat release mechanisms is investigated using a general heat conduction equation obtained from nonequilibrium thermodynamics. We demonstrate how the equation greatly simplifies for steady state operation of the fuel cell. For the metallic external circuit, we naturally find that Joule heating and the Peltier and Thomson effects are responsible for heat evolution and absorption. In the bulk electrolyte, we also have Joule heating, but in addition we find two terms, apparently novel, that can be interpreted as Peltier and Thomson effects in solution and a third term arising from what we call in Sec. II the measurable part of the thermal diffusion potential in the wider sense (of Haase¹). Finally, we find an explicit expression for the heat released/absorbed in the vicinity of an individual

electrode arising from the electrode reactions and concomitant transport of reactants and products in the electrode region. In Sec. IV, we analyze more thoroughly and simplify the expressions for individual electrode heat release. In Sec. V, we demonstrate the consistency of our results with the First Law of thermodynamics. Concluding remarks are presented in Sec. VI. Finally, the physical significance of our two principal results is considered further in an appendix.

From an electrochemical standpoint, a fuel cell's distinctive feature is that the electrode reactions proceed without any net change in the amount of electrolyte in the cell. We are, of course, ignoring losses from evaporation or leakage or from side chemical reactions that might occur in corrosion. Electrolyte composition and temperature gradients may, and often will, arise during operation, and these are responsible for the novel bulk electrolyte heat effects mentioned above.

In this analysis, we treat the class of fuel cells involving only gaseous reactants and products in the overall cell reaction. Furthermore, we consider only electrolyte mixtures with a single anionic species which is also the only electroactive ionic species in the overall electrode half-reactions. The latter two conditions are not very restrictive, but they do help simplify the analysis. Two other simplifying assumptions are made: first, that the electrodes have equal active areas and that conditions at each of the active electrode surfaces do not vary from point to point; second, that the gas-electrolyte interfaces are in close proximity to the electrolyte-electrode interfaces. The first assumption guarantees that uniform current density is produced, reducing the problem to a one-dimensional analysis. The second facilitates the identification of several terms contributing to the individual electrode heat release. The first condition should be attainable to a high degree with small lab size cells and the second almost always holds when porous gas diffusion electrodes are used. Finally, as mentioned, only steady state operation of the cell will be dealt with.

Regarding notation, the subscript k will be used to denote both ionic and neutral species; n , α , and γ will be used only for neutral species; i will designate only ionic species with N reserved for the anions; and the special subscript e will signify electrons. Subscripts a and c denote anodic and cathodic properties or regions,

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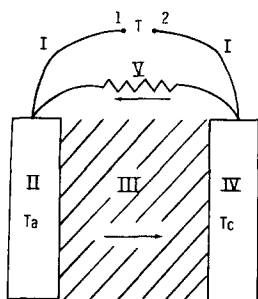


FIG. 1. Schematic cell diagram. For labeling of components, see Table I. Arrows indicate direction of current flow in normal operation.

respectively, and g will indicate the gas-electrolyte interfacial region.

Finally, we introduce a set of "functions" $s'_{a,c}$, $s''_{a,c}$, $s_{a,c}$, and s_g that will be formally useful in the developments of Sec. III. These functions are zero everywhere except at an appropriate interface where they act like delta functions at each point of the interface:

$$\int f s dv \equiv \int f da .$$

In this equation, the left hand side is a volume integral and the right hand integration is carried out only over the appropriate interfacial area. We define $s'_{a,c}$ to act at an interface just inside the metal electrode where bulk properties can be defined but close to the electrode-electrolyte interface; $s''_{a,c}$ acts at the (somewhat arbitrary) interface between the diffuse double layer and the bulk electrolyte; $s_{a,c}$ acts at both of the just mentioned interfaces; and s_g acts at the gas-electrolyte interface.

II. VOLTAGE OF NONISOTHERMAL CELL

The measurable voltage of an operating cell depicted in Fig. 1 will be the potential drop between points 1 and 2 of the reference leads, both at temperature T , which differs from either the anode or cathode temperatures T_a or T_c , respectively. As noted, we assume that conditions do not vary across the electrode faces so that a uniform current density is produced. In order to simplify some of the less important details of the calculation, we will also further assume that the electrodes and the external circuitry consist of the same metal which may differ from that used in the two identical reference leads. It will also be helpful to use Roman numerals to designate the various components of the cell as shown in Table I.

In traversing the circuit through the cell from 2 to 1, we may write the total potential drop (pd) as the sum of the pd's occurring in each cell component:

$$\Delta\phi = \phi_2 - \phi_1 = (\phi_2 - \phi_{c,I}) + (\phi_{c,I} - \phi_{c,IV}) + (\phi_{c,IV} - \phi_{a,IV}) + (\phi_{a,IV} - \phi_{a,II}) + (\phi_{a,II} - \phi_{a,I}) + (\phi_{a,I} - \phi_1) . \quad (2.1)$$

Here, $\phi_{a,I}$ and $\phi_{c,I}$ are the electrical potentials in the reference leads at temperatures T_a and T_c , respectively; $\phi_{a,II}$ and $\phi_{c,IV}$ are the electrical potentials in the metallic electrodes; and ϕ_1 and ϕ_2 are the potentials at points 1 and 2. The first and last terms of the above expression arise from the thermal diffusion potentials in the metallic reference leads; the second and fourth terms are the contact potential differences be-

tween the reference leads and the electrodes; and the middle term is the potential difference between the two electrodes. These pd's are all readily expressible in terms of familiar thermodynamic quantities:

$$\phi_2 - \phi_{c,I} = F^{-1} \int_{T_c}^T (*Q_{e,I}/T) dT , \quad (2.2)$$

$$\phi_{a,I} - \phi_1 = F^{-1} \int_T^{T_a} (*Q_{e,I}/T) dT , \quad (2.3)$$

$$\phi_{c,I} - \phi_{c,IV} = F^{-1} [\mu_{e,I}(T_c) - \mu_{e,IV}(T_c)] , \quad (2.4)$$

$$\phi_{a,II} - \phi_{a,I} = F^{-1} [\mu_{e,II}(T_a) - \mu_{e,I}(T_a)] , \quad (2.5)$$

$$\phi_{c,IV} - \phi_{a,II} = \Delta\phi_c + \int_a^c (\nabla\phi_{III}) \cdot d\mathbf{l} - \Delta\phi_a . \quad (2.6)$$

In the above expressions, $*Q$ is a heat of transport and μ is a chemical potential; T is the absolute temperature; and F is the Faraday. Next, $\Delta\phi_a$ and $\Delta\phi_c$ are the pd's between the metal electrodes and the bulk electrolyte just outside (at) the diffuse double layer, and the integral in Eq. (2.6) is carried out over a path through the bulk electrolyte between points just outside (at) the diffuse double layer of each electrode. This integral gives the pd arising from electrolyte resistivity, the diffusion or liquid junction potential, and the thermal diffusion potential. The quantity $\nabla\phi_{III}$ is written explicitly as

$$\nabla\phi_{III} = -j\kappa_{III}^{-1} + \nabla\phi_{TD} , \quad (2.7)$$

where κ_{III} is the specific conductivity ($\text{ohm}^{-1} \text{cm}^{-1}$) of the electrolyte, j is the current density (A/cm^2), and

$$F\nabla\phi_{TD} = - \sum_i \tau_i [(\nabla\mu_i)_{T,P} + (*Q_i/T)\nabla T] . \quad (2.8)$$

The quantity, ϕ_{TD} has been termed by Haase¹ the "thermal diffusion potential in the wider sense." In future use, we refer to it as TDPWS. In Eq. (2.8), the sum extends over all ionic species; and the reduced transference numbers are defined as

$$\tau_i = t_i/z_i ,$$

where t_i and z_i are the Hittorf transference number (relative to solvent) and charge of the i th ionic species. For simplicity, we assume that the τ_i for undissociated species are zero or, equivalently, that there are no undissociated species. We will shortly indicate how to interpret the results obtained in order to relax this assumption.

We next recall that the anionic transference number t_N is related to the remaining t_i by the equation

TABLE I. Designations of various cell components.

Cell components	Designation
Reference leads	I
Anode	II
Electrolyte	III
Cathode	IV
External circuit	V

$$t_N = 1 - \sum_{i \neq N} t_i \quad (2.9)$$

Then, if ν_i and $\nu_N^{(i)}$ are the stoichiometric coefficients of the cations (i) and anion (N) in a neutral combination of these species, we have the relations

$$\nu_i z_i = \nu_N^{(i)} z \quad (2.10)$$

where

$$z = |z_N|$$

Next we define the chemical potential μ_{iN} and heat of transport $^*Q_{iN}$ of the neutral species corresponding to the just mentioned combinations of ions:

$$\mu_{iN} = \nu_i \mu_i + \nu_N^{(i)} \mu_N \quad (2.11)$$

$$^*Q_{iN} = \nu_i ^*Q_i + \nu_N^{(i)} ^*Q_N \quad (2.12)$$

Then we note that the identity

$$(\nabla \mu)_{T,P} + (^*Q/T) \nabla T = \nabla \mu + ^*S \nabla T \quad (2.13)$$

follows from the definition of the transported entropy *S in terms of the partial molar entropy S and the heat of transport

$$^*S = S + ^*Q/T \quad (2.14)$$

and a familiar thermodynamic identity

$$(\partial \mu / \partial T)_{P,X} = -S \quad (2.15)$$

Equations (2.13) and (2.14) are valid for both ionic and neutral species.

Now, with the aid of Eqs. (2.9)–(2.14), it is possible to rewrite $\nabla \phi_{TD}$ as

$$\nabla \phi_{TD} = \nabla \phi'_{TD} + (zF)^{-1} (\nabla \mu_N + ^*S_N \nabla T) \quad (2.16)$$

where

$$\begin{aligned} \nabla \phi'_{TD} = & -(zF)^{-1} \sum_{i \neq N} (t_i / \nu_N^{(i)}) \\ & \times [(\nabla \mu_{iN})_{T,P} + (^*Q_{iN}/T) \nabla T] \end{aligned} \quad (2.17)$$

The expression for $\nabla \phi'_{TD}$ consists of measurable/independently calculable quantities; hence, we will call ϕ'_{TD} the measurable part of the TDPWS. In fact, when Eq. (2.17) is integrated as required by Eq. (2.6), the term involving the sum of the μ_{iN} can be recognized immediately as the formal classical expression for the potential of a concentration cell with transference. Similarly, when integrated, the sum involving the $^*Q_{iN}$ can be identified as the formal expression for the difference between the initial and steady state values of the potential of a thermocell in which the species N is the only ionic participant in the electrode half-reactions.

If undissociated species are present, the t_i in Eq. (2.17) should be reinterpreted as the stoichiometric transference numbers¹ and the results will hold in precisely the same form as that presented. This remark holds throughout the remainder of this article wherever t_i occurs.

So, with the aid of Eqs. (2.16) and (2.17), we integrate Eq. (2.7) to obtain

$$\int_a^c (\nabla \phi_{III}) \cdot dl = -j Z_{III} + (zF)^{-1} [\mu_{N,c}(T_c) - \mu_{N,a}(T_a)]$$

$$+ \int_a^c [\nabla \phi'_{TD} + (zF)^{-1} ^*S_N \nabla T] \cdot dl \quad (2.18)$$

where the electrolyte impedance Z_{III} (ohm cm²) is defined by

$$Z_{III} = \int_a^c \kappa_{III}^{-1} dl \quad (2.19)$$

and

$$j = |j|$$

In writing Eq. (2.18), we have used our assumption of uniform current density, but have left κ under the integral to account for possible changes in the conductivity with variations in the electrolyte composition.

Of all the terms in Eq. (2.18), only $\mu_N(T_c) - \mu_N(T_a)$ does not depend on thermodynamically well defined and measurable quantities, but it fortunately will shortly be combined with similar terms present in the expressions for the pd's across the double layers. These two quantities can be written as

$$\Delta \phi_a = E_a(T_a) + \eta_a(T_a) + (zF)^{-1} [\mu'_{N,a}(T_a) - \mu_{N,a}(T_a)] \quad (2.20)$$

and

$$\begin{aligned} \Delta \phi_c = & E_c(T_c) - \eta_c(T_c) \\ & + (zF)^{-1} [\mu'_{N,c}(T_c) - \mu_{N,c}(T_c)] \end{aligned} \quad (2.21)$$

Here, E_a and E_c are the Nernst half-cell potentials calculated with all species at open circuit concentrations at the indicated temperatures. The primed and unprimed chemical potentials are to be evaluated at open circuit conditions and under load, respectively.

It is important to note that the variation in $\Delta \phi_a$ and $\Delta \phi_c$ that arises from changes in the activity of the anionic species just "at" the double layer has been deliberately excluded from the overvoltages η_a and η_c (defined so both are positive). Although this is perhaps noncanonical, the reason for so doing can be inferred from our remarks regarding the term $\mu_N(T_c) - \mu_N(T_a)$ in Eq. (2.18). By explicitly displaying these terms, we simply facilitate the algebraic reduction of the expression for the cell emf into a sum of terms that have unambiguous thermodynamic significance.

To avoid any possible confusion, it is worth emphasizing that the overvoltages (or overpotentials) are not the usual quantities that appear in treatments of electrochemical kinetics.⁴ These latter quantities refer to changes in the pd across the compact double layer attributable to charge transfer, reaction, concentration, etc. overpotentials. Our quantities η_a and η_c do comprise, in part, the familiar components just mentioned, aside from the large contribution to the concentration overpotential from the anions that was excluded for thermodynamic reasons. However, they also include the additional ohmic drops across the diffuse layers and any other changes from the open circuit value of the pd across the diffuse layer arising from the passage of current.

Let us next reference the cathode open circuit half-

cell potential to the anode temperature. We first write the general form

$$zFE_c = - \left(\sum_{\gamma} \nu_{\gamma} \mu'_{\gamma} + \mu'_N - z \mu'_{e,II} \right), \quad (2.22)$$

where the sum includes each nonionic species appearing in the half-reaction with its signed stoichiometric coefficient ν_{γ} . The stoichiometric coefficient of species N has been arbitrarily set equal to one and the other ν_{γ} 's have been normalized accordingly. Also, note that μ'_{γ} is the chemical potential of neutral species γ in the gas phase. We then use the standard thermodynamic identity (2.15) to rewrite this expression as

$$zFE_c(T_c) = zFE_c(T_a) + \mu'_N(T_a) - \mu'_N(T_c) + \int_{T_a}^{T_c} (S_{\Gamma} - zS_{e,II}) dT, \quad (2.23)$$

where

$$S_{\Gamma} = \sum_{\gamma} \nu_{\gamma} S_{\gamma} \quad (2.24)$$

and S_{γ} is a gas phase partial molar entropy.

Upon adding together Eqs. (2.18), (2.20), and (2.21), we find the following expression for the potential drop between the two electrodes:

$$\phi_{c,IV} - \phi_{a,II} = V - F^{-1} \int_{T_a}^{T_c} S_{e,II} dT, \quad (2.25)$$

where

$$V = E(T_a) - jZ_{III} - \eta_a(T_a) - \eta_c(T_c) + (zF)^{-1} \int_{T_a}^{T_c} S_{\Gamma} dT + \int_a^c [\nabla \phi'_{TD} + (zF)^{-1} *S_N \nabla T] \cdot dl, \quad (2.26)$$

and

$$E(T_a) = E_c(T_a) - E_a(T_a).$$

We hasten to add that because of the presence of S_e , the pd given by Eq. (2.25) is not, in principle, a measurable quantity. The actual cell emf can be found by adding in the potential drops in the reference leads and the contact potentials. Because the phases II and IV are assumed to be identical, the sum of Eqs. (2.2)–(2.5), denoted as $\Delta\phi_{I,II}$, can be simplified to read

$$F\Delta\phi_{I,II} = \int_{T_a}^{T_c} (S_{e,II} - *S_{e,I}) dT. \quad (2.27)$$

Finally, upon combining Eqs. (2.25) and (2.27), we obtain the desired expression

$$\Delta\phi = V - F^{-1} \int_{T_a}^{T_c} *S_{e,I} dT. \quad (2.28)$$

This equation is easy to check in one limiting case. In the currentless steady state (Soret steady state), besides having $\mathbf{j} = 0$ we also have $\eta_a = \eta_c = 0$ and

$$0 = (\nabla \mu_{iN})_{T,P} + (*Q_{iN}/T) \nabla T.$$

With these simplifications, it is easy to see that Eq. (2.28) correctly reduces to the steady state value of the emf of a nonisothermal cell at open circuit.⁶

The physical origins of the terms in this equation

should be apparent from the derivation presented. Each of the terms is independently measurable or calculable from standard auxiliary thermodynamic measurements. (See the appendix for further comment on this point.) An estimate of the typical order of magnitude of each term in this equation for a molten carbonate fuel cell has been presented elsewhere.⁸

For future use, it is also worthwhile to obtain a second expression for $\Delta\phi$ by traversing the system through the external circuit. In this case, following the same procedure used to obtain Eq. (2.1), we find

$$F\Delta\phi = [\mu_{e,I}(T_c) - \mu_{e,V}(T_c)] + [\mu_{e,V}(T_a) - \mu_{e,I}(T_a)] + \int_{T_c}^{T_a} (*Q_{e,I}/T) dT + F \int_a^c (\nabla \phi_V) \cdot dl', \quad (2.29)$$

where dl' indicates a path through the external circuit, and

$$\nabla \phi_V = -j\kappa_V^{-1} + F^{-1}(\nabla \mu_e + *S_e \nabla T). \quad (2.30)$$

As before, noting the identity of phases II, IV, and V, we can simplify the above equation to read

$$\Delta\phi = jZ_V + F^{-1} \int_{T_a}^{T_c} (*S_{e,V} - *S_{e,I}) dT, \quad (2.31)$$

where Z_V is the impedance (ohm cm^2) of the external circuit

$$Z_V = \int_a^c \kappa_V^{-1} dl'. \quad (2.32)$$

From Eqs. (2.28) and (2.31), we find the identity

$$V = jZ_V + F^{-1} \int_{T_a}^{T_c} *S_{e,V} dT, \quad (2.33)$$

which will be useful in Sec. V.

III. HEAT RELEASE

A. Metallic contributions

The analysis in this section is similar to that of Haase,¹ but here we specifically recognize that an electrode acts as a source or a sink of electrons for the external circuit. The general heat conduction equation for the metallic components of the system takes the form [Haase, Eqs. (4-24.54) and (4-25.9)]:

$$(\bar{C}_p / \bar{V})(\partial T / \partial t) = \nabla \cdot (\lambda_V \nabla T) + F^{-1} \mathbf{j} \cdot \nabla H_e + F^{-1} \nabla \cdot (*Q_e \mathbf{j}) - \mathbf{j} \cdot \nabla \phi_V, \quad (3.1)$$

where \bar{C}_p is the local constant pressure molar heat capacity, \bar{V} is the molar volume, λ_V is the thermal conductivity, H_e is the partial molar electron enthalpy, and the potential gradient $\nabla \phi_V$ is given by Eq. (2.30). From mass balance for the electron concentration c_e in the steady state, we have

$$0 = F(\partial c_e / \partial t) = \nabla \cdot \mathbf{j} + j(S'_a - S'_c), \quad (3.2)$$

where the "functions" S'_a and S'_c were introduced in Sec. I. The term jS'_a thus acts as a source of electrons for the metal circuit while jS'_c acts as a sink. We combine Eqs. (3.1) and (3.2) and note the definition of the transported enthalpy

$$*H_e = H_e + *Q_e \quad (3.3)$$

and that

$$\nabla \mu_e + {}^*S_e \nabla T - \nabla {}^*H_e = -T \nabla {}^*S_e, \quad (3.4)$$

in order to obtain in the steady state

$$-\nabla \cdot (\lambda_V \nabla T) = j^2 \kappa_V^{-1} + F^{-1} T \mathbf{j} \cdot \nabla {}^*S_e + F^{-1} j^* Q_c (s'_c - s'_a). \quad (3.5)$$

The Joule heating term is easily recognized, and the second term can be expanded to give

$$T \mathbf{j} \cdot \nabla {}^*S_e = T \mathbf{j} \cdot (\nabla {}^*S_e)_{T,P} + T (\partial {}^*S_e / \partial T)_{P,X} \mathbf{j} \cdot \nabla T. \quad (3.6)$$

In this equation, both the continuous Peltier effect (first term) and the Thomson effect (second term) are represented. Because sensible concentration gradients of electrons do not exist in a metallic conductor, the Peltier term will be zero for a pure metal. The most familiar example of a system showing a nonzero Peltier effect is a bimetallic junction, but an alloy with a composition gradient will also exhibit this phenomenon. The terms of Eq. (3.5) involving the electronic heat of transport *Q_e will shortly be combined with related terms in the next section to complete the quantitative prescription of the individual electrode heat release.

B. Electrolyte contribution

We begin with the general heat conduction equation which can be found, for example, in Haase [Eq. (4-24.47)]:

$$\begin{aligned} & (\bar{C}_p / \bar{V}) (\partial T / \partial t + \mathbf{v}_0 \cdot \nabla T) \\ &= -\nabla \cdot \mathbf{J}_Q - \mathbf{j} \cdot \nabla \phi_{III} - \sum_k \mathbf{J}_k \cdot \nabla H_k \\ & - (zF)^{-1} (j_c \Delta \bar{H}_c s_c + j_a \Delta \bar{H}_a s_a) + \sum_n b_n \Delta H_n s_g. \end{aligned} \quad (3.7)$$

In writing Eq. (3.7), we have invoked the simplifying condition that no pressure change occurs in the cell and we have used the identity

$$(\nabla H_k)_{T,P} + C_{pk} \nabla T = \nabla H_k, \quad (3.8)$$

where H_k and C_{pk} are the partial molar enthalpy and constant pressure heat capacity of species k . Other undefined symbols have the following meanings: \mathbf{v}_0 is the solvent velocity, \mathbf{J}_Q is the heat current density, and \mathbf{J}_k is the Hittorf flux (relative to solvent) of species k . The final three terms of Eq. (3.7) account for the enthalpy changes accompanying the electrode reactions and for the dissolution and "evaporation" of neutral species at the gas-electrolyte interfaces. Because charge transfer occurs across the double layer, the enthalpy changes at the electrodes must be expressed in terms of the electrochemical enthalpies \bar{H}_i of all participating charged species⁴:

$$\bar{H}_i = H_i + z_i F \phi_i, \quad (3.9)$$

where ϕ_i is the electrical potential of the phase in which species i is found. We thus write

$$\Delta \bar{H}_c = \sum_\alpha \nu_\alpha H_\alpha + z \bar{H}_{e,IV} - \bar{H}_{N,a} \quad (3.10)$$

and

$$\Delta \bar{H}_c = \sum_\gamma \nu_\gamma H_\gamma + \bar{H}_{N,c} - z \bar{H}_{e,II}, \quad (3.11)$$

where α and γ serve as summation indices for the neutral species at the anode and cathode, respectively. The enthalpy changes in Eqs. (3.10) and (3.11) have been written for the reactions as they would actually occur in an operating cell, i.e., as a reduction at the cathode and as an oxidation at the anode. The enthalpy change associated with the dissolving of the n th neutral gas species in the electrolyte is denoted as ΔH_n . The rates of electron transfer at the anode and cathode are expressed as the current densities j_a and j_c , respectively, and b_n (<0 for a reactant, >0 for a product) is the rate of transfer of the n th neutral species across the gas/liquid interface in moles per $\text{cm}^2 \text{sec}$. Finally, recall that the s functions were previously defined in Sec. I.

We now specialize to convection-free steady state conditions, recognizing first that $\partial T / \partial t = 0$ and $\mathbf{v}_0 = 0$. We next use Haase' Eq. (4-24.36a):

$$\mathbf{J}_Q = \sum_{k=1}^N {}^*Q_k \mathbf{J}_k - \lambda_{III} \nabla T$$

and the identity

$$\mathbf{J}_k \cdot \nabla H_k + \nabla \cdot (\mathbf{J}_k {}^*Q_k) = {}^*Q_k \nabla \cdot \mathbf{J}_k + \mathbf{J}_k \cdot \nabla {}^*H_k \quad (3.12)$$

to simplify Eq. (3.8). We obtain

$$\begin{aligned} \nabla \cdot (\lambda_{III} \nabla T) &= \sum_k ({}^*Q_k \nabla \cdot \mathbf{J}_k + \mathbf{J}_k \cdot \nabla {}^*H_k) + \mathbf{j} \cdot \nabla \phi_{III} \\ &+ (zF)^{-1} (j_c \Delta \bar{H}_c s_c + j_a \Delta \bar{H}_a s_a) - \sum_n b_n \Delta H_n s_g, \end{aligned} \quad (3.13)$$

where λ_{III} is the local steady state electrolyte thermal conductivity and *H_k is the transported enthalpy of species k :

$${}^*H_k = H_k + {}^*Q_k. \quad (3.14)$$

By assumption only anionic species N participates in the overall electrode reactions. We therefore find for the remaining ionic species that

$$\mathbf{J}_i = 0, \quad \nabla \cdot \mathbf{J}_i = 0, \quad i \neq N. \quad (3.15)$$

For species N , we have

$$-zF \mathbf{J}_N = \mathbf{j}, \quad (3.16)$$

and from mass balance that

$$0 = (\partial c_N / \partial t) = -\nabla \cdot \mathbf{J}_N + (zF)^{-1} j (s'_c - s'_a). \quad (3.17)$$

For the neutral species involved in the overall electrode reactions, we also have the mass balance relations

$$0 = (\partial c_n / \partial t) = -\nabla \cdot \mathbf{J}_n + (zF)^{-1} j \nu_n (s'_{c,a} - s'_g). \quad (3.18)$$

The assumed uniformity of conditions in the vicinity of each electrode has been used in the above equations in order to write

$$j = |\mathbf{j}| = j_c = j_a = zF b_n / \nu_n. \quad (3.19)$$

In addition to Eqs. (3.15)–(3.19), we also use Eqs. (2.7) and (2.16) to further reduce Eq. (3.13). In so doing, we must define the quantities $\Delta {}^*Q_a$ and $\Delta {}^*Q_c$ by

analogy with Eqs. (3.10) and (3.11), and we need one additional identity

$$\nabla \mu_N + {}^*S_N \nabla T - \nabla {}^*H_N = -T \nabla {}^*S_N \quad (3.20)$$

to combine terms arising from the TDPWS with the transported enthalpy gradient of species N . Finally, we wish to "add" Eq. (3.5) to Eq. (3.13) in order to obtain the desired result:

$$\begin{aligned} -\nabla \cdot (\lambda \nabla T) = & j^2 \kappa^{-1} + F^{-1} T j \cdot \nabla {}^*S_e - j \cdot \nabla \phi'_{TD} \\ & + (zF)^{-1} T j \cdot \nabla {}^*S_N - \sum_n \mathbf{J}_n \cdot \nabla {}^*H_n - (zF)^{-1} j \left[(\Delta \bar{H}_c + \Delta {}^*Q_c) s_c \right. \\ & \left. + (\Delta \bar{H}_a + \Delta H {}^*Q_a) s_a - \sum_n \nu_n (\Delta H_n + {}^*Q_n) s_n \right]. \end{aligned} \quad (3.21)$$

With proper interpretation, Eq. (3.21) applies to the entire system: electrolyte-electrode-external circuit. Clearly, in the electrodes and circuit, only metallic and electronic properties will be nonzero, terms referring to electrolyte and dissolved species must be considered absent, and κ and λ must be taken equal to κ_v and λ_v . In the solution phase, κ and λ are, of course, properties of the electrolyte and generally only *S_e and *Q_e will be zero. Thus, the right hand side represents the net heat evolved (or absorbed) that must be balanced locally by conduction in order to maintain the steady state.

The first four terms obviously represent volume evolution or absorption of heat in the metallic and solution phases. Joule heating of either phase is readily identified with the term $j^2 \kappa^{-1}$. The second term, as discussed in Sec. IIIA, comprises both the Peltier and Thomson effects in a metal. The next two terms arise from the passage of current through an electrolyte containing steady state composition and temperature gradients. These gradients give rise to the TDPWS [cf. Eq. (2.8)] and to the transported enthalpy gradients which are apparent in Eq. (3.13). Equations (2.16) and (3.20) show quite clearly how we have rearranged these contributions into the form seen in Eq. (3.21). Thus, $j \cdot \nabla \phi'_{TD}$ represents heat evolved or absorbed by the passage of current through what we termed the measurable part of the "TDPWS." The other term $(zF)^{-1} T j \cdot \nabla {}^*S_N$ that arises from the electrolyte composition and temperature gradients is also conceptually interesting. The formal resemblance of this term to the one occurring for electrons in the metallic phase is readily apparent. We will thus succumb to the temptation to interpret this term by analogy with its metallic/electronic counterpart. As in Eq. (3.6), we write

$$\nabla {}^*S_N = (\nabla {}^*S_N)_{T,P} + (\partial {}^*S_N / \partial T)_{P,X} \nabla T,$$

from which we associate $T j \cdot (\nabla {}^*S_N)_{T,P}$ with a continuous Peltier heat effect arising from the electrolyte composition gradient through which migrate the anions, the only ionic species with a nonzero flux in the steady state. Similarly, we associate the term $T(\partial {}^*S_N / \partial T)_{P,X} j \cdot \nabla T$ with a Thomson heat effect which occurs if a temperature gradient exists in the solution through which current is passing.

Although the existence of these effects is physically

not surprising, being based on the movement of charge carriers in a conducting medium, we have found only one prior literature reference to them. In a review of thermogalvanic cells with a pure fused salt, Markov and Kuzyakin⁹ mention a thermal effect which they call a Thomson effect that arises when current is passed through a single fused salt in which a potential gradient (the usual thermal diffusion potential) exists as a result of an imposed temperature gradient. This is partially correct, but as we have seen in the above derivation, the transported enthalpy gradient also makes a conceptually important contribution to what we have termed the Peltier and Thomson effects in solution.

The remaining terms of Eq. (3.21) represent all of the heat liberated or absorbed at the electrodes because of electrochemical reactions and the transport of reactants and products to the electrode surfaces. We have included the terms involving the transport, dissolution, and "evaporation" of neutral species because of the assumed proximity of the electrolyte/electrode interface to the gas/electrolyte interface. Further development and simplification of these terms continues in the next section.

IV. SINGLE ELECTRODE HEAT RELEASE

The terms representing the heat release (in W/cm^3) "at" the anode and cathode, designated as \dot{Q}_a and \dot{Q}_c , can be obtained by inspection of Eq. (3.21):

$$\begin{aligned} \dot{Q}_a = & (zF)^{-1} j (\Delta \bar{H}_a + \Delta {}^*Q_a) s_a \\ & + \sum_\alpha [\mathbf{J}_\alpha \cdot \nabla {}^*H_\alpha - (zF)^{-1} j \nu_\alpha (\Delta H_\alpha + {}^*Q_\alpha) s_{\alpha,a}], \end{aligned} \quad (4.1)$$

$$\begin{aligned} \dot{Q}_c = & (zF)^{-1} j (\Delta \bar{H}_c + \Delta {}^*Q_c) s_c \\ & + \sum_\gamma [\mathbf{J}_\gamma \cdot \nabla {}^*H_\gamma - (zF)^{-1} j \nu_\gamma (\Delta H_\gamma + {}^*Q_\gamma) s_{\gamma,c}], \end{aligned} \quad (4.2)$$

where we have again used α and γ as summation indices for the neutral species at the anode and cathode. As mentioned, the energy dissipation arising from the transport of neutral species across the gas/electrolyte interface and to and from the electrode surface has been included in the above expressions because of the assumed smallness of the regions containing neutrals and their proximity to the electrodes.

In the above form, these equations are primarily of conceptual interest. In order to obtain a more practically useful form, we integrate these expressions, wherever they are nonzero, over the electrolyte volume and divide the result by the electrode area to find average power densities \dot{q}_a and \dot{q}_c (W/cm^2) absorbed or released at the electrodes. It is straightforward to show that many of the terms in the above expressions cancel upon integration, leaving us with just the equations

$$zF \dot{q}_a = j (\Delta \bar{H}'_a + z {}^*Q_e - {}^*Q_N), \quad (4.3)$$

$$zF \dot{q}_c = j (\Delta \bar{H}'_c + {}^*Q_N - z {}^*Q_e). \quad (4.4)$$

Here we have used a prime on the electrochemical enthalpy changes to indicate that the partial molar enthalpies of the neutral species refer to gaseous states characteristic of the uniform conditions just outside the gas/

electrolyte interfacial region. The partial molar enthalpy and heat of transport of the anions are, however, evaluated for the actual steady state conditions in the electrolyte, just outside the diffuse layer. By using the definitions of the electrochemical enthalpy and the transported enthalpy [Eqs. (3.9) and (3.14)], we may rewrite the above two expressions in another physically appealing way. We first note that

$$zF\dot{q}_a/j = \sum_{\alpha} \nu_{\alpha} H'_{\alpha} + z *H_{e,II} - *H_{N,a} - zF\Delta\phi_a, \quad (4.5)$$

$$zF\dot{q}_c/j = \sum_{\gamma} \nu_{\gamma} H'_{\gamma} + *H_{N,c} - z *H_{e,IV} + zF\Delta\phi_c. \quad (4.6)$$

The potential drops $\Delta\phi_a$ and $\Delta\phi_c$ have been defined earlier in Eqs. (2.20) and (2.21); with the aid of Eq. (2.22) and its anodic counterpart, we can write the pd's as

$$zF\Delta\phi_a = \sum_{\alpha} \nu_{\alpha} \mu'_{\alpha} - \mu_{N,a} + z\mu_{e,II} + zF\eta_a, \quad (4.7)$$

$$zF\Delta\phi_c = - \sum_{\gamma} \nu_{\gamma} \mu'_{\gamma} + z\mu_{e,IV} - \mu_{N,c} - zF\eta_c. \quad (4.8)$$

Now, after substituting for $\Delta\phi_a$ and $\Delta\phi_c$ with Eqs. (4.7) and (4.8), and using the standard identities

$$*H = \mu + T *S, \quad (4.9)$$

$$H = \mu + TS, \quad (4.10)$$

we obtain for each electrode an expression of the form

$$zF\dot{q} = j(T\Delta S^P - zF\eta), \quad (4.11)$$

where ΔS^P is the steady state Peltier entropy change for the electrode half-reaction given by the equation

$$\Delta S_a^P = \sum_{\alpha} \nu_{\alpha} S_{\alpha} - *S_N + z *S_e \quad (4.12)$$

for the anode, and by

$$\Delta S_c^P = \sum_{\gamma} \nu_{\gamma} S_{\gamma} + *S_N - z *S_e \quad (4.13)$$

for the cathode. Here it may be helpful to recall that S_n is the partial molar entropy of a neutral species in the gas phase just outside of the gas-electrolyte interface, $*S_N$ is the transported entropy of the anion under actual steady state conditions just outside the diffuse double layer, and $*S_e$ is the transported entropy of electrons in the metal electrodes. The overvoltage η appearing in Eqs. (4.7), (4.8), and (4.11) is defined consistently with our previous usage, as discussed in Sec. II.

Equations (4.11)–(4.13) are in substantial agreement with the results of Jacobsen and Broers⁵ who also considered the problem of heat release at an individual electrode, but from a less fundamental viewpoint than that presented here. There is one small difference that occurs in the expressions for ΔS^P because Jacobsen and Broers⁵ consider the initial uniform state of the electrolyte, as opposed to the present steady state analysis.

The electrode Peltier entropies, both initial and steady state, are experimentally obtainable from measurements

on thermocells.^{1,5,6,9,10} Furthermore, values of $*S_e$ are available from other thermoelectric experiments in conjunction with an extended statement of the Third Law.¹ Then, because entropies of the neutral species are also available from familiar Third Law considerations, we see that it is possible to determine values of the transported entropy for the individual anionic species, in contrast to the situation that exists regarding the partial molar entropy alone (but see the appendix for a related comment).

In general, only in the case of isothermal cell operation with identical electrolyte composition at each electrode will the transported entropies of the ions be equal. Interestingly, this implies that the sum of electrode Peltier entropies does not equal the total entropy change for the overall cell reaction. This difference is made up by the changes in transported entropies caused by temperature or composition gradients in the electrolyte.

Additional discussion of the electrode Peltier entropies, including size estimates, has been presented in another publication.⁸

V. INTEGRAL HEAT PRODUCTION

In this section, we calculate the total heat release of the cell in the steady state by integrating Eq. (3.21) over the volume of the system. We show that the result obtained agrees with the intuitive application of the First Law of thermodynamics.

The rhs of Eq. (3.21) is the net local heat release of the cell per unit volume. Integrating that equation over the cell volume to find the net heat production or absorption rate of the system \dot{u} , we easily obtain

$$\dot{u} = \dot{u}_{III} + \dot{u}_{a,c} + \dot{u}_V, \quad (5.1)$$

where

$$\dot{u}_{III} = I^2 R - I \int_a^c [\nabla \phi'_{TD} - (zF)^{-1} T \nabla *S_N] \cdot d\mathbf{l}, \quad (5.2)$$

$$\dot{u}_V = I^2 r + IF^{-1} \int_{T_c}^{T_a} T d *S_{e,v}, \quad (5.3)$$

$$\dot{u}_{a,c} = -\alpha(\dot{q}_a + \dot{q}_c). \quad (5.4)$$

Equations (5.2)–(5.4) display the physically significant contributions to \dot{u} arising from the electrolyte (III), the electrodes (a, c), and the external circuit (V). In the above equations, I is the current, R and r are the electrolyte and circuit resistances

$$R = Z_{III} \alpha^{-1},$$

$$r = Z_V \alpha_V^{-1},$$

α and α_V are the electrode and circuit cross-sectional areas, the impedances Z_{III} and Z_V are defined in Eqs. (2.19) and (2.32), and \dot{q}_a and \dot{q}_c are defined in Eqs. (4.5) and (4.6).

Now note that even when the two electrodes are at different temperatures, the change in enthalpy ΔH for the overall cell reaction is still given as

$$\Delta H = \sum_n \nu_n H'_n = \sum_{\alpha} \nu_{\alpha} H'_{\alpha} + \sum_{\gamma} \nu_{\gamma} H'_{\gamma}. \quad (5.5)$$

We now use Eqs. (2.15), (2.24), and (4.5)–(4.10) in order to rewrite the total electrode heat release as

$$zF\dot{u}_{a,c} = -I \left\{ \Delta H + zF[E(T_a) - \eta_a(T_a) - \eta_c(T_c)] + \int_{T_a}^{T_c} S_T dT + T_c(*S_{N,c} - z*S_{e,IV}) - T_a(*S_{N,a} - z*S_{e,II}) \right\}. \quad (5.6)$$

With this equation and two identities found through integrating by parts, i. e.,

$$\int_{T_c}^{T_a} T d*S_{e,v} = T_a*S_{e,II} - T_c*S_{e,IV} + \int_{T_a}^{T_c} *S_{e,v} dT, \\ \int_a^c T(\nabla*S_N) \cdot d\mathbf{l} = T_c*S_{N,c} - T_a*S_{N,a} - \int_a^c *S_N \nabla T \cdot d\mathbf{l},$$

Eq. (5.1) can finally be expressed as

$$zF\dot{u} = -I \left[\Delta H + zFV - z \int_{T_a}^{T_c} *S_{e,v} dT - Ir \right], \quad (5.7)$$

where V is defined by Eq. (2.26). However, recall the identity that we had established earlier in Sec. II, Eq. (2.33), as

$$V = Ir + F^{-1} \int_{T_a}^{T_c} *S_{e,v} dT$$

and we see that Eq. (5.7) reduces to just the expected form of the First Law applied to the total system:

$$F\dot{u} = -I\Delta H.$$

All of the enthalpy of the overall cell reaction is eventually converted to heat which must be removed from the system to maintain the steady state.

VI. DISCUSSION

This paper's principal result is an equation for the local heat release in fuel cells operating on gaseous fuel and oxidant mixtures. This result facilitates the identification of the nature of the heat release occurring in different regions of the cell and external circuit. Thus, contributions to the local heat release in the metallic circuit are attributed to Joule heating and to the Peltier and Thomson effects. Steady state heat release at individual electrodes is characterized in terms of measurable and therefore physically significant thermodynamic quantities. Local heat release in the bulk electrolyte is seen to arise from Joule heating, from current passing through the measurable TDPWS and from electrolyte Peltier and Thomson effects.

Some readers may object to our somewhat arbitrary classification of these latter three effects. As explained in Sec. III, the Peltier and Thomson terms were named by appealing to the formal analogy between $\nabla*S_N$ and $\nabla*S_e$. That $\nabla\phi'_{TD}$ can also be related to separately measurable quantities as discussed in Sec. II also influenced our choice of terminology. Regardless of how the individual terms are named, the important point is that composition and temperature gradients in the electrolyte give rise to the TDPWS and to transported enthalpy gradients that are responsible for heat release when current passes through the solution.

Finally, we risk belaboring the obvious to point out

that aside from Joule heating and overpotential losses, none of the heat release mechanisms discussed is intrinsically exo- or endothermic. The sign of the heat release depends on the values of the thermodynamic quantities involved and on the direction of current flow. Size estimates for the various contributions to the heat release in molten carbonate fuel cells have been presented elsewhere.⁸ In that case, for example, the single electrode heat release terms dominate the heat budget and are of opposite sign. In normal operation, the cathode is exothermic; the anode is endothermic.

APPENDIX: PHYSICAL SIGNIFICANCE OF EQS. (2.28) AND (3.21)

In Eqs. (2.28) and (3.21) the physical significance of the terms involving $*S_N$ and $*S_e$ might be questioned because they apparently require thermodynamic properties of individual ionic species. This is in fact not a problem, and the issue can furthermore be resolved without reference to the extended Third Law statement mentioned in Sec. IV.

First consider Eq. (2.28). Here it is apparent that we can rewrite the questionable portion of that equation as

$$\int_a^c *S_N \nabla T \cdot d\mathbf{l} - z \int_{T_a}^{T_c} *S_e dT = \int_a^c (*S_N - z*S_e) \nabla T \cdot d\mathbf{l}$$

because $*S_e$ is independent of the electrolyte composition and therefore of the integration path. As noted in Sec. IV, the quantity $(*S_N - z*S_e)$ is directly obtainable from thermocell measurements.

In Eq. (3.21) only the gradients of $*S_N$ and $*S_e$ are required. Because of this $*S_N$ and $*S_e$ need to be specified only to within an arbitrary constant, e. g., as $(*S_N - *S'_N)$ and $(*S_e - *S'_e)$ where $*S'_N$ and $*S'_e$ are evaluated at a fixed electrolyte composition (for N) and at fixed temperatures T' and T'' . The quantity $(*S_e - *S'_e)$ can be obtained from experiments on the Thomson effect in the appropriate metal. The other quantity $(*S_N - *S'_N)$ can be found by combining results of thermocell measurements with values of $(*S_e - *S'_e)$.

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