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Thermal Energy Production in an Electrochemical Cell and Heat Transfer to Its Dark Surroundings

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ABSTRACT

The theoretical formulation presented in this abridged paper was developed to predict the transient cell average temperature of a lithium-based cell during its discharge in dark, extremely low material density surroundings where the predominant mechanism of heat exchange between its shroud surface and surroundings is the thermal radiation process for a given cell discharge current and its initial temperature. The average computed temperature of an ideal lithium-based button cell, such as Li(s)/electrolyte/CF(s), is presented as a function of time in the form of plots at two discharge currents as an example of the application of the derived formulation. The presented data are briefly discussed in light of the lithium-based cell component stability and its safe discharge operation.

KEYWORDS: Lithium-based cell, thermal energy production, radiative heat exchange, thermally-safe cell discharge operation

I. INTRODUCTION

At the onset, it is mentioned that the theoretical formulation presented here is in continuation of the formulation reported in the reference [1] where the formulation accounted for the thermal energy production and heat exchange via both the natural convection and radiative heat transfer mechanisms during the discharge of the cell Li(s)/electrolyte/CF_x(s) as an example for the application of the formulation presented there to calculate the cell transient temperature as a function of time during its discharge on the earthly surface. The derived formulation presented in this paper is for the lithium-based button cell, shown in Figure 1, discharging in a dark, extremely low-density environment where the only mechanism for heat exchange is the radiative heat transfer process. The discharge operation of a galvanic cell of the type shown in Figure 1 is briefly explained below. Dimensions, masses, and physical property information about the major components of the button cell shown in Figure 1 are provided in the Supplementary Material.

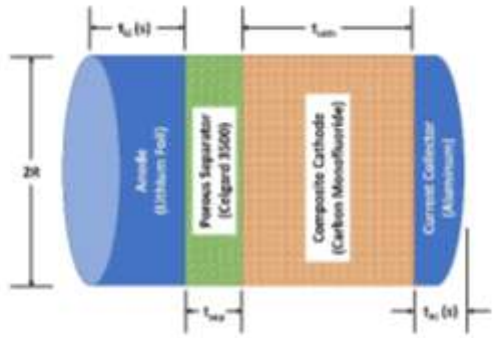

Figure 1. Sketch of the 'model' button cell: $Li(s)/electrolyte/CF_x\,(s), x = 1$ (not to scale). The button cell, as shown here, is uncased (bare) with no leads.

During the discharge period at a cell current level, the electrochemical reaction-generated lithium ions are transferred from the solid lithium foil to the electrolyte solution held in the cell porous separator, whereas the reaction-generated electrons are transferred to an external circuit (to provide the electric power for various applications such as in national defense systems, deep space explorations, cars and trucks, laptops, cell phones, calculators, smoke detectors, subway back-up power, hearing aids, clocks, etc.). Lithium ions migrate through the electrolytic solution to the electrochemically active reaction sites of the active material carbon monofluoride, CF(s), of the cell composite cathode to react with CF(s) in the presence of electrons provided by the current collector, aluminum foil, via an electronic conductor such as carbon black or graphene powder; noting that the current collector receives electrons from the cell external electrical circuit. Thermal energy is generated in the cell due to the occurrence of irreversible ionic and electronic transport processes in the cell electrolyte solution and electrodes as well as due to the electrochemical reaction kinetics charge-transfer polarization processes proceeding at the cell electrode-electrolyte solution interfaces depending on the discharge current level. The rate of change of the entire cell mass-averaged temperature depends on the thermal energy production and heat transfer from its outer skin surface to the environment surrounding it.

II. FORMULATION

The developed formulation presented in this section has been exclusively employed to predict the temperature versus time behavior of the ‘model’ button cell depicted in Figure 1. The formulation, however, with some adjustment, can be applied for the prediction of the transient average temperature for any type of galvanic cell during its discharge as a function of time or its capacity exhausted to store charge in its cathode active material.

During the cell discharge period at a constant current, I amperes, the thermal energy production rate [2] is given by:

$$\dot{P}_{thermal} = I\left[E - E_{OCV} + T\left(\frac{\partial E_{OCV}}{\partial T}\right)_{P,DOD}\right] \qquad (1)$$

where E is the actual cell electric potential [volt], E_{OCV} is the open-circuit cell potential [volt], $\left(\frac{\partial E_{OCV}}{\partial T}\right)_{P,DOD}$ is the change of E_{OCV} per unit change in cell temperature at the constant pressure and depth of cell discharge (DOD). If the information on $\left(\frac{\partial E_{OCV}}{\partial T}\right)_{P,DOD}$ is either not available or its value is so small that the numerical value of $\left[T\left(\frac{\partial E_{OCV}}{\partial T}\right)_{P,DOD}\right]$ is insignificant relative to $(E - E_{OCV})$ for a given electrochemical cell; then, it is appropriate to assume that

$$\dot{P}_{thermal} = (E - E_{OCV}) \qquad (2)$$

II. A Heat exchange between the outer surface of a galvanic cell and its surroundings via the radiative heat transfer process as if the cell is being operated in a dark perfect vacuum (extremely low mass density) space

The radiative heat flux from the outer surface of a part or component j is given by:

$$\dot{q}_{r,j} = \varepsilon_{s,j}(\sigma T^4) \qquad (3)$$

where $\sigma = Stefan - Boltzmann\ constant = 5.67051 \times 10^{-12}\ [W cm^{-2} K^{-4}]$,

$\varepsilon_{s,j} = emissivity\ of\ the\ outer\ surface\ of\ the\ cell\ component\ j$

$T = absolute\ temperature\ of\ the\ cell = absolute\ temperature\ of\ the\ cell\ component\ j, [K]$.

The rate of exchange of thermal energy between the galvanic cell and the surrounding vacuum space is given by:

$$\dot{q}_{r,cell,tot,T} = \left[\sum_j\left(\varepsilon_{s,j}A_{surf,j}\right)\right](\sigma T^4) \qquad (4)$$

where $A_{surf,j} = outer\ 'skin'\ surface\ area\ of\ the\ cell\ component, j, [cm^2]$

$$\dot{q}_{r,cell,tot,T=T_{ini}} = \left[\sum_j\left(\varepsilon_{s,j}A_{surf,j}\right)\right](\sigma T_{ini}^4) \qquad (5)$$

and $\dot{P}_{thermal} = |I(E - E_{OCV})|$ (6)

are calculated and compared.

If $\dot{P}_{thermal} > \dot{q}_{r,cell,tot,T=T_{ini}}$; then, from the very start of the ‘button’ cell discharge, cell heating would occur. If $\dot{P}_{thermal} < \dot{q}_{r,cell,tot,T=T_{ini}}$; then, from the very start of the galvanic cell discharge, cooling of the cell body would occur. For this reason, the model equation to predict the galvanic cell temperature as a function of time is developed for each of these two situations as follows.

Case 1: $\dot{P}_{thermal} > \dot{q}_{r,cell,tot,T=T_{ini}}$:

Transient thermal energy balance over a galvanic cell, such as the model ‘button’ cell (see Figure 1):

$$(rate\ of\ thermal\ energy\ accumulation) = (rate\ of\ thermal\ energy\ production) - \begin{pmatrix} rate\ of\ thermal\ energy\ loss\ from\ the\ outer\ surface \\ via\ radiative\ heat\ transfer\ process\ to\ the \\ surrounding\ vacuum \end{pmatrix} \qquad (7)$$

Representing Eq. (7) in ‘mathematical’ symbols,

$$\left[\sum_j\left(m_j C_{p,j}\right)\right]\frac{dT}{dt} = \dot{P}_{thermal} - \dot{q}_{r,cell,tot} = |I(E - E_{OCV})| - \left[\sum_j\left(\varepsilon_{s,j}A_{surf,j}\right)\right](\sigma T^4) \qquad (7\text{-a})$$

$$\left(\frac{dT}{dt}\right) = \left[\frac{|I(E-E_{OCV})|}{\sum_j(m_j C_{p,j})}\right] - \left\{\frac{\left[\sum_j(\varepsilon_{s,j}A_{surf,j})\right]\sigma}{\sum_j(m_j C_{p,j})}\right\}T^4 \qquad (8)$$

where m_j and $C_{p,j}$ are the mass and heat capacity of component j, respectively.

$$\left(\frac{dT}{dt}\right) = \alpha - \beta T^4 \qquad (9)$$

where $\alpha = \left[\frac{|I(E-E_{OCV})|}{\sum_j(m_j C_{p,j})}\right], [K s^{-1}]$ and $\beta = \left\{\frac{\left[\sum_j(\varepsilon_{s,j}A_{surf,j})\right]\sigma}{\sum_j(m_j C_{p,j})}\right\}, [K^{-3}s^{-1}]$ (10-a, 10-b)

Or, $$\left(\frac{dT}{dt}\right) = (-\beta)\left[T^4 - \frac{\alpha}{\beta}\right] \qquad (11)$$

where $$\frac{\alpha}{\beta} = \left\{\frac{|I(E-E_{OCV})|}{\left[\sum_j(\varepsilon_{s,j}A_{surf,j})\right]\sigma}\right\}, [K^4] = \left[\gamma, [K]\right]^4 \qquad (12)$$

Hence, $$\gamma = \left\{\frac{|I(E-E_{OCV})|}{\left[\sum_j(\varepsilon_{s,j}A_{surf,j})\right]\sigma}\right\}^{0.25}, [K] \qquad (13)$$

Rewriting Eq. (11) as:

$$\left(\frac{dT}{dt}\right) = (-\beta)[T^4 - \gamma^4] \qquad (14)$$

For the situation of $\dot{P}_{thermal} = |I(E - E_{OCV})|$ varying with an increase in time during the call discharge period; consequently, γ would change with time. Then, Eq. (14) should be solved for the cell temperature as a function of time using a numerical method, such as the Euler or Runge-Kutta method [3]. If $\dot{P}_{thermal} = |I(E - E_{OCV})|$ varies slowly over a significant portion of the cell discharge period that its effect is relatively small with respect to the assumption of constant $\dot{P}_{thermal}$, then Eq. (14) can be solved analytically. An example of this type of cell discharge situation at a fixed current is the discharge of a $Li(s)/electrolyte/CF_{x=1}$ cell [4].

For constant β with the assumption of invariant γ, the differential Eq. (14) is solved as follows:

$$\int_{T=T_{ini}}^{T=T} \frac{dT}{(T^4-\gamma^4)} = (-\beta)\int_0^t dt \tag{15}$$

The left-hand side integral of Eq. (15) is obtained [5] and the resultant equation is given below after simplification.

$$ln\left[\left(\frac{T-\gamma}{T+\gamma}\right)\left(\frac{T_{ini}+\gamma}{T_{ini}-\gamma}\right)\right] - 2\theta + 2\theta_{init} = -(4\gamma^3\beta)t = -\zeta t \tag{16}$$

where $$\theta_{ini} = tan^{-1}\left(\frac{T_{ini}}{\gamma}\right), [radians] \tag{17-a}$$

$$\theta = tan^{-1}\left(\frac{T}{\gamma}\right), [radians] \tag{17-b}$$

$$\beta = \left\{\frac{[\sum_j(\varepsilon_{s,j}A_{surf,j})]\sigma}{\sum_j(m_jC_{p,j})}\right\}, [K^{-3}s^{-1}] \tag{18}$$

$$\gamma = \left\{\frac{|I(E-E_{OCV})|}{[\sum_j(\varepsilon_{s,j}A_{surf,j})]\sigma}\right\}^{0.25}, [K] \tag{19}$$

$\zeta = (4\gamma^3\beta), [s^{-1}]$ and $\zeta t = (4\gamma^3\beta t), [dimensionless]$, with t in seconds. Eq. (16) can be solved to predict the cell temperature as a function of time during the cell discharge period for the case of $\dot{P}_{thermal} > \dot{q}_{r,cell,tot,T=T_{ini}}$.

Case 2: $\dot{P}_{thermal} < \dot{q}_{r,cell,tot,T=T_{ini}}$:

Transient thermal energy balance over a galvanic cell during its discharge period is given as:

$$\begin{pmatrix} rate\ of\ decrease\ of\ thermal\ energy \\ content\ of\ the\ cell\ material \end{pmatrix}$$
$$= \begin{pmatrix} rate\ of\ loss\ of\ thermal\ energy\ from\ the\ cell\ skin \\ surface\ via\ thermal\ radiation\ to\ its \\ surrounding\ vacuum\ or\ deep\ space\ environemnt \end{pmatrix}$$
$$- \begin{pmatrix} rate\ of\ thermal\ energy\ production \\ in\ the\ cell\ material \end{pmatrix} \tag{20}$$

Representing Eq. (20) in mathematical symbols,

$$\left[\sum_j(m_jC_{p,j})\left(-\frac{dT}{dt}\right)\right] = \left[\sum_j(\varepsilon_{s,j}A_{surf,j})\right](\sigma T^4) - \dot{P}_{thermal} \tag{21}$$

$$\left(-\frac{dT}{dt}\right) = \left\{\frac{[\sum_j(\varepsilon_{s,j}A_{surf,j})]\sigma}{\sum_j(m_jC_{p,j})}\right\}T^4 - \left[\frac{\dot{P}_{thermal}}{\sum_j(m_jC_{p,j})}\right] \tag{22}$$

$$\left(-\frac{dT}{dt}\right) = \beta T^4 - \alpha \tag{23}$$

where $\beta = \left\{\frac{[\sum_j(\varepsilon_{s,j}A_{surf,j})]\sigma}{\sum_j(m_jC_{p,j})}\right\}, [K^{-3}s^{-1}]$ and $\alpha = \left[\frac{\dot{P}_{thermal}}{\sum_j(m_jC_{p,j})}\right] = \left[\frac{|I(E-E_{OCV})|}{\sum_j(m_jC_{p,j})}\right], [Ks^{-1}]$ (24-a, 24-b)

Eq. (23) is expressed as:

$$\left(\frac{dT}{dt}\right) = (-\beta)\left[T^4 - \frac{\alpha}{\beta}\right] \tag{25}$$

Where $$\frac{\alpha}{\beta}\left\{\frac{|I(E-E_{OCV})|}{[\sum_j(\varepsilon_{s,j}A_{surf,j})]\sigma}\right\}, [K^4] = [\gamma, [K]]^4 \tag{26}$$

thus, $$\gamma = \left\{\frac{|I(E-E_{OCV})|}{[\sum_j(\varepsilon_{s,j}A_{surf,j})]\sigma}\right\}^{0.25}, [K] \tag{27}$$

From Eq. (25) and Eq. (26),

$$\left(\frac{dT}{dt}\right) = (-\beta)[T^4 - \gamma^4] \tag{28}$$

For constant β with the assumption of invariant γ, Eq. (28) is analytically solved as follows:

$$\int_{T=T_{ini}}^{T=T} \frac{dT}{(T^4-\gamma^4)} = (-\beta)\int_0^t dt = (-\beta t) \tag{29}$$

The left-hand side integral of Eq. (29) is obtained [5] and the resultant equation, upon simplification, leads to:

$$ln\left[\left(\frac{T-\gamma}{T+\gamma}\right)\left(\frac{T_{ini}+\gamma}{T_{ini}-\gamma}\right)\right] - 2\theta + 2\theta_{init} = -(4\gamma^3\beta)t = -\zeta t \tag{30}$$

where $$\theta_{ini} = tan^{-1}\left(\frac{T_{ini}}{\gamma}\right), [radians] \tag{31-a}$$

and $$\theta = tan^{-1}\left(\frac{T}{\gamma}\right), [radians] \tag{31-b}$$

$\zeta = (4\gamma^3\beta), [s^{-1}]$ and $\zeta t = (4\gamma^3\beta t), [dimensionless]$, with t in seconds.

Hence, Eq. (30) can be used to predict the cell average temperature as a function of time during its discharge period for the situation of $\dot{P}_{thermal} < \dot{q}_{r,cell,tot,T=T_{ini}}$; the case of the cell body-material cooling until the steady-state cell temperature is reached or the cell cathode active material capacity to store charge or lithium is exhausted.

III. COMPUTATION OF THE NUMERICAL DATA USING THE MODEL EQUATIONS

The parametric information about the 'model' button cell depicted in Figure 1 was employed to calculate the cell average temperature versus time for typical cell currents of 0.0182, 4.55×10^{-4} and the corresponding $|E - E_{theoretical,OCV}| = |E - 4.57|$ volt values. For the nonadiabatic cell discharge operation of the button cell in a dark "perfect vacuum" (i.e. extremely low mass density environment) or deep space, the cell average temperature versus time was computed from Eq. (16) and Eq. (30), respectively, for $(\dot{P}_{thermal} > \dot{q}_{tot,ini})$ and $(\dot{P}_{thermal} < \dot{q}_{tot,ini})$. At the cell discharge current of 0.0182 A (1C rate), the assumption of the loss of almost the entire cell emf was made to observe the effect of maximum thermal energy production rate on the average cell temperature.

IV. DISCUSSION OF THE PREDICTED CELL TEMPERATURE VERSUS TIME DATA

Figure 2 shows the cell average temperature plotted versus the cell discharge time for the currents of $0.0182\ A$ and $4.55 \times 10^{-4}\ A$ for the 'model' button cell discharging in a black, very low mass density environment where the heat exchange between the cell 'skin surface' and its surrounding space is only via the radiative heat transfer process. For the discharge current of $0.0182\ A$, the cell average temperature increases and reaches a steady-state value of 248°C; whereas for the discharge current of $4.55 \times 10^{-4}\ A$, the cell average temperature decreases to -100°C long before the cathode active material capacity to store charge is completely exhausted.

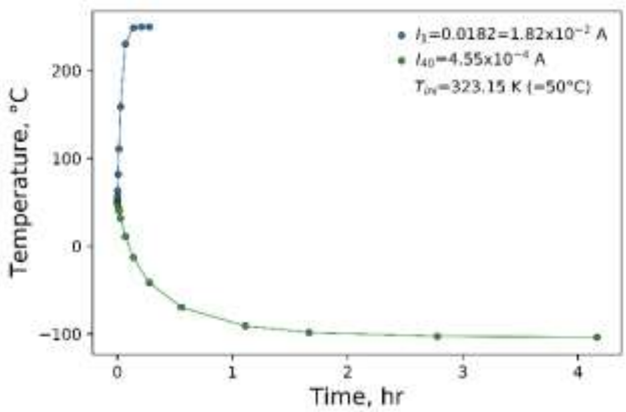

Figure 2. Cell average temperature, T [°C], versus time, t [hr], for the nonadiabatic discharge operation of the galvanic 'model' button cell shown in Figure 1.

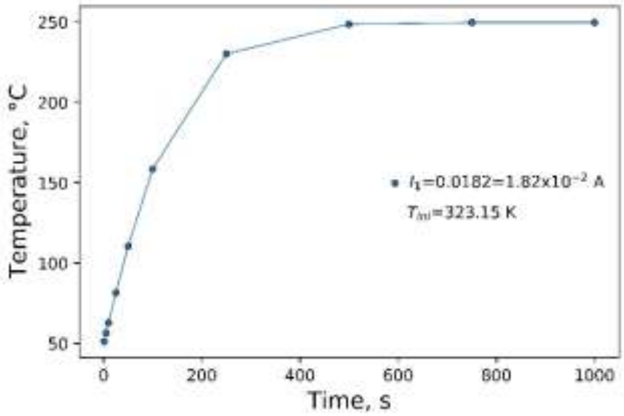

Figure 3. Cell average temperature, T [°C], versus time, t [s], for the nonadiabatic discharge operation of the galvanic 'model' button cell (amplification).

V. CONCLUDING REMARKS

The formulation presented in this paper was developed to predict the average cell temperature of a lithium-based electrochemical cell for its discharge at a given cell current and an initial temperature for nonadiabatic conditions. The predicted cell average temperature as a function of time; for the model button cell discharge for the cell current of $0.0182\ A$ and initial temperature of 323.15 K in a dark, very low mass density environment or 'deep space' where the only mode of heat transfer is the radiative process; increases and reaches a steady-state value of 248°C long before the cell capacity to store charge is exhausted. Cell operation at this current should only be continued to the extent that the cell average temperature is less than the melting point of lithium metal anode as well as the melting points of other cell components. At the discharge current of 4.55×10^{-4} A, cell cooling is predicted and the cell temperature decreases to a value of 0°C in about 5.1 minutes.

Finally, it is stated here that the developed analytical formulation presented in this paper, with some adjustment, can be employed to predict the average cell temperature as a function of time for any galvanic cell during its discharge at a fixed cell current level for operation under nonadiabatic conditions in dark, extremely low mass density environment. The predicted cell average temperature versus time information is of paramount importance for the safe operation of discharge of a galvanic cell at any cell current level. It is strongly recommended to determine the cell temperature versus time through a carefully designed experimental program to validate the model presented above.

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