



Estimation of the heat generation rates in electrochemical cells



Henry A. Catherino

Electrical and Computer Engineering Department, Oakland University, Rochester, MI 48063, USA

H I G H L I G H T S

- The heat generation rate for single cells and multi-cell batteries is estimated.
- The heat generation rate during cell venting is estimated.
- The heat generation rate is estimated without requiring a temperature measurement.
- The thermal response of a battery is a measure of its state of health.
- A simple first order differential equation models the dynamic thermal response.

A R T I C L E I N F O

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One of the earliest attempts to estimate the heat production rate in an electrochemical cell is that of Sherfrey and Brunner [1]. Their methodology and the developments that followed generated models of greater or lesser sophistication that are difficult to apply because of notation problems. In many cases, the modeling equations are referenced in subsequent papers but the cell's thermal response continues to be determined experimentally. A computationally simpler approach is developed and evaluated. This methodology follows essentially the original methodology but begins at a more fundamental level, i.e., the energy conservation law. By doing this, the critical parameters are easily addressed in a more systematic way and produce quantitative results suitable for more extended modeling and simulation exercises. These quantitative parameters include (1) the heat generation rate in multi-cell batteries, (2) the heat generation rate during cell venting, (3) the thermal response as a measure of the state of health of a battery, (4) an estimator of the heat generation rate that does not require a temperature measurement and (5) a first order differential equation that models the dynamic thermal response as a function of the power input (or output) of the battery.

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1. Introduction

The objective of this effort is to develop a method for estimating the rate of heat generation in an electrochemical cell during charge and discharge. It is understood that this objective has been the focus of a number of earlier studies. The early paper that is most often referenced as the starting point for estimating the thermal response of electrochemical cells is that of Sherfrey and Brunner [1].

The methodology presented there is to break the heat generation rate into a reversible and an irreversible part. The reversible heat component is associated with the Entropic changes taking place in the cell as current passes and the electrochemical reaction proceeds. The irreversible part is the contribution of Joule heating resulting from the fixed resistive components within the cell and

the consequence of the polarization at each of the cell electrodes. Basically,

$$Q_{\text{cell}} = Q_{\text{Entropic}} + Q_{\text{Joule}} + Q_{\text{Electrode Polarization}} \quad (1)$$

The studies that followed focused on determining the power components associated with each of these parts. A sampling of applications of this methodology appears in the following references [2–8].

As a practical matter, the developed models used to estimate the heat generation rate are mathematically barely tractable. There also appears to be a tendency only to reference the modeling equations and then the sought after heat generation data is measured experimentally. In this study, a methodology is being sought to allow for a more convenient way to estimate the thermal response of electrochemical cells.

As a point of clarification, the polarization resistance used in the text that follows includes the summation of all of the resistances. The polarization resistance is determined as the difference between

E-mail address: henry.catherino@comcast.net.

Nomenclature			
A	area (m^2)	Q_{Entropic}	rate of heat generation of absorption associated with Entropic changes (W)
C_p	heat capacity ($\text{J}^\circ\text{C}^{-1}$)	$Q_{\text{irreversible}}$	rate of irreversible heat generation (W)
E	cell or battery voltage (V)	$Q_{\text{Polarization}}$	rate of heat generation associated with cell polarization (W)
E_{EQ}	equilibrium voltage (V)	Q_{Joule}	rate of heat generation from resistive components (W)
F	Faraday	$Q_{\text{reversible}}$	rate of reversible heat generation (W)
h	heat transfer coefficient ($\text{W m}^{-2} \text{ }^\circ\text{C}^{-1}$)	R	the gas constant ($\text{LAtm mol}^{-1} \text{ K}^{-1}$)
I	current (A)	T	cell temperature ($^\circ\text{C}$)
m	number of cells wired in series	T_a	ambient temperature ($^\circ\text{C}$)
n	number of equivalents per mole	T^*	absolute temperature (K)
n^*	number of moles	V	volume (L)
P	pressure (Atm)	ΔG	Gibbs Free Energy of Reaction (J mol^{-1})
Q_{battery}	rate of heat generation in a battery (W)	ΔH	Enthalpy of Reaction (J mol^{-1})
Q_{cell}	rate of heat generation in a cell (W)	ΔS	Enthalpy of Reaction (J mol^{-1})
$Q_{\text{ElectrodePolarization}}$	rate of heat generation associated with electrode polarization (W)		

the equilibrium voltage (at zero applied current) and the voltage measured at any specific applied current. So, in the discussion that follows

$$Q_{\text{cell}} = Q_{\text{Entropic}} + Q_{\text{Polarization}} \quad (2)$$

and so for the net polarization

$$Q_{\text{polarization}} = Q_{\text{Joule}} + Q_{\text{Electrode Polarization}} \quad (3)$$

The Entropic term refers to the heat generated by virtue of the structural changes taking place in the transition from reactants to products resulting from the electrochemical reaction taking place in the cell. This transition involves the energy changes associated with the changes in the Entropy between the reactants and the products. Since this quantity is independent of how fast the reaction takes place (it depends only on the initial and final states), it is the reversible part of the heat generated in the reaction.

$$Q_{\text{cell}} = Q_{\text{reversible}} + Q_{\text{irreversible}} \quad (4)$$

In the text that follows, the Joule heating effect is understood to include the entire heating consequence of current passing through all of the resistances in the cell including the resistance associated with the electrode polarizations. Although the discussion that follows addresses battery systems, it is to be understood that the analysis can apply to electrochemical cells generally.

2. Method

The methodology developed here basically takes a slightly different tack on the estimation of the heat generation. Rather than attempt to determine the heat generation rate directly, the approach is to back it out of the conservation laws. It is worthy of note, this methodology gives no information about the mechanistic descriptions that are dealt within substantial detail in the cited references. The energy conservation law requires that

$$C_p \frac{dT}{dt} + hA(T - T_a) + \frac{I}{nF} \Delta H = EI \quad (5)$$

Many of the terms from this equation are well known but in some of the terms there are some tricky details that are easily overlooked. The first term on the left is the power involved in heating the thermal mass of the cell. The heat capacity at constant pressure (C_p) of the cell is the summation of the specific heat–mass product of the individual cell components. This term also identifies

the equation as a first order differential equation for the rate of temperature (T) change with respect to time. The second term on the left is the power lost to (or gained from) the environment by the cell across a thermal gradient. The term, hA , is the heat transfer coefficient (h) multiplied by the area (A) of the mass undergoing the heat transfer. It is critical to note that h is not the convective heat transfer coefficient. It is unfortunate that the same symbol is used in textbooks to represent both quantities without sufficient explanation. In this case, h , includes the power contributions of conduction, convection and radiative heat transfer. Although the radiative component is known to occur across a thermal gradient of absolute temperatures where the temperatures are raised to the fourth power, it can be shown that in the ranges of temperature normally experienced by batteries, the usual temperature gradient as shown in Equation (5) is an excellent approximation. As a point of explanation, this approximation applies whenever the absolute temperature of the cell is approximately equal to the absolute temperature of the environment. The third term on the left hand side is the power involved in driving the chemical reaction in the battery. It is normally the case that this is a single process so that the Enthalpy term is that of the energy storage reaction in the battery. Perhaps a better way of stating this is to say that, in this case, a single chemical process is the major and predominating contributor to the observed Enthalpy of Reaction during the charging and discharging of the cell. One measure of the fidelity of this approximation is the current efficiency of the reaction. F , is the Faraday and n is the number of moles of electrons produced per mole of reactant involved in the reaction. Or more precisely, n is the number of equivalents per mole of reactant. The Enthalpy of Reaction is understood to be a one dimensional vector quantity so as to signify that its sign changes depending on the direction of the reaction. By convention, its magnitude is given a negative sign whenever the thermodynamic system under consideration loses energy and positive when it gains energy. The Enthalpy of Reaction is not to be confused with the Heat of Reaction. The former is a vector whereas the latter is a scalar. The absolute value of the Enthalpy of Reaction equals the Heat of Reaction. The current, I , can also become a problem here. Current is normally considered a scalar quantity. However, in the application of Kirchhoff's Laws as applied in circuit analysis, the current is given a positive or negative value depending on its direction. This makes the current magnitude appear to have a vector-like property. What complicates this is that the selection of the initial reference direction is arbitrary. That is, the direction of the positive current is arbitrarily selected and once it has been selected, the negative current is then established as

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