

A General Formulation for Theoretical Study of Thermal Runaway in Batteries

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1 Introduction

Thermal-runaway (TRA) is one of the most challenging phenomena in valve regulated lead-acid (VRLA) batteries. Although many researches have been done on this topic (see for example [1–3]), its exact cause is not well known yet. In the present work, a general thermal-electrochemical formulation is presented by which thermal runaway in any battery type including lead-acid batteries can be studied. The main heat sources arising from electrochemical reactions are divided into reversible and irreversible parts and it is shown that only irreversible parts contributes to heat generation and the reversible parts are canceled out in the positive and negative electrodes. This formulation is applied to lead-acid batteries and the results are discussed.

2 Governing equations

A battery can be considered as a porous, multi-phase and multi-component medium whose energy content varies during charge and discharge. Generally, batteries are made of two porous electrodes with a separator in between. Either sides of the separator may have some ribs which acts as an electrolyte reservoir and provides more electrolyte for the electrodes. A general model of such a battery can be seen in Figure 1. This model includes a current collector at the center of positive electrode ($x = 0$), a porous positive electrode, and electrolyte reservoirs (the rib space), separator, a porous negative electrode and a current collector at the center of the negative electrode ($x = l$). As it was mentioned, the electrolyte reservoir may also exist in contact with the negative electrode depending on the design of the separator.

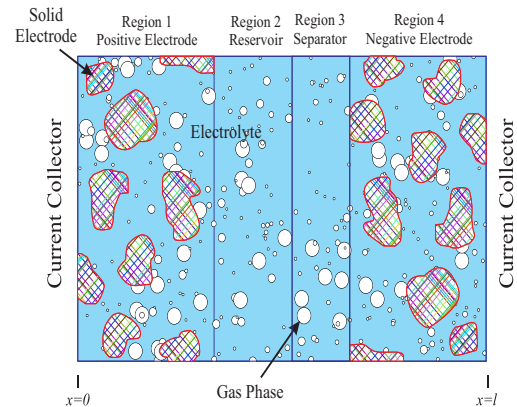


Fig. 1. Schematic illustration of an electrochemical cell.

Different phases are in contact according to chemical and electrochemical reactions, mixing and phase change. During charge and discharge, a set of surface reactions occur at the electrode/electrolyte interface as follows:

$$\sum_j \nu_j M_j^{z_j} = n_j e^- \quad (1)$$

in which ν_j is the stoichiometric coefficient, M_j is a general formula for each species, z_j is the charge number and n_j is the number of transferred electrons.

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Table 1

The governing equations of battery dynamics.

$$\frac{\partial(\varepsilon_k \rho_k)}{\partial t} + \nabla \cdot (\varepsilon_k \rho_k \langle \vec{v}_k \rangle^k) = \sum_m \Gamma_{km} \quad m \neq k \quad (2)$$

$$\frac{\partial}{\partial t} (\varepsilon_k \rho_k \langle \vec{v}_k \rangle^k) + \nabla \cdot (\varepsilon_k \rho_k \langle \vec{v}_k \rangle^k \langle \vec{v}_k \rangle^k) = -\varepsilon_k \nabla \langle p_k \rangle^k + \nabla \cdot (\mu_k^* \varepsilon_k \nabla \langle \vec{v}_k \rangle^k) + \varepsilon_k \langle \vec{B}_k \rangle^k - \varepsilon_k^2 \frac{\mu_k}{K k_{rk}} \cdot \langle \vec{v}_k \rangle^k \quad (3)$$

$$\frac{\partial(\varepsilon_k \langle c_k \rangle^k)}{\partial t} + \nabla \cdot (\varepsilon_k \langle c_k \rangle^k \langle \vec{v}_k \rangle^k) = \nabla \cdot [(D_k^{\text{eff}} + D_a) \nabla \langle c_k \rangle^k] + \sum_m (J_{km}^d + J_{km}^\Gamma) - \langle \vec{i}_k \rangle \cdot \nabla \left(\frac{t_k}{zF} \right) \quad (4)$$

$$\nabla \cdot (\sigma^{\text{eff}} \nabla \langle \phi_e \rangle^e) + \sum_m I_{sm} = 0 \quad m \neq s \quad (5)$$

$$\nabla \cdot (k^{\text{eff}} \nabla \langle \phi_e \rangle^e) + \nabla \cdot (k_D^{\text{eff}} \nabla \langle \ln c_i^e \rangle^e) + \sum_m I_{em} = 0 \quad m \neq e \quad (6)$$

$$\frac{\partial(\rho_k c_{pk} \langle T_k \rangle^k)}{\partial t} + \nabla \cdot (\langle \vec{v}_k \rangle^k \langle T_k \rangle^k) = \nabla \cdot \lambda_k \langle T_k \rangle^k + q_k \quad (7)$$

The system of governing equations of battery dynamics shown in Table 1, consists of the following equations: (a) Conservation of mass (Eq. (2)), (b) Conservation of momentum (Eq. (3)), (c) Conservation of species (Eq. (4)), (d) Conservation of electrical charge (Eqs. (5) and (6)) and (e) Balance of energy (Eq. (7)). This system of equations, the necessary auxiliary equations and different parameters together with the methods of solution are repeatedly discussed in the literature (just for some example [4,5]), hence will not given here.

As it is obvious from Eq. (7) that the only source term in the energy equation is q_k which is responsible for temperature rise in a battery. This term is a summation of Joule heating and the heat generated from chemical and electrochemical reactions. As a consequence, if one wants to study the temperature rise in a battery, this term should be focused in detail. Therefore, in the present work the source term in energy equation is considered and studied with more detail.

3 Heat Generation Inside the Battery

The source term can be divided into generation and dissipation. Generation is due to the electrochemical reactions and Joule heating inside the battery. In addition to heat generation, heat removal also occurs by dissipation of energy to the ambient. Therefore, to have a complete study, both terms should be considered.

A general heat balance for any battery system was studied by Bernardi et al. [6]. According to Bernardi and neglecting the enthalpy of mixing, heat capacity and phase change, the general heat balance of a battery can be simplified as:

$$q = IV + \sum_l \bar{i}_l \left[T^2 \frac{d}{dT} \left(\frac{U_{l,\text{avg}}}{T} \right) \right] \quad (8)$$

During discharge of a battery, the chemical energy converts to electrical energy. The maximum electrical energy can be obtained when the reaction is reversible. In that case, the reversible electrical work can be calculated from the following equation:

$$IV_{\text{rev}} = \sum_l \bar{i}_l [U_{l,\text{avg}}] \quad (9)$$

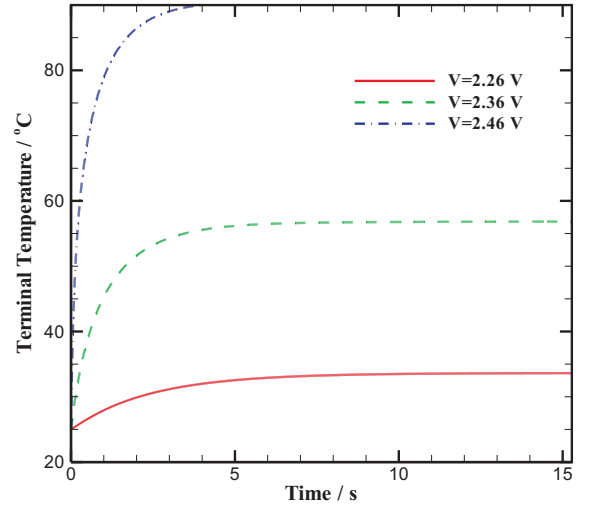


Fig. 2. Variation of temperature vs. time.

The difference between the actual voltage and reversible voltage is called overvoltage ($\eta = V - V_{\text{rev}}$) which represents the irreversibility such as Ohmic drop, charge transfer overpotential and mass transfer limitations. The production of overvoltage and current is called polarization heat which consists of Joule heating inside the battery and energy loss at electrodes.

In addition to polarization heat, the reaction enthalpy term includes the entropic heat which is

$$q_{\text{rev}} = - \sum_l \bar{i}_l \left[T \frac{\partial U_{l,\text{avg}}}{\partial T} \right] \quad (10)$$

Equation (9) and (10) represent the generated power and heat in a reversible, isothermal process. The reversible work can be calculated by means of the variation of Gibbs free energy and the reversible entropic heat which is related to the change of the system entropy. Substituting the equations (9) and (10) into equation (8) results into:

$$q = \left[IV - \sum_l \bar{i}_l U_{l,\text{avg}} \right] + \sum_l \bar{i}_l \left[T \frac{\partial U_{l,\text{avg}}}{\partial T} \right] = \sum_l \bar{i}_l \eta_l + \sum_l \bar{i}_l \Pi_l \quad (11)$$

where η is the surface overpotential and Π is called Peltier coefficient. The above equation shows that the generated heat in an electrochemical electrode consists of two parts; namely $\sum_l \bar{i}_l \eta_l$, which is the irreversible part which is always positive and contribute to thermal rise. and $\sum_l \bar{i}_l \Pi_l$ which is the reversible part and changes sign in charge and discharge.

According to Newmann [7], and by neglecting the Dufour energy flux, the Peltier coefficient can be written as: $\Pi_l = T \frac{\partial U_l}{\partial T} = \frac{T}{nF} \sum_l \nu_l \bar{S}_l$, in which, \bar{S}_l is the partial molar entropy of species l .

Beside the heat generated by electrochemical reactions, Joule heating should also be considered as a main source of heat generation inside the batteries.

In addition to heat generation in an electrochemical cell, heat dissipation plays an important role in its thermal behavior. There are different heat dissipation mechanisms in a battery cell namely: heat convection to surrounding, radiation to ambient and dissipated heat by exhausting gases. Therefore, the total heat dissipation can be calculated as $q_{\text{diss.}} = q_{\text{conv.}} + q_{\text{rad.}} + q_{\text{exh.}}$

4 Case Study

To show the application of the above general formulation, a VRLA cell is chosen as a test case. The cell is charged from a fully-charged state ($SoC = 1$). Therefore, main reactions exist no more and all the input charges are spent for driving the side reactions.

The simulation is carried on for three different float charging voltages namely $V = 2.26, 2.36$ and 2.46 Volts. For each floating voltage, the irreversible and reversible parts of heat sources expressed by Eq. (11) are integrated over the positive and negative electrodes and plotted.

Not presented in this paper, the Joule heating part is negligible since the cell is fully charged hence the internal resistance of the cell is very small.

5 Results and Discussion

The variation of cell temperature for different floating voltages is plotted in Fig. 2. As it can be seen, for floating voltages $V = 2.26$ and 2.36 the cell temperature reaches a steady state below 60°C . This means that for this cell, under such condition, TRA never happens. But when the

floating voltage is 2.46, the cell temperature rises rapidly and over 60°C. This means that the cell undergoes TRA.

To have a better understanding about the cause of TRA, let us examine the different parts of heat sources inside the cell. Figures 3(a) to 3 show these parts. In all the cases, it is obvious that the reversible parts of heat sources in the positive and negative electrodes cancel out each other hence do not contribute to heat generation.

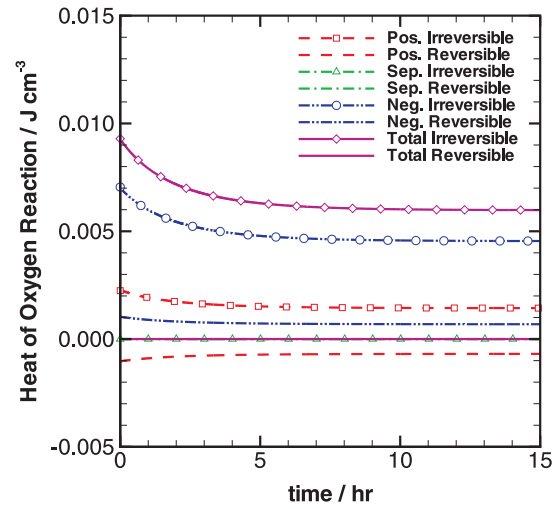
On the other hand, from the result one can conclude that the only heat source that remains inside the battery is the irreversible part of oxygen cycle. This part in both electrodes generates a specific amount of heat which in turn causes the temperature rise of the cell.

6 Acknowledgements

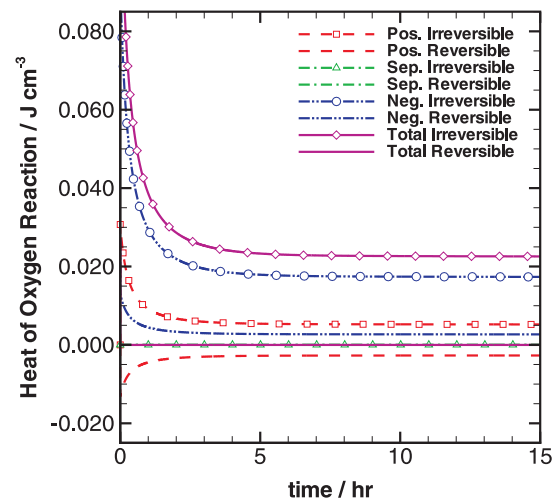
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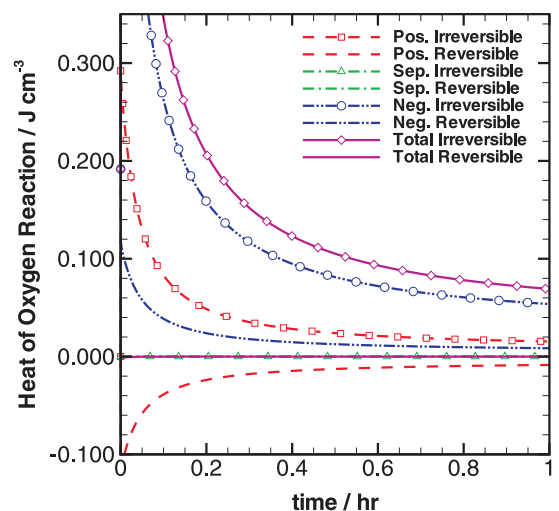
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(a) $V = 2.26 \text{ V}$



(b) $V = 2.36 \text{ V}$



(c) $V = 2.46 \text{ V}$

Fig. 3. Variation of different parts of heat source for different float charging.