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Simulation of temperature rise in Li-ion cells at very high currents

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HIGHLIGHTS

- A radial mass-transport coefficient is used to modify the thermal-electrochemical Dualfoil model.
- Simulation of current and temperature under very-high-current discharge is achieved.
- Mass-transport limitation decreased by high cell temperature causes a rapid temperature rise.
- Effective heat transfer outside the cell center is critical.

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ABSTRACT

The Dualfoil model is used to simulate the electrochemical behavior and temperature rise for MCMB/ $LiCoO_2$ Li-ion cells under a small constant-resistance load, approaching a short-circuit condition. Radial mass transport of lithium from the center of the pore to the pore wall has been added to the model to describe better current limitations at very high discharge currents. Electrolyte and solid-surface-concentration profiles of lithium ions across the cell at various times are developed and analyzed to explain the lithium-ion transport limitations. Sensitivity tests are conducted by changing solution and solid-state diffusion coefficients, and the heat-transfer coefficient. Because diffusion coefficients increase at high temperature, calculated discharge curves can show currents dropping initially but then rising to a second peak, with most of the available capacity being consumed in the second peak. Conditions which lead to such a second peak are explored.

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1. Introduction

Li-ion batteries are widely used in mobile technologies because of their high energy and power density. The usage extends from small cell phones to electric vehicles, and even to airplanes. With bigger batteries, more concern on battery safety is aroused. Reviews of thermal issues in Li-ion batteries point out that the safety problem results from thermal runaway causing fire and explosion, and it is clear that no existing thermal-management strategy or technology meets all these requirements [1,2].

The key to battery safety is to manage the temperature properly. A battery can be safe under moderate operating condition (e.g., low current), but is compromised for larger cells and higher currents (low-resistance loads). The temperature rise of a Li-ion cell is determined by heat produced internally and heat exchanging with the environment during operation, and can be predicted using a thermal-electrochemical-coupled model. The coupling of thermal and electrochemical models arises from temperature-dependent physicochemical properties and the heat-generation equation. The history of thermal-electrochemical-coupled models has been given in Refs. [3,4]. Internal and external short-circuit tests are routine for Li-ion-battery safety tests in industry, and high temperatures that result from extremely high discharge current are sometimes observed during short-circuit tests [5–8]. It is urgent to interpret the various experimental phenomena fundamentally by simulation. The goal of this work is to use the thermal-electrochemical-coupled Dualfoil model to simulate the temperature rise in Li-ion cells at very high currents and understand fundamentally the quick temperature rise to above 120 °C during short-circuit tests.

The Dualfoil model is a powerful and flexible mathematical model that can be used to treat the coupled phenomena in a

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porous-electrode battery system (including Ni-MH and Li-ion batteries). It has six coupled differential equations (a material balance on the electrolyte, a material balance on the solid intercalant, Ohm's law in the liquid phase, Ohm's law in the solid phase, a current balance that relates the flow of current between the solid and liquid phases, and a Butler−Volmer kinetics expression) [9]. Review of the Dualfoil model and more detailed descriptions are given in Refs. [10−12]. A clear schematic of the Li-ion cell in Dualfoil modeling has been given in a recent reference [13]. Unlike other commercial simulation programs, such as COMSOL, MATLAB, the Dualfoil program based on Dualfoil model is open access, and can be downloaded from our website and has low computational demands [14]. The Dualfoil software employs Newman's BAND (j) subroutine, which is a finite-difference method (FDM) used to simulate electrochemical systems for more than four decades. The model has been improved over the years to include impedance [15,16], a better thermal balance [17−21], additional battery chemistries [22−25], etc., and has more and more applications [13,26−29]. When discharging under nonequilibrium conditions such as very high currents, the distribution of current, potential, and lithium concentration inside the porous electrode is nonuniform, leading to increased internal resistance, producing large heat, and thus increasing the cell temperature. The transport properties in the electrolyte and solid phases and the electrochemical reaction rate can be increased by temperature rise following some empirical relationship, and an Arrhenius exponential relationship is usually adopted. This temperature rise in turn will cause more current to pass the cell. This kind of positive feedback between temperature and those physicochemical properties can lead to overheating issues and must be dealt with [30]. Simulation can give deep insight into the internal behavior of batteries, and can provide information that is difficult or impossible to obtain by experiment [31]. A good review of model development and simulation of Li-ion cells at different length and time scales is given by reference [29].

When simulating the thermal and electrochemical behavior of a Li-ion cell at abnormally large discharge currents, there are two difficult problems for the Dualfoil model. The first problem is that the salt concentration can be reduced substantially and even try to go negative locally when the discharge current is very high, and the Dualfoil program has shown a tendency to stop short of the full simulation due to lack of convergence. For a real electrolyte system, the local salt concentration cannot be zero or negative. This issue has always been present in the model, and various approximations have been developed to bypass the issue for a given set of conditions. In this work, we develop a radial mass-transport coefficient of solution diffusion to solve the convergence problem. Most previous porous-electrode models consider only mass transport along the pores and ignore radial transport in the pores. This means that the absence of a radial transport limitation allows even the most dilute solutions to support large currents. To address this issue, a radial mass-transport condition (i.e., limiting current) has been introduced into the model. With discharge at extremely high currents, the local salt concentration can only get very close to zero, and the transfer current will approach its limit. This modification to the Dualfoil model results in smooth operation and allows the program to run at virtually all currents, and dramatically reduces the running time. The model modification and derivation are presented in the next section.

The second problem is how to compute the variable solid diffusion for lithium ions with more accuracy and in short computational time. In this work, lithium ions are still assumed to diffuse radially in the spherical solid particle following Fick's laws; and with a solid diffusivity which does not vary, the concentration profile can be computed efficiently by the Duhamel superposition integral (which is an advanced mathematical method [32]) as done in the original Dualfoil model. There are many mathematical methods for treating solid diffusion in simulation research, and the usage of some approximate approaches for simulations of Li-ion solid transport in batteries is reviewed [33]. More detailed discussion of the advantages and disadvantages of using Duhamel superposition integral to compute with a variable solid diffusion is shown in a later section.

In this paper, the thermal-electrochemical model (Dualfoil) is used to simulate the electrochemical behavior and temperature rise for an MCMB/$LiCoO_2$ cell discharging under a constant-resistance load. A set of parameters is used in the base-case simulation for a small resistance load (R_{load}) of 0.2 × 10^{-3} Ω m^2. Then sensitivity tests on some parameters are conducted and investigated. By looking at very high currents (approaching a short-circuit condition), we hope to learn more about parameters which can impact overheating in batteries.

2. Model

In the Dualfoil model, the six coupled differential equations are solved numerically and simultaneously at each time step. A summary of the equations is presented in Table 5 in the appendix; it is noted that only the kinetic equation is modified by a denominator. A function has been developed which describes the radial mass transport of lithium ions in the pore. Starting with the original kinetic B−V (Bulter−Volmer) equation in the model, (i is transfer current density, j is transfer flux)

$$i = jF = i_0\left[\exp\left(\frac{\alpha_a F}{RT}\eta_s\right) - \exp\left(-\frac{\alpha_c F}{RT}\eta_s\right)\right] \qquad [1]$$

insert a new term in front of the cathodic term

$$i = jF = i_0\left[\exp\left(\frac{\alpha_a F}{RT}\eta_s\right) - \left(1-\frac{i}{i_{lim}}\right)\exp\left(-\frac{\alpha_c F}{RT}\eta_s\right)\right] = \frac{\left[\exp\left(\frac{\alpha_a F}{RT}\eta_s\right) - \exp\left(-\frac{\alpha_c F}{RT}\eta_s\right)\right]i_0}{1-\frac{i_0}{i_{lim}}\exp\left(-\frac{\alpha_c F}{RT}\eta_s\right)} \qquad [2]$$

Physically this is intended to represent a term like $c_0/c_{bulk} = 1-i/i_{lim}$, where i_{lim} is proportional to the bulk or average concentration in the pore and can be calculated roughly by equation (3). c is the average concentration already calculated by Dualfoil in the pores, and r is the radius of the pore, which represents a diffusion-layer thickness and can only be estimated. At the cathode, the transfer current is negative, and i_{lim} should be negative.

$$|i_{lim}| = \frac{FcD}{r} \qquad [3]$$

The new term denominator is added in the new B−V equation as following.

$$i = jF = i_0\left[\exp\left(\frac{\alpha_a F}{RT}\eta_s\right) - \exp\left(-\frac{\alpha_c F}{RT}\eta_s\right)\right]\Big/\text{denominator} \qquad [4]$$

where

$$\text{denominator} = 1+\frac{coef}{c}\exp\left(-\frac{\alpha_c F\eta_s}{RT}\right) = 1-\frac{i_0}{i_{lim}}\exp\left(-\frac{\alpha_c F}{RT}\eta_s\right) \qquad [5]$$