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A nonlinear equivalent circuit model for lithium ion cells

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HIGHLIGHTS

- ► Nonlinear equivalent circuit model for lithium ion cells.
- ► The circuit elements are based on charge transfer reaction and variable resistances.
- ► The potential drops are the natural state variables rather than cell state-of-charge.
- ► A pulse protocol was predicted accurately within an error of 50 mV.
- ► Voltage predicted without parameter re-estimation, amenable as an on-board algorithm.

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ABSTRACT

A nonlinear equivalent circuit model for lithium ion cells is developed where the circuit elements are based on electrochemical processes like charge transfer reaction, and variable resistances that are functions of the state variables. The potential drops are the natural state variables rather than cell state-of-charge (SOC). A commercial pouch cell consisting of composite positive and meso-carbon microbeads (MCMB) negative electrodes is analyzed. The state space model developed consists of the current balance which forms the state variable evolution equation and voltage balance which forms the output equation. The global set of parameters for a two pair resistor–capacitor circuit is calculated by solving the model equations consistently and minimizing the error with HPPC (Hybrid Pulse Power Characterization) pulse voltage at few SOCs. The entire HPPC protocol is predicted by the model accurately within an error of 50 mV. The model is validated using the full depth charge–discharge experiments. The model is used to resolve the overall cell potential into potential drops due to individual processes, yielding insights into controlling mechanisms. The variable resistor formalism enables cell voltage prediction without parameter re-estimation and hence can be developed as an on-board algorithm.

1. Introduction

The lithium ion battery technology has been proven as an alternate energy source in electric vehicle or hybrid electric vehicle applications due to its high energy density, light weight, low self-discharge and other features [1]. To exploit the advantages of different lithium compounds, recent positive electrode compositions consider multiple active materials. Although the technology has proven successful [2], and there are modeling efforts from an electrochemical approach [3], an accurate model that can be used as a predictive and on-board tool that represents various cell processes of a commercial cell is still wanting.

Equivalent electric circuit representations for cells [4,5] have received much importance due to the conceptual simplicity that enables the models to be integrated with control algorithms at a system level, and is potentially suitable for on-board applications in an automobile. The pertinent variables do not have spatial dependence, and the model equations based on electrical circuit theory are solved as a set of ordinary differential equations (ODEs). An equivalent circuit model should be robust, accurate over a wide range of operating conditions, and easy to compute.

The equivalent circuit model equations can be formulated and solved either in the time domain or in the frequency domain. In the time domain formulation, although the models are successful in representing the cell charge–discharge data, most of the approaches are purely empirical. A direct connection of the

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parameters with the electrochemical processes is seldom attempted restricting the predictability of the model. The equations are often linearized and solved as difference equations, and the parameters are estimated at every solution time step. This solution procedure results in a large number of uncorrelated parameters, which often lead to unphysical values that depend on the time step used in the solution method. The model parameters are reported in terms of a system variable [6,7], typically the cell state-of-charge (SOC). The functional dependence is typically built-in posteriori and ad hoc.

In the frequency domain formulation, the physical basis of the parameters is sought predominantly through impedance analysis [8]. Impedance analysis is conducted around an equilibrium state and parameters so obtained cannot be used directly to non-equilibrium scenarios like constant power or constant current or pulse cell charge–discharge data. Hence, there are only a few approaches where impedance spectrum [9–13] is used to predict the discharge behavior of commercial cells. In the present work, a time domain formulation of the equivalent circuit model with physics-based functional forms for the model parameters is proposed.

The state space approach represents the state of the system using a minimal set of state variables. Each state variable is obtained by solving its own evolution equation, and the remaining process variables are obtained from the state variables. The state space approach is used extensively in the control systems theory and is amenable for large scale system simulations as in vehicle models. State space models are applied to equivalent circuit cell models predominantly in association with a Kalman filter algorithm, thus making the solution scheme inherently discrete in time [14], with varying parameter values. This approach is used to estimate the equilibrium potential V_0 and the corresponding SOC [15–19] leading to various SOC estimation algorithms [20] applied to drive profiles [21]. The state space approach in conjunction with Kalman filter algorithm is also used with the electrochemical model [22–24].

An approach that combines the mathematical simplicity of the equivalent circuit model and the rigor of the state space approach, with functional forms of parameters from electrochemical or physical processes, would result in numerically robust models. Such models could be used to obtain insights into the controlling processes and potentially be used as a predictive or a design tool, in addition to a characterization tool.

In this work a nonlinear equivalent electric circuit model for a commercial cell is developed. The zero current regime of the HPPC (hybrid pulse power characterization, explained later) data is analyzed to establish the adequate circuit to be used. A general equation for an N pair RC is derived, and analytical solutions for special cases obtained. The key step of identification of the state variables is done by analysis of the electrochemical processes. The electric circuit thus considered in this work consists of elements that represent the Butler–Volmer reaction and nonlinear variable resistances. It is observed that the overpotential, or the potential drops across the circuit elements are the natural state variables rather than the cell state-of-charge. It is to be noted that the effects of overpotential on cell processes have not been studied in detail till recently [25]. This formulation enables a direct solution procedure, reduces the number of parameters and empiricism. The parameters are estimated by minimizing the error between the model output and the HPPC data at select SOCs. The predictability of the model is demonstrated at other SOCs as well as the entire HPPC protocol. The model is validated using full depth charge–discharge data that includes Ragone (constant power) and constant current charge–discharge data.

2. *N* pair *RC* equivalent circuit model development

The equivalent circuit approach represents the cell in terms of electric circuit elements that corresponds to the ionic or electronic flow in the cell. The various processes are identified and modeled using resistors (R), capacitors (C) and its generalizations (Constant Phase Element or CPE) [9], and in rare cases inductors. The most general representation that arises from electrochemical impedance spectrum of the cell is that of a sequence of RC (R is parallel to C) or R-CPE circuits with a Warburg element representing diffusion [9,10]. However, this circuit does not have a direct solution in the time domain. As the present approach is to model the time domain data, simplifications of this model are sought, without sacrificing the electrochemical basis of the parameters. A simplification that has been successful is to consider the circuit as consisting of a fixed number of RC elements, the generalization being an N pair RC (Fig. 1).

2.1. Overall voltage balance and individual RC pair current balance

The voltage balance for the cell, represented by an N pairs of RC circuits, where the cell voltage V is related to the equilibrium potential V_0, the voltage drop across the resistor due to the current I and resistance R, and the voltage drop across the nth RC pair, V_n, is

$$V = V_0 + IR + \sum_{n=1}^{N} V_n \tag{1}$$

The current balance for the nth pair RC is

$$I = I_{C_n} + I_{R_n}, \tag{2}$$

where the current through the capacitor is

$$I_{C_n} = \frac{\mathrm{d}Q_n}{\mathrm{d}t}, \tag{3}$$

with $Q_n = V_n \cdot C_n$, and the current through the resistor is

$$I_{R_n} = \frac{V_n}{R_n} \tag{4}$$

Substituting these expressions in Eq. (2) the current balance is

$$I = \frac{\mathrm{d}}{\mathrm{d}t}[C_n V_n] + \frac{V_n}{R_n} \tag{5}$$

Equation (5) is applied to all the RC pairs in the circuit. Thus the system is a set of N ordinary differential equations (ODEs) involving the voltage drops across individual pairs of RCs and the voltage balance for the cell, Eq. (1). It is interesting to note that the

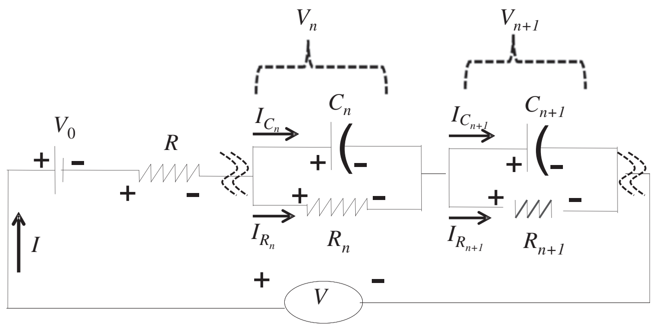

Fig. 1. The *N* pair *RC* model.