

MODELLING OF CHARGE/DISCHARGE CYCLE OF LITHIUM ION BATTERY SYSTEM

(Pemodelan Kitaran Cas/Discas Sistem Bateri Litium Ion)

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ABSTRACT

In this paper, a general model of lithium ion battery based on specific charge/discharge profile of the battery has been developed. The governing equations are solved by explicit numerical method. The partial differential numerical simulation is performed using MATLAB software. The charge/discharge model is capable of predicting the total discharge time of a battery under various discharge rates. The simulated result is also compared to experimental data of specific condition from a specified journal. Then an equation that represents the simulation result is formulated.

Keywords: battery; lithium ion; modelling; charge/discharge; simulation

ABSTRAK

Dalam makalah ini, suatu model bateri ion litium berdasarkan profil cas/diskas tertentu untuk bateri telah dibangunkan. Persamaan menakluk diselesaikan dengan menggunakan kaedah berangka tak tersirat. Simulasi berangka pembezaan separa dilakukan menggunakan perisian MATLAB. Model cas/diskas ini mampu untuk meramalkan jumlah masa dicas bateri di bawah pelbagai kadar discas. Keputusan simulasi telah dibandingkan dengan data yang diperoleh daripada eksperimen untuk keadaan khusus daripada jurnal tertentu. Kemudian suatu rumus yang mewakili hasil simulasi diterbitkan.

Kata kunci: bateri; ion litium; pemodelan; cas /discas; simulasi

1. Introduction

A battery is defined as an electrochemical storage device that stores electricity in chemical bonds. It converts the chemical energy contained in its active materials directly into electric energy by means of an electrochemical redox reaction. This reaction involves the transfer of electrons from one material to another through an electric circuit. Scientifically, battery is referred to as electrochemical or galvanic cell which stores electrical energy in the form of chemical energy and the electrochemical reactions that take place termed galvanic (Whittingham *et al.* 2004). The materials with lower positive standard reduction potential undergo an oxidation reaction providing electrons by the external circuit to the material with higher positive standard reduction potential. This electrochemical process then undergoes a reduction reaction. The conversion of chemical energy to electrical energy is performed by electron transfer through external circuit.

In 1991, Sony released the world's first commercial lithium ion rechargeable battery product (Sony 2013). This commercial lithium ion battery offers high energy density and excellent low temperature as well as load and cycle characteristics (Texas Instruments 2011). The features of a lithium ion battery include:

- High energy density. US18650 size have energy density per volume of approximate 440Wh/l
- Three types of carbonaceous materials can be used as anode active materials, i.e. graphite, graphitisable carbon and nongraphitisable carbon (the so-called hard carbon).

High voltage Lithium ion batteries with average operating voltages at 3.6V for hard carbon and 3.7V for graphite batteries. This is about three times higher than the cut off voltage for nickel cadmium and nickel metal hydride batteries (Srinivasan & Wang 2003).

- Excellent charge/discharge cycle characteristic which can go through 500 or more cycles.
- No memory effect which occur in other nickel batteries.

Lithium possesses lightest weight of all metals, has the greatest electrochemical potential and provides the largest specific energy per weight. Rechargeable batteries with lithium metal on the anode (negative electrodes) could provide extraordinarily high energy densities (Buchmann 2013). The positive electrodes in a lithium ion battery are normally made of lithium intercalation compounds. Intercalation compound have a lattice structure in which certain species will be inserted and extracted without changing the structure of the host material significantly (Bruce 2008). The mechanism of Li-ion battery is based on the transport of lithium ions from positive electrode to the negative electrode during charging and opposite direction while discharging. This is general referred as rocking chair principle. Charging and discharging of lithium ion battery occur through the migration of lithium ions between the cathodes and anodes and the exchange of electrons through doping and dedoping. During the charging process, lithium ion is dedoped from cathodes (positive electrodes) consisting of a lithium containing compound. Lithium ion is then doped or intercalates into the interlayers of carbon in anodes (negative electrodes). On the other hand, during discharging lithium is dedoped from interlayers of carbon in anodes (negative electrodes) and the compound layers in cathodes (positive electrode) are doped with lithium (Dees *et al.* 2002).

A lithium ion battery system mathematical model based on specific charge/discharge behaviour is developed in this study. The model is developed using the MATLAB R2011a software. The simulated results are then tested to validate the model developed.

A lithium ion battery consists of three core regions which are negative electrode, separator and positive electrode and boundary region. The boundary region is the copper current collector at negative terminal and aluminium current collector at positive terminal. The negative and positive electrodes are composite materials and there are represented as spherical particles. A lithium ion cell is shown schematically in Figure 1.

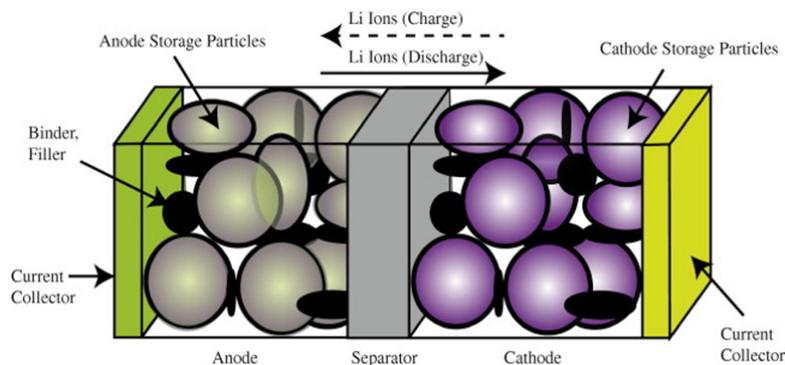


Figure 1: Schematic diagram of a lithium ion battery (Purkayastha & McMeeking 2013)

In this study, the active material of both electrodes is assumed to be spherical and both electrodes are porous contained in non-flat surfaces. Solid phase diffusion coefficient is also independent of concentration. The design of Lithium charge/discharge model has various

phase of super imposed electrode and therefore it has perfect connectivity between all points. More important is no volume changes of host structure upon insertion and extraction of lithium ion. Thermal effect is assumed to be negligible in this model.

2. Lithium Ion Battery System Mathematical Model Based On Specific Charge/ Discharge Behaviour

This battery system is modelled based on porous electrode theory and concentrated solution theory (Newman & Tiedemann 1975). The theories are chosen as it associates the equations to the diffusion process in porous electrode and electrochemical systems. According to concentrated solution theory, the mass balance of electrolyte present in three regions of battery can be deduced by considering migration and diffusion effects. The values of the parameters are given in Tables 1, 2 and 3.

Table 1: Cell specific parameters for cell 1 (Ning *et al.* 2006)

Parameter	Symbol	Value	Unit
Capacity of cell	I	19.0	Ah/m ²
Porosity of negative electrode	ϵ_-	0.440	-
Porosity of positive electrode	ϵ_+	0.338	-
Length of negative electrode	δ_-	74	μm
Length of positive electrode	δ_+	75	μm
Length of separator	δ_{SEP}	25	μm

Table 2: Values for parameters for the baseline case for cell 1 (Ning *et al.* 2006)

Parameter	Symbol	Value	Unit
Transfer number of positive ion	t_+^o	0.2	-
Area	A	0.011	m ²
Particle diffusivity coefficient of negative electrode	D_-	3.8×10^{-14}	m ² /S
Particle diffusivity coefficient of positive electrode	D_+	1.0×10^{-13}	m ² /S
Initial concentration of electrolyte	c_o	1000	mol/m ³
Conductivity of negative electrode	σ_-	100	S/m
Conductivity of positive electrode	σ_+	10	S/m
Temperature	T	298	K

Table 3: Universal standard value

Parameter	Unit	Value
Faraday Constant, F	C/mol	96487
Molar Gas Constant, R	J/K-mol	8.3145

The equation for the total mass transport flux is given by

$$N = -D \left(1 - \frac{d \ln c_o}{d \ln c} \right) \bullet \nabla c + \frac{i_2 t_+^\circ}{F} \quad (1)$$

Where i_2 is current density in the electrolyte phase and D is particle diffusivity coefficient of negative electrode .

The reaction term of the mass balance equation that occurs at the electrodes can be expressed as

$$R = \frac{a}{v_+} (1 - t_+^\circ) j_{Li} \quad (2)$$

where v_+ is cell capacity for positive electrode.

From porous electrode theory, the overall mass balance is

$$\frac{\partial c}{\partial t} = -\nabla \bullet N + R \quad (3)$$

Upon substitution, a general equation for concentration of lithium ion in the electrolyte is obtained. The resulted equation is only valid for continuous region of the battery. Thus, to take into account the porosity of medium in electrode region, the equation is modified so that it will be applicable to all three regions in a battery system (Doyle & Newman 1995).

$$\varepsilon \frac{\partial c}{\partial t} = D \left(1 - \frac{d \ln c_o}{d \ln c} \right) \bullet \nabla^2 c - \frac{i_2 \nabla \bullet t_+^\circ}{F} + \frac{a}{v_+} (1 - t_+^\circ) j_{Li} \quad (4)$$

The model can be simplified by means of consideration of the constant and null terms in the battery system. The term $\frac{d \ln c_o}{d \ln c}$ is neglected due to lack of experiment data while t_+° is

constant. v_+ is constant due to the electrolyte used in this battery is dissociated in a 1:1 ratio (Martinez-Rosas *et al.* 2011). Thus, lithium ion diffusion in electrolyte is expressed by the equation

$$\varepsilon \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial t^2} + a(1 - t_+^\circ) j_{Li} \quad (5)$$

While the equation for the pore wall flux of lithium ions can also be written as

$$j_{Li} = \frac{IR_s}{3\varepsilon F\delta} \quad (6)$$

where R_s is radius of electrode spherical particle and I is total current density.

The diffusion coefficient of salt in the solution phase is used as the parameter to fit the experimental data. The diffusion coefficient in the porous media is evaluated by the Bruggeman relation. Effective diffusion coefficient of electrode can be expressed through a relationship

$$D^{eff} = D\varepsilon^{1.5} \quad (7)$$

Since in this model the particles of both electrodes are assumed to be spherical, the specific surface area in terms of porosity is given as

$$a_+ = \frac{3}{R_{s,+}}(1 - \varepsilon_+ - \varepsilon_{f,+}) \quad (8)$$

where $R_{s,+}$ is the radius of active material sphere in positive electrode and $\varepsilon_{f,+}$ is the volume fraction of filler in electrode.

The boundary condition can be written as Eq. (9) at $x = \delta_+ + \delta_s + \delta_-$ and at $x=0$. The concentration for the cell at $t=0$ equals to initial concentration of electrolyte.

$$\frac{\partial c}{\partial t} = 0 \quad (9)$$

In this study, the model developed is validated by experimental results obtained from Ning *et al.* 2006. Besides that, curve fitting tool in MATLAB R2011a is also used.

3. Results and Discussion

Figures 2 and 3 show the change of electrolyte concentration across distance x for positive and negative electrode. The figures are plotted for cell during 1C discharging rate. From Figure 2, the electrolyte concentration of negative electrode increases as time increases.

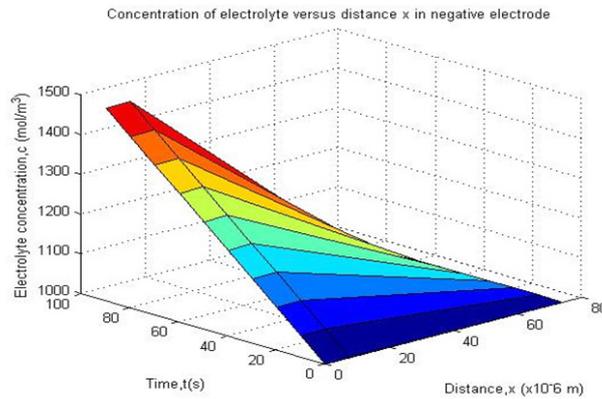


Figure 2: Graph of concentration versus time, t , and distance, x , in negative electrode

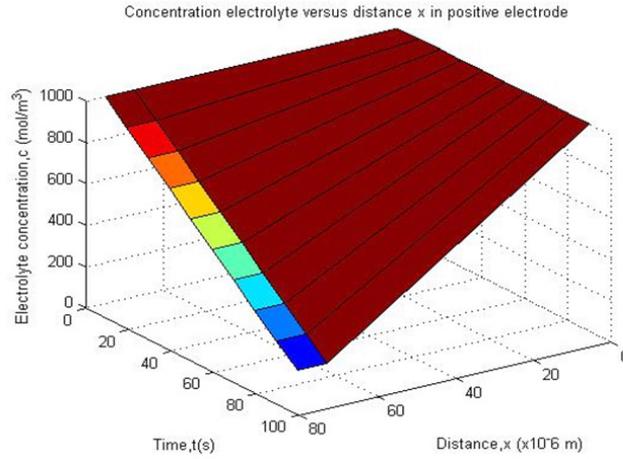


Figure 3: Graph of concentration versus time, t , and distance, x , in positive electrode

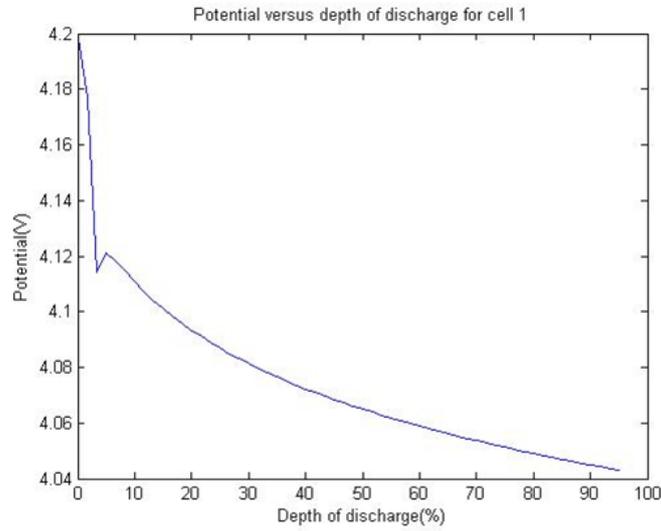


Figure 4: Graph of potential against depth of discharge in cell 1

This is because the lithium ion is formed when discharging as in (11) (Newman & Tiedemann 1975). In positive electrode, electrolyte concentration decreases as time increases. This is due to lithium ion is consumed during discharging process to form lithium metal oxide as in (10). The half cell reactions for both electrodes while discharging are:

Positive electrode:



Negative electrode:

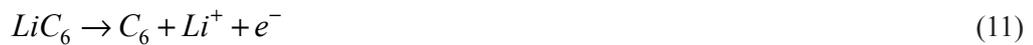


Figure 4 shows a graph of potential of a lithium ion cell versus depth of discharge. In the figure, the potential of the battery system decreases drastically at the first region of discharge curve. At the range depth of discharge around 0% to 5%, there is drop from 4.2 V to 4.11V.

At the second region of the curve, the potential of the cell decreases slowly from 8% depth of discharge to the end of depth of discharge. The curve plotted has a similar discharge pattern as a general discharge curve of battery system. There is a slightly unstable voltage variation when the battery is discharge 5% of its capacity. This may due to the side reaction as cell oxidation, electrolyte decomposition and self discharge process occur. The cell oxidation leads to film grown on electrode. This cell oxidised film causes non reversibility to the discharge process and increases the internal resistance of lithium ion batteries.

Figure 5 shows the graph of experimental data and simulated data. It can be seen that the experimental data are distributed around the simulated curve. The pattern of changes of the potential when depth of discharge is increased is similar for simulated result and experimental data. To further evaluate the simulated results, some data from simulated results are used. The results are then further processed with curve fitting tool in MATLAB R2011a. Figure 6 shows the curve plotted for the simulated results.

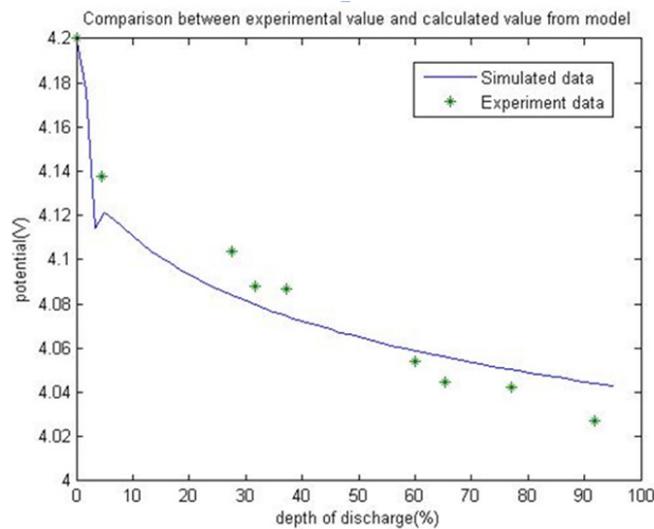


Figure 5: Comparison of experimental data with simulated data

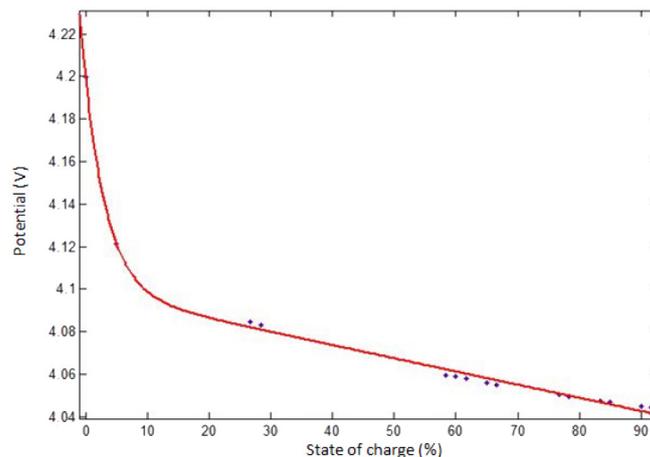


Figure 6: Fitting curve plotted for simulated results

The curve plotted is well fitted to the data points. By using the curve fitting tool, the exponential equation is chosen. The equation generated from the specific simulation data which can represent the group of data extracted from model developed is

$$\text{Potential} = 0.1012\left(xe^{-0.2734}\right) + 4.099\left(xe^{-0.0001526}\right) \quad (12)$$

The R^2 value of this equation is 0.9979, which means the curve plotted has a good fitness. A new set of potential data is calculated using this equation. Besides from the method above, the reliability of model developed can also be tested out by plotting the discharge curve of potential versus time at various discharge rates. The graph plotted is shown in Figure 7.

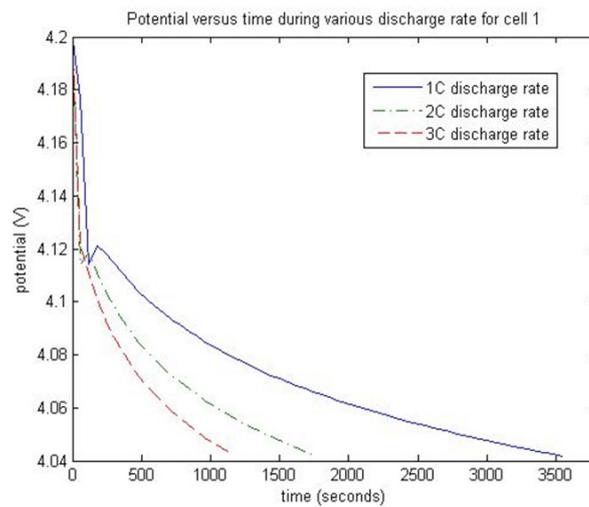


Figure 7: Graph of potential versus time for various discharge rates

From Figure 7, it shows that for 1C discharge rate, the cell is fully discharge at around 3550 seconds (theoretical 3600) which is approximate 1 hour. On the other hand, the discharge curve for 2C discharge rate fully discharge at time 1750 seconds (theoretical 1800). It will takes around half an hour for the cell to fully discharge. The discharge curve for 3C rate shows the battery fully discharge at 1150 seconds (theoretical 1200). Hence it shows that the simulation results match the theoretical ones.

4. Conclusion

In this model, concentration of electrolyte is first modelled to study the transportation of lithium ion in electrolyte. The changes of concentration in positive and negative electrodes at the boundary region are examined. We can conclude that the changes of electrolyte concentration along the time at boundary regions matched well with theoretical expected condition. The model of discharging profile for a battery is then developed based on the concentration profile of both electrodes. The governing equations applied in this model are based on porous electrode theory, concentrated solution theory and Fick's law as well. In order to develop this model, some assumptions are made as there are several variables which are unavailable due to lack of experimental data. The plotted discharge curve shows a similar pattern with most of the lithium ion battery in the market. Besides, in order for the developed model to be established, the governing equations are solved using explicit numerical method. The simulated discharge

potential of model built can be extracted from the model. The experimental data is obtained using digitiser plot software. An equation which may represent the modelled discharge behaviour is produced from the simulated data. This is done by using the curve fitting tool in the MATLAB R2011a. The formulated equation is able to calculate the potential cell for specific condition stated which is almost similar to experimental potential. A model is then developed to plot the potential of cell versus time. We therefore has proved that the discharging time of the battery at various discharging rates matched the discharge rate applied.

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