

Lithium Ion Battery Performance for Different Size of Electrode Particles and Porosity



Ra hifa Ranom, Hawa N. A. Rosszainily

Abstract: Nowadays, the interest of high proficiency of Lithium ion batteries is increasing as they provide high volumetric energy densities and to meet the demand of exponentially growth of electronic devices. Furthermore, LIB has shown their potential to offer high performance rechargeable battery in the research of electric vehicles. Electrochemical process of Lithium ion batteries encompasses a complex ion transport between the anode and cathode within an electrolyte. The multiscale LIB model consists of charge transport within electrode particle and in electrolyte and the reaction rate at the electrolyte-electrode particle interface which directly relating the geometry of microstructure (the size of particles, about 1nm) to the behaviour in macroscopic model (within the thickness of electrode, about 1 μm). Thus, the geometry of cell and the interfacial behaviour are significantly control the rate of reaction rate. This study concerns about the effect of geometry variations of cell upon the discharge curve of LiFePO₄ cathode material. The electrochemical model is solved using Method of Lines technique by discretising the spatial variable using Finite Difference Method. The simulation result is verified with experimental data of LiFePO₄ cell by Yu et. al. [14]. The effect of different sizes of particles and volume fractions upon the cell performance are examined. It has been shown that decreasing the size of electrode particles produce high cell potential but slightly low capacity. On the other hand, the optimal volume fraction is shown to be $\epsilon_v = 0.4763$ provided that all the particles are spherical and of the same size. Smaller volume fractions resulted in low capacity.

Keywords : Lithium Ion battery, Mathematical model, Volume fractions, Porosity.

I. INTRODUCTION

Lithium-Ion Battery or LIB is an art of rechargeable battery which provides high energy density. The consistency in supplying DC voltages while discharging process makes battery such as Lithium-Ion Battery a suitable replacement of portable power generator. Moreover, features exhibit by the cell such as low cost, large capacity, high durability, intrinsic stability, design flexibility and outstanding environmental compatibility makes LIB an excellent choice for its use in

electric vehicles [1].

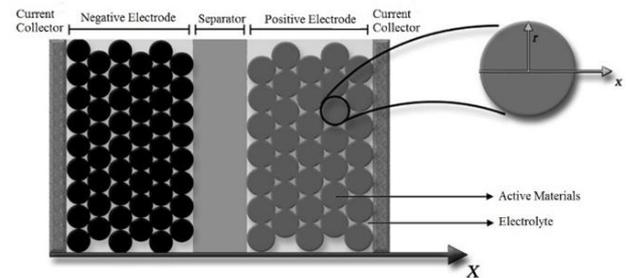


Fig 1. Schematic Diagram of the Structure of LIBs [15]

Essentially, LIB has three main components; an anode (negative electrode), a cathode (positive electrode) which are bathed in an electrolyte and current collectors at the end of both electrodes. During discharge, the electrode materials are selected so that the anode donates electrons (and thus also lithium ions), while the cathode accepts electrons (and thus lithium ions). The preferential of a material to donate or accept electrons is determined by its standard electrode potential which gives the voltage of the cell at equilibrium. Separator is a porous polymeric film that lies between two electrodes that acts as insulator and prevents the direct electrical contact to avoid faulty while allowing passage of ions within electrode in electrolyte. An electrolyte consists of “ionically conductive” organic solvent that provide pathway to transport Li^+ . The current collector plays important role in transferring the electrons charge to the outer circuit efficiently. During discharge, Lithium (Li) diffuses to the solid-electrolyte anode interface (in the particle scale) and undergoes the charge transfer reaction (refer Fig 1). The reaction transfers the Lithium ion (Li^+) into the electrolyte and releases the electron (e^-) which travel via the outer circuit to generate electricity. The Li^+ diffuses and is conducted through the electrolyte solution to the cathode. Another similar reaction on the solid-electrolyte cathode interface insert the Li^+ into the cathode (by a process known as intercalation). Thus the Lithium ions, Li^+ carry the charge through the non-aqueous electrolyte (and separator diaphragm) from the anode to cathode.

To accommodate the numerous chemical process in LIB, the multiscale battery modelling must account for conservation of ions in the electrolyte, charge reaction at the electrolyte/electrode particle interface and transport of Lithium within the electrode particles [2]-[3]. Richardson et.al. [3] has derived the macroscopic LIB model in dilute electrolyte which accounts the microscopic system (the size of electrode particles) by homogenization technique.

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The model is described in the form of Newman phenomenological battery model [4]-[5] which has been used in battery research worldwide. Several authors adapted the Newman electrochemical models of lithium-ion batteries and their use towards the design of better batteries [6]-[8]. Mehrdad et. al. [6] has simplified the Newman's full-order porous electrode using polynomial approximations to increase the simulation efficiency of any composite electrode with non-uniform transport properties of active-material particles. Therefore, solution to the model provides a useful tool to understand LIB behavior and consequently to study how can we produce high performance LIB.

Krewer et. al. [10] have given available options to select the most suitable model taking into account the multiscale processes in LIB for a specific purpose. In terms of accuracy the electrochemical modeling can definitely predict the LIB behavior with high accuracy however it's very expensive. Safari et al. [12] simulated the ageing behavior in a commercial graphite/LiFePO₄ cell. Ashiqur et. al. [11] used particle swarm optimization to identify four battery parameters that demonstrate major variation under extreme operating situations namely solid phase diffusion coefficient and intercalation/deintercalation reaction rate at the cathode and anode. Dargaville [9] demonstrated the Lithium phase transport in electrode particle of LiFePO₄ cathode which was found to be the main limiting factor of capacity loss of LiFePO₄.

This study concerns about the effect of geometry variations of cell upon the discharge curve of LiFePO₄ cathode material. LiFePO₄ exhibits a flat discharge curve characteristic that shows hardly any variation of voltage until it is fully discharged. Here, we manipulated the radius of particles (r) and volume fraction while other parameters are fixed.

II. MATHEMATICAL MODEL OF LITHIUM ION BATTERY

The mathematical model of LIB in moderately dilute electrolyte in the form of Newman model [4] demonstrates the electrochemical process of LIB ranging from microscopic to macroscopic length scale in 1D averaged model. The electrolyte model [4, 13] consists of (i) drift-diffusion equation of Li⁺ (see Equation 1) that explains their diffusion (resulting from concentration gradient) and advection (resulting from electric field), (ii) flux of current density (Equation (2)), (iii) reaction rate equation by Butler Volmer equation (Equation (4) - (5)). The equations are coupled with the solid state model by (vi) the diffusion equation in spherical particle (where we assume all the particle are sphere of the same sizes) and conservation equation for the flux of Lithium in the solid (see Equation (6)-(8)). The model is closed by supplying (vii) the Ohmic boundary conditions on the current collector and on the separator (Equation (9)) and as well as at the electrode particle (Equation (10)). The present study is conducted for half-cell cathode ($0 \leq x \leq L$), where L is the thickness of cathode. The model of LIB can be summarized as follows:

$$\varepsilon_v \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D(c) \beta \frac{\partial c}{\partial x} \right) - \partial t_+^0 \frac{j}{F} + (1 - t_+^0) b_{et} G \quad (1)$$

$$\frac{\partial j}{\partial x} = F b_{et} G \quad (2)$$

$$j = \beta \kappa(c) \left(\frac{\partial \phi}{\partial x} - \frac{2RT}{F} (1 - t_+^0) \frac{\partial \log c}{\partial x} \right) \quad (3)$$

$$\eta = \phi - \phi_s - U_{eq}(c_s|_{r=a_0}) \quad (4)$$

$$G = k_0 c^{\frac{1}{2}} (c_{s, \max} - c_s|_{r=a_0}) \left(\exp \left(-\frac{F\eta}{2RT} \right) - \exp \left(\frac{F\eta}{2RT} \right) \right) \quad (5)$$

$$\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_s(c_s) \frac{\partial c_s}{\partial r} \right) \quad (6)$$

$$\frac{\partial j_s}{\partial x} = -F b_{et} G \quad (7)$$

$$j_s = -\sigma_s \frac{\partial \phi_s}{\partial x} \quad (8)$$

$$c|_{x=0} = C_0, \quad \frac{\partial c}{\partial x}|_{x=L} = 0 \quad (9)$$

$$j|_{x=0} = -\frac{I}{A}, \quad j|_{x=L} = 0$$

$$\frac{\partial c_s}{\partial r}|_{r=0} = 0, \quad D_s \frac{\partial c_s}{\partial r}|_{r=a_0} = -G \quad (10)$$

where the definition of all parameters are listed in Table – I.

Table – I: List of symbols

Symbols			
ε_v	Volume fraction	ϕ_s	Solid potential of cell
C	Li ⁺ concentration (electrolyte)	ϕ	Electrolyte potential of cell
C_s	Li concentration (electrode)	j_s	Current density (electrode)
t	Time	j	Current density (electrolyte)
L	Cell thickness	U_{eq}	Equilibrium cell potential
b_{et}	BET surface area	G	Reaction rate
F	Faraday constant	t_+^0	Transference number
R	Universal gas constant	D	Diffusion coefficient
T	Temperature	σ_s	Ionic conductivity (electrode)
κ	Conductivity of ions	β	Permeability factor
η	Cell over-potential	a_0	Radius of particle
$c_{s, \max}$	Maximum concentration of Li		

Note that, by homogenization technique, the permeability factor β appears in the equation which explains the detailed microstructure geometry of the electrode in the macroscopic model. Thus, the model describes the effective conductivity and diffusion equation of the Li⁺ concentration within the electrolyte in terms of the properties of the microstructure. The reaction rate as stated in equation (5) indicates that there are two mechanisms of capacity loss and voltage drop which is when the electrolyte $c = 0$ (electrolyte depletion) or no vacancy in the electrode particles to react at the electrode surface (fully discharged), $c_s = c_{s, \max}$.

In this study, the half-cell

cathode of LiFePO₄ bathed in LiPF₆ salts dissolve in a mixture 1:1 EC:DMC is chosen. The equilibrium cell potential of LiFePO₄ varies with the intercalated lithium concentrations at electrode surface is given by [13]

$$U_{eq}(c_s|_{r=a_0}) = 3.11455 \dots + 4.4388 \tan^{-1}(-71.7352 c_s|_{r=a_0} + 70.8533) - 4.2402 \tan^{-1}(-68.5605 c_s|_{r=a_0} + 67.73) \quad (11)$$

The diffusivity and conductivity of the electrolyte as concentration dependant are fitted to the equations [13]

$$D(c) = 5.253 \times 10^{-10} e^{-0.0003017c} m^2 s^{-1} \quad (12)$$

$$\kappa(c) = 10^{-4} c (5.2069 - 2.14 \times 10^{-3} c + 2.3440 \times 10^{-7} c^2) AV^{-1} m^{-1} \quad (13)$$

Equation (1) – (10) with the transport properties (11) – (13) were solved numerically using Method of Lines technique which discretized the spatial variable by Finite Difference Method to reduce the PDE into a series of coupled ODEs. The resulting ODES were then being solved forward in time using an implicit scheme ODE solver, ode15s to generate the results.

III. GEOMETRY OF MICROSTRUCTURE OF THE ELECTRODE

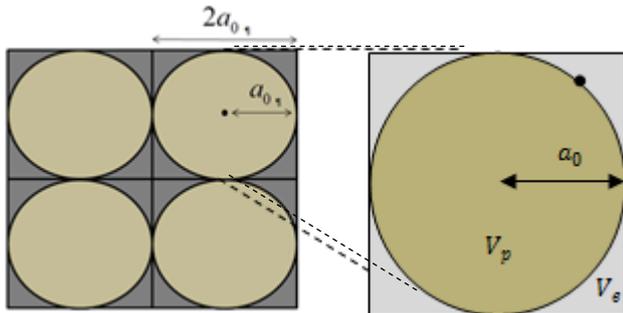


Fig 2. The microstructure of particles arrangement in electrode in 2D

The ϵ_v, β and b_{et} in equations (1) – (3) and equation (7) have been derived using homogenisation technique [3] describe the effective parameters in the underlying microstructure of particles. Here V_p is the region filled by the electrode particles and V_e is the region filled by the electrolyte. It is assumed that the microstructure is locally periodic inside a completely periodic array of boxes, $V_p \cup V_e$ (refer Fig 12). The arrangements of solid particles are assumed as uniform while considering each spherical particles with radius, $r = a_0$ are positioned inside a cube where each particle just touches its neighbours. The volume fraction, ϵ_v is in the form [13]:

$$\epsilon_v = \frac{|V_p|}{|V_e| + |V_p|} \quad (1)$$

The formula for a sphere radius a_0 is $V_p = \frac{4}{3} \pi a_0^3$ and the volume of periodic cube are determined by the cuboid volume formula which is

$$|V_e| + |V_p| = (2a_0)^3 = 8a_0^3 \quad (2)$$

Therefore, the optimal volume fraction from (10) can be

written as

$$\epsilon_{v,max} = 1 - \frac{|V_p|}{8a_0^3} = 1 - \frac{\pi}{6} = 0.4763 \quad (3)$$

The permeability factor which can be calculated from the underlying microstructure given by the Bruggeman relation [16] so that

$$\beta = \epsilon_v^{1.5} \quad (4)$$

The bet surface area (the surface area of particles per unit volume of electrode) is calculated as

$$b_{et} = \frac{\text{surface area of particle}}{\text{volume of periodic cube}} = \frac{4\pi a_0^2}{8a_0^3} = \frac{\pi}{2a_0} \quad (18)$$

IV. RESULTS AND ANALYSIS

A. Model – experimental comparison

Table- II: The transport properties of electrode particle and electrolyte

Transport properties	Electrolyte (LiPF ₆)	Electrode (LiFePO ₄)
Diffusivity ($m^2 s^{-1}$)	$D = 3 \times 10^{-10}$ [14]	$D_s = 6 \times 10^{-18}$ [14]
Conductivity ($AV^{-1} m^{-1}$)	$\kappa_{max} = 100$ [14]	$\sigma_s = 0.5$ [14]
Volume fraction, ϵ_v	0.31 [14]	-
Radius of particle, a_0 (m)	-	5.2×10^{-8} [14]
Transference number, t_+^0	0.363 [14]	
Concentration ($mol m^{-3}$)	$c_{s,max} = 18850$ [14]	$C_0 = 1000$ [14]
Thickness, L (μm)	76 [14]	
Reaction rate constant, k	3.5×10^{-14} [14]	
Cross-sectional area of cathode, A	$1 \times 10^{-4} m^2$ [9]	

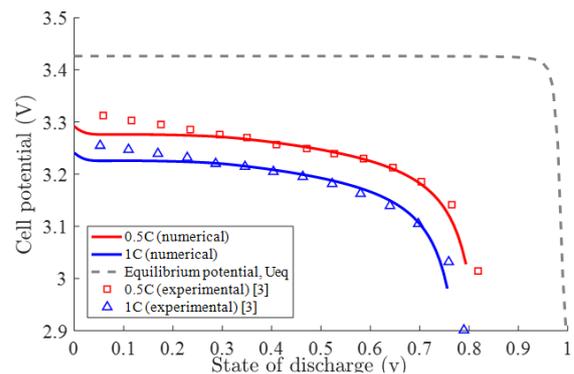


Fig 3. The comparison of numerical simulation (solid lines) of LiFePO₄ half-cell cathode with full-cell experimental data at 0.5C (70 mAh/g) and 1C (140 mAh/g). In order to verify the numerical simulation, a comparison of the model with LiFePO₄ experimental data by Yu et. al [14] is plotted in Figure 2 at different C-rates; which are 0.5C and 1C. The battery parameters used for simulation are listed in Table – II. The electrolyte diffusion is taken to be $10^{-10} m^2 s^{-1}$ based on the value calculated by Riemers et al. [17].

This reflects that the tortuosity and porosity of the composite electrode structure for particle sizes less than 1 micrometre which reduce the effective diffusion coefficient in the electrolyte [18]. Values for the lithium diffusion coefficient in LiFePO_4 takes the value $10^{-18} \text{m}^2 \text{s}^{-1}$ that demonstrates fast diffusion in electrode particles.

It can be seen that the numerical simulation compares reasonably well to the experimental data except at early discharge. This might happen due to the electrode particle resistance is taken to be small in this model. The drop of voltage occurs due to the capacity loss which is caused by transport limitation in the electrolyte and in the solid particles. The Li^+ depletion in electrolyte prevents the active material in electrode particles being discharged in the depletion region. In solid particles, the process of intercalation at particle surface increases very fast which makes the particle becomes saturated with Lithium, thus hampering the discharge.

B. Effect of Particles Size upon the Performance of LIB

This section discusses the effect of varying the size of particles upon the performance of LIBs. The radius of particles are varied to $a_0, \frac{1}{2}a_0$ and $2a_0$ where $a_0 = 5.2 \times 10^{-8} \text{m}$. Other parameters remain the same values as stated in Table 2. At 1C discharge rate, the smallest particles offer higher capacity then the other two sizes of electrode particles as shown in Fig 4. However, at the early discharge, the biggest particles generate slightly higher cell potential as compared to the other sizes. As smaller particles size provides larger surface area, more reactions are able to occur at the electrode surface and more Li^+ can be transported into cell. Consequently, as the rate of reaction at the electrode particles is high, it contributes to the loss of capacity due to the electrolyte depletion.

Moreover, equation (18) indicates that the value of b_{et} is decreased with every increment of a_0 . Therefore, the ability to intercalate at the electrode surface becomes higher as b_{et} appears in front of the reaction rate, G in equation (1),(2) and (7). This proves that by decreasing the size of electrode particles can improve high rate capabilities of the cells. On the other hand, large particle results in lower reaction rate, G yet higher capacity is produced.

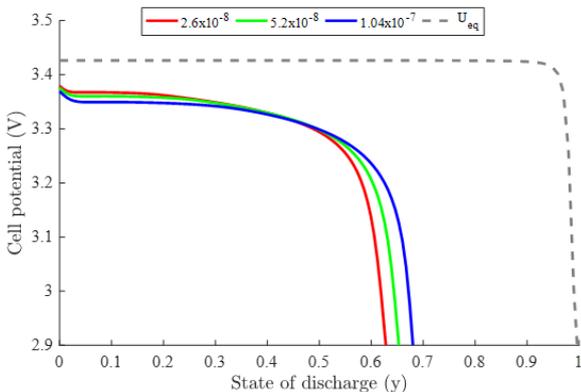


Fig 4. The discharge curve of the 1C cell when particles sizes are varied into a_0 (green), $\frac{1}{2}a_0$ (red) and $2a_0$ (blue).

C. Effect of Porosity Distribution upon the Performance of LIB

Fig 5. shows the discharge curves of the cell when the volume fraction, ϵ_v varies from 0.228 (calculated by $\frac{1}{2} \epsilon_{v,max}$), 0.31 (value provided by Yu et. al.[14]) and 0.4763 (calculated from equation (16)) while other parameters are fixed as listed in Table 2. Note that it is assumed that the sizes of spherical particles are uniform and in the same radius.

It is observed that the cell with optimal volume fraction shows the best performance with highest capacity compared to lower volume fraction. The lowest volume fraction $\epsilon_v = 0.228$ shows significant potential drop followed by $\epsilon_v = 0.31$ while $\epsilon_{v,max} = 0.4763$ offers the smallest potential drop and the highest capacity for LIBs. This observation is reflected by the permeability factor which is related to volume fraction by the Bruggeman relation (see equation (17)). As volume fraction increases, the permeability increases which in turn resulted in an improvement of the effective diffusivity and conductivity of ions in electrolyte.

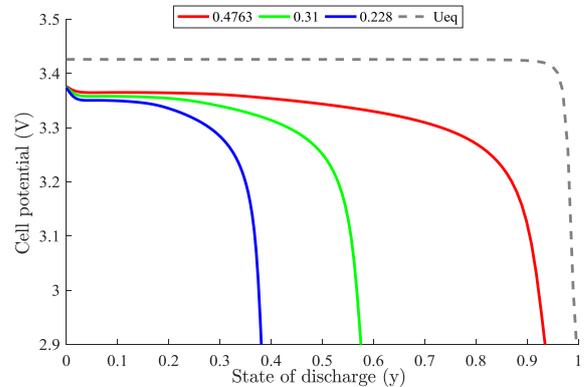


Fig 5. The discharge curve of the 1C discharge rate for different values of volume fractions, $\epsilon_v = 0.4763$ (red line), 0.31 (green line) and 0.228 (blue line).

V. CONCLUSION

This study revisits the Newman mathematical model of LIB which is then be solved for half-cell LiPeFO_4 cathode in non-aqueous LiPF_6 electrolyte. The numerical scheme of Method of Lines Technique by using Finite Difference Method has been used to generate the simulation results which are then being compared against the experimental data measured by Yu et. Al. [14]. The effect of geometry variations namely volume fractions and electrode particle sizes were investigated. It is proven that the geometry variations give an impact to LIB performance. Smaller particle size generates slightly higher of cell potential but slightly lower of capacity. On the other hand, the optimal volume fraction is shown to be $\epsilon_v = 0.4763$ provided that all the particles are spherical and of the same size. It is found that if the volume fraction lower than the optimal volume fraction, will result in low capacity. Therefore, smaller particle size is suitable to achieve high rate capabilities of the cell while higher volume fraction provides larger cell capacity. Thus, it is believed that the results of this study prove beneficial in electrode design.

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Wire Industry as Production Planner.

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