

Impact of Electrode Surface/Volume Ratio on Li-ion Battery Performance

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Abstract: The adoption of micro- and nano-structured electrodes is a promising technique to improve the performance of Li-ion battery, which increases the electrode surface area and improves the efficiency of ion exchange between the electrode and electrolyte. This performance improvement is supported by the results of our numerical simulation based on COMSOL Li⁺ battery simulator. The results also indicate that this performance improvement saturates when the electrode surface/volume ratio (ESVR) reaches a certain level. Charge and discharge characteristics of Li⁺ battery and heat dissipation strongly depend on the structure of the current collector, which is theoretically and numerically studied as a function of ESVR.

Keywords: Li-ion battery, heat dissipation.

1. Introduction

Li-ion battery (LIB) is considered as one of the key components for energy storage in portable electronic devices and systems [1, 2]. The energy capacity and power density are important parameters of battery performance [3]. Heat generation and dissipation are also key factors defining the overall battery performance, and particularly its safe operation in high temperature environment [4]. Electrochemical reaction and ion exchange processes in a Li-ion battery not only depend on the material properties of electrode and electrolyte, but also strongly depend on the geometric structure and size of the electrodes [5]. In recent years, the maturity of micro- and nano-fabrication techniques provided much more flexibilities in battery design, and thus performance improvements [6-8]. Numerical simulation is an important step in battery design and performance optimization [9]. In this paper we report the results of our numerical simulation based on COMSOL Li-ion battery simulator. A special focus is to understand the impact of electrode size on battery performance such as energy capacity and heat generation/dissipation at the current collector in a novel interdigitated architecture

[8]. The results indicate that reducing the electrode thickness helps increasing energy capacity of the battery of the same amount of electrode materials because of the increased electrode surface/volume ratio (ESVR). However, this energy capacity increase saturates when ESVR reaches a certain level at which the electrode thickness becomes comparable to the diffusion length of Li⁺ into the electrode. Meanwhile, increasing the number of electrodes reduces heat generated by each current collector, and therefore reducing the effect of local heating. In addition, the increased ESVR helps heat dissipation so that the overall temperature of the battery can be reduced. The thermal effect is investigated both theoretically and numerically as a function of ESVR.

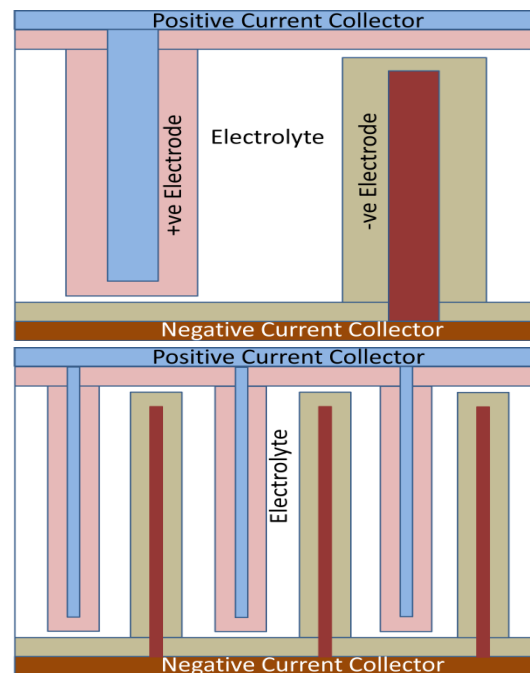


Figure 1. Illustration of Li⁺ battery with 1 (top) and 3 (bottom) pairs of electrodes

2. Energy Capacity of the Battery

The simplest structure of a Li-ion battery consists of two parallel electrodes separated by

electrolyte. In this study, an interdigitated architecture is used in which the electroactive materials are coated on highly conductive micro/nano- sheets extended from opposite current collectors with electrolyte filled between them as illustrated in Figure 1(top). If the number of electrodes is increased while keeping constant volumes of both the electrodes and the electrolyte, the surface area of electrodes will be increased accordingly. As the consequence of the increased number of electrodes, the thickness of each electrode will decrease accordingly as shown in Figure 1(bottom).

Consider that the initial condition of the battery is fully charged, and a constant current is drawn from the battery for discharging. During this discharge process the Li^+ concentration increases inside the negative ($-v_e$) electrodes while decreases inside the positive ($+v_e$) electrodes. As an example, Figure 2 shows the comparison of Li^+ concentration for a battery with one pair of electrodes (Fig. 2(top)) and with three pairs of electrodes (Fig. 2(bottom)). Li^+ concentration corresponding to several different states in the discharge process are displayed which have been normalized by their initial values before discharging.

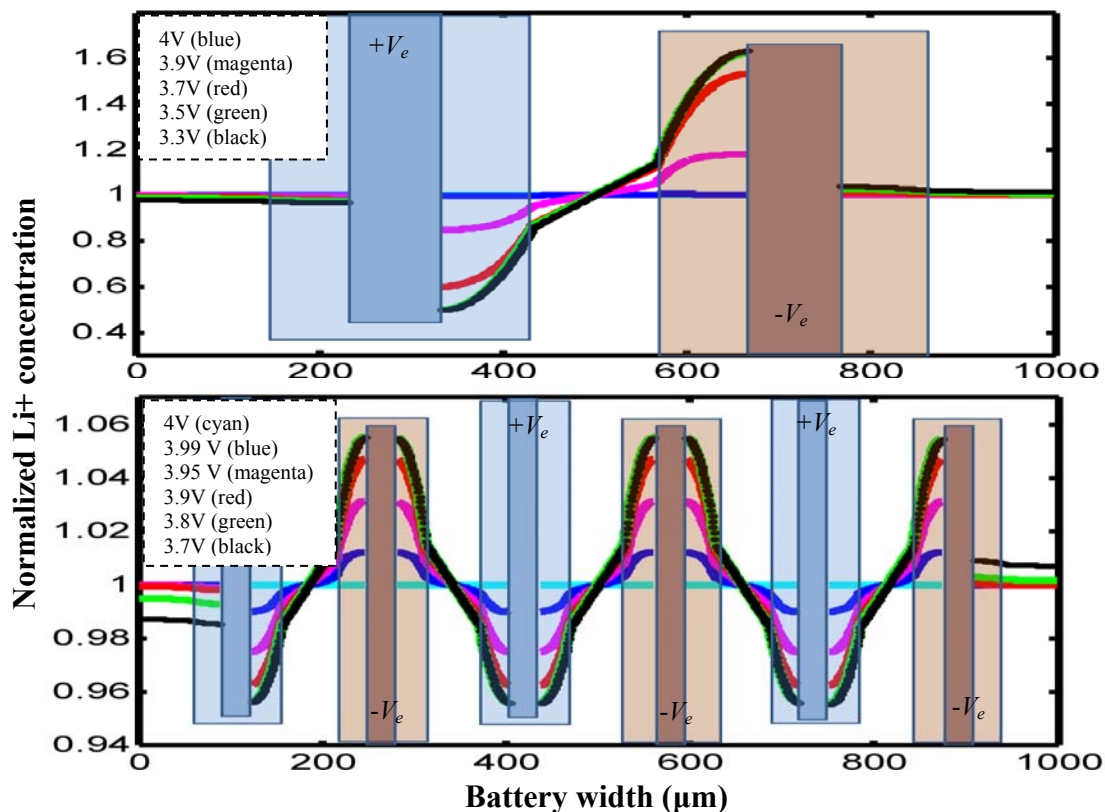


Figure 2. Normalized Li^+ concentration for one (top) and 3 (bottom) pairs of electrodes during discharge process at various voltage levels.

It is evident that the relative variation of Li^+ concentration becomes smaller with the increase of the number of electrodes from 1 pair to 3 pairs. This is due to the reduced current density of each electrode when increasing the number of electrodes. In addition, the variation of Li^+ concentration tends to saturate earlier when the electrodes become thinner. By increasing the number of electrodes while keeping a fixed

volume, the surface area of electrodes increases, which helps improve the efficiency of electrochemical reaction and facilitates ion-exchange between electrode and electrolyte. The penetration depth of Li^+ into the electrode is determined by the diffusion length, which in turn depends on the material property and the surface morphology. It is known that the diffusion coefficient of Li^+ in solid electrode can be many

orders of magnitude lower than that in liquid

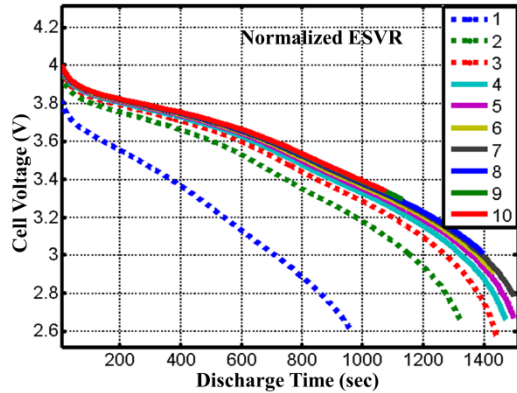


Figure 3. Discharge graphs for different normalized ESVRs

electrolytes, for example $5.1 \times 10^{-12} \text{ cm}^2/\text{s}$ in nanostructured Si [10] vs. $\sim 1 \times 10^{-5} \text{ cm}^2/\text{s}$ in volatile organic electrolyte [11]. Reducing the electrode thickness will, in general, allow more efficient use of the entire volume of the electrode material at higher charge/discharge rates. Therefore the energy capacity and power density can be increased by using micro- or nano-structured electrodes with large ESVR values.

Consider the battery configuration shown in Figure 1 with a total width of 1 mm. By increasing the number of electrodes from 1 pair to 10 pairs, the thickness of each electrode is reduced from $300 \mu\text{m}$ to $30 \mu\text{m}$, the thickness of current collector in the middle of each electrode is reduced from $100 \mu\text{m}$ to $10 \mu\text{m}$, and the normalized ESVR value is thus increased from 1 to 10. Figure 3 shows the calculated cell voltage depletion during the discharge process for 10 different normalized ESVR values.

The discharge current is kept constant at 200mA. The time it takes for the voltage to drop from the initial value of 4V to 2.6V increases with the increase of ESVR as shown in Figure 4. Note that this time increase is saturated when the normalized ESVR reaches 5, corresponding to the electrode thickness of $60 \mu\text{m}$.

Considering that the thickness of current collector of $20 \mu\text{m}$ corresponds to the normalized ESVR of 5, the width of electrode on each side of the current collector is $20 \mu\text{m}$. Figure 5 shows the distribution of Li^+ concentration inside an electrode with different thicknesses. In a conventional battery with the electrode thickness much larger than the diffusion length of Li^+ , only

a small region close to the surface participates in the electrochemical reaction. This is illustrated in Figure 5(a) in which large variation of Li^+ only happens near the surface during the discharge process. On the other hand, when the electrode is thin enough, the entire volume of the electrode can be efficiently utilized as shown in Figure 5(b). The energy capacity of the battery is determined by the integration of power over time, which is the integrated area underneath each discharge curve shown in Figure 3. In fact the normalized energy capacity increases as the function of normalized ESVR follows the same trend as the discharge time as also shown in Figure 4. Eventually, when the thickness of the electrode is much smaller than the diffusion length, this efficiency improvement with increasing the number of electrodes saturates.

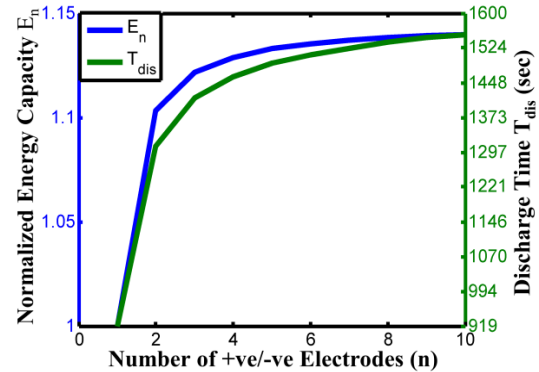


Figure 4. Normalized energy capacity and discharge time for different number of electrode pairs.

3. Thermal Model

In addition to the impact on energy capacity, the increase of ESVR also affects the thermal behavior of battery operation. To simplify the analysis, we only consider heat generated from current collectors inside battery electrodes [4] as schematically illustrated in Figure 6.

Assume the thickness of each current collector is T , the height of each current collector is L , the width of each current collector is W , the total current of the battery is I , the resistivity of the positive and the negative current collectors are ρ^+ and ρ^- , respectively. ρ^+ and ρ^- may not be equal because different materials may be used for the positive and the negative current collectors. The

resistance of each positive and negative current collector can be defined as:

$$R^+ = \rho^+ \frac{L}{WT} \quad \text{and} \quad R^- = \rho^- \frac{L}{WT}$$

Due to current continuity, the current flowing through the positive and the negative collectors are equal, which is I , so that the total power consumed by current collectors should be $P = I^2 R^- + I^2 R^+ = I^2 R$, where $R = R^- + R^+$ is the resistance of each pair of current collectors. Keeping a fixed total volume of the electrode while increasing the number of electrode pairs from 1 to n , the thickness of each current collector will be reduced from T to T/n . Then the resistance of each current collector pair will be increased from R to nR . As the total current I remains constant, the current i flowing through each current collector is $i = I/n$.

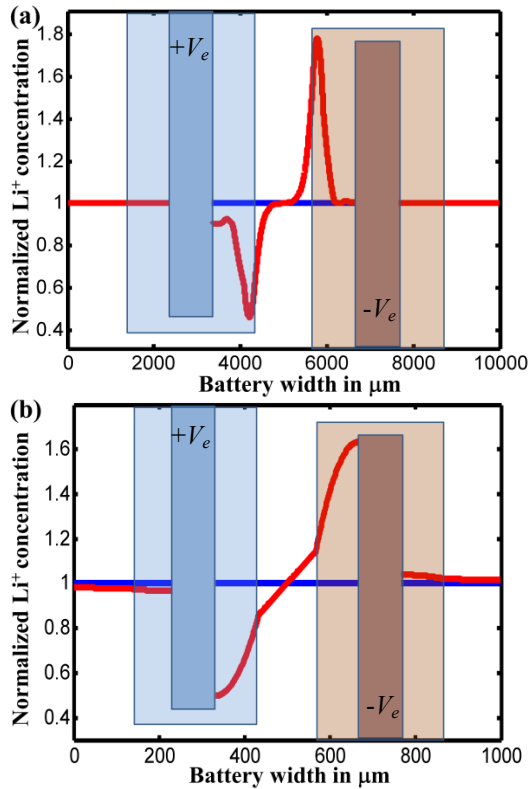


Figure 5. Normalized Li^+ ion concentration during discharge process for different thickness of electrodes

Thus, the power consumed by each current collector pair should be $p = (I/n)^2 nR = P/n$, which is inversely proportional to the number of current collector pairs n . Although the total

power consumption remains constant, the power consumption of each current collector decreases with increasing the number of electrodes. Therefore, the effect of excessive local heating can be avoided.

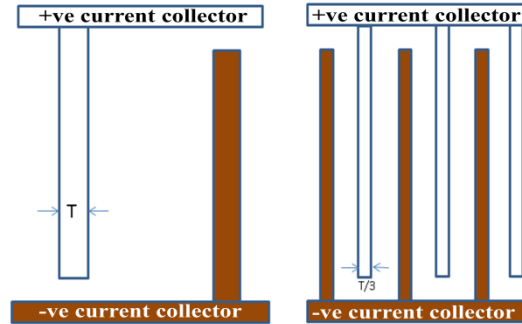


Figure 6. Battery structures used for thermal modeling with a single pair (left) and multiple pairs (right) of current collectors

Meanwhile, battery temperature increase during discharge also depends on the efficiency of heat dissipation. In this 2D battery model, the surface area of current collector increases linearly with the increase of the number of electrodes, and the efficiency of heat dissipation increases with the increase of surface area. Therefore the battery temperature is expected to reduce when the number of electrodes is increased. Figure 7 shows an example of simulated temperature distribution of negative current collectors. In the simulation the initial temperature is 293.15K (room temperature) before discharge, the total current is kept constant at $I = 200$ mA, and the temperatures are measured 900s after discharge started. The maximum temperature increases by 28.85 K for the battery with two pairs of electrodes, whereas the temperature increase is

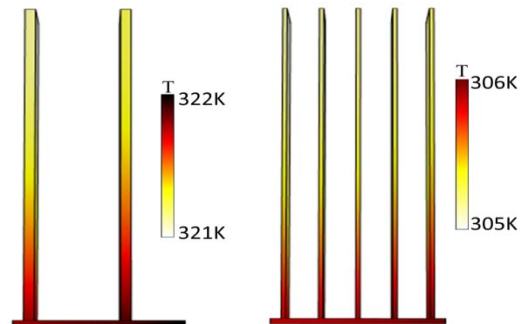


Figure 7. Example of simulated temperature distribution of negative current collectors in batteries with two (left) and five (right) pairs of electrodes, but with the same total current.

reduced to 12.85 K for the battery with 5 pairs of current collectors.

Figure 8 shows the simulated power consumption of each pair of current collectors and the temperature increase versus the number of electrode pairs. Both of these curves have been normalized to their values of a battery with single pair of current collectors. Evidently, the normalized temperature follows the same rule of the power consumption of each current collector, which is inversely proportional to the number of current collectors n . This verifies that large surface area due to the increased number of electrodes helps heat dissipation and reduces the rise of temperature.

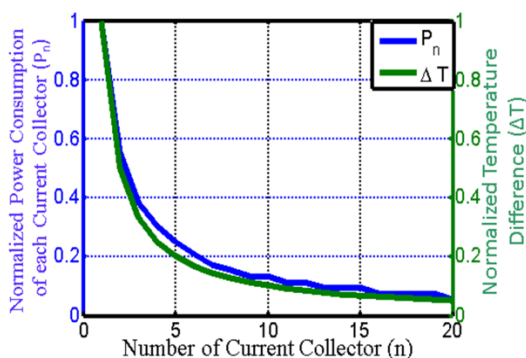
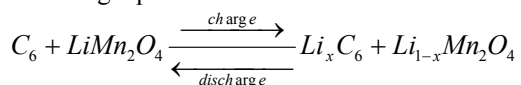


Figure 8. Normalized power consumption of each current collector, and normalized temperature versus the number of current collectors.

4. Use of COMSOL Multiphysics

Numerical simulation of Li^+ battery is carried out using COMSOL 2-D “Lithium-ion Battery module” and “joule heating module” to investigate the discharge time and heat distribution. Copper and aluminum are used as negative and positive current collectors; Carbon and LiMn_2O_4 are used as electrode materials, and 1:2 EC:DMC (with 1.0 mole/Ltr LiPF_6 salt) is used as the electrolyte. The basic electrochemical reaction for a Li^+ battery for charge and discharge is interpreted by the following equation:



Properties of those materials are taken from COMSOL material library. The battery is initially fully charged and then a constant current is set for discharging.

5. Conclusions

The results of COMSOL Multiphysics simulation indicate that increasing ESVR of a Li^+ battery is an effective way to enhance the battery energy capacity per unit volume. This energy capacity improvement is attributed to the more efficient diffusion of Li^+ into the electrode. The increased ESVR also helps heat dissipation because of the increased surface area of current collectors, and therefore the temperature increase during discharge can be reduced.

6. References

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6. Acknowledgements

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