Selection of charge methods for lithium ion batteries by considering diffusion induced stress and charge time

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Abstract

This article demonstrates the design of charging strategies for lithium ion batteries with considering the balance between diffusion induced stress and total charge time for two- and three-stage charge methods. For the two-stage galvanostatic-potentiostatic charge method the low mechanical stress can be achieved without increasing total charge time by switching the galvanostatic to the potentiostatic at the time moment when the lithium concentration at the surface of particles reaches the limit $\bar{c}_{\text{surf}} = 0$. A three-stage method, which consists of an initial galvanostatic stage of high current, a galvanostatic stage of low current and a potentiostatic ending stage, is suggested. Employing the initial galvanostatic stage of high current is helpful not only in accelerating the charge process, but also in controlling the mechanical stress once the electrical current and time duration of the initial galvanostatic stage are properly designed.

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1. Introduction

Lithium ion (Li-ion) battery is widely used in many applications nowadays due to its advantages such as high energy density, high operating voltage and low self-discharge rate. It is also one of the most promising technologies that meet the demands of electric vehicles (EV) [1]. There are many aging mechanisms, such as lithium metal plating, formation and growth of solid electrolyte interphase (SEI), mechanical failures and structural changes etc., that affect battery life-time [2]. Diffusion induced stress (DIS), which arises during charge and discharge, is considered as the direct cause of mechanical failures which may leads to loss of capacity and degradation of cyclic performance [2,3]. Although the battery aging does not originate from one single cause, it is believed that reducing and controlling DIS would improve the battery life-time.

Evolution of diffusion induced stress in electrodes depends significantly on charge/discharge operations. There are two kinds of elementary operations, i.e. galvanostatic and potentiostatic, corresponding to constant current and constant potential, respectively. Cheng et al [4] formulated DISes in a spherical particle under galvanostatic and potentiostatic operations, which were shown quite different. The stress increases initially and then decreases with time in potentiostatic operation, whereas it keeps increasing until a steady-state in galvanostatic operation. Zhang et al.

[5] performed similar works for layered electrodes and suggested an optimized charge procedure, i.e. galvanostatic first and potentiostatic followed.

In real battery operations, charge/discharge usually follows complex procedures including galvanostatic and potentiostatic operations [6]. However, in literature, a large amount of works simulated the DISes under a single operation. For example, under the assumption of galvanostatic operation, Christensen and Newman calculated the concentration and stress profiles in spherical particles [7,8], Zhang et al. discussed the impacts of aspect ratio on DISes in an ellipsoidal particle [9], Bhandakkar and Gao investigated crack nucleation in thin strip and nanowire electrodes [10,11], as well as the works on electrode critical size by Zhao et al. [12] and Lu et al. [13-15]. These works, although provided important insights on DISes in electrodes, are incapable of revealing the DISes under real combinational galvanostatic and potentiostatic charge/discharge procedure of a battery.

In recent years, the combinational operations have been considered in several works. For example, Song et al [16] discussed the effects of plasticity of current collector on battery performance in the cycles consisting galvanostatic and potentiostatic operations. Purushothaman et al. [6,17] proposed a pulsed currents charging method that contains multiple galvanostatic stages with different currents so as to accelerate charging process. However, it is still vacant comprehensive discussions on optimization of the combinational operation, including the current flux in galvanostatic stage and the switch time to potentiostatic stage, with consideration of both DIS and charge time.

In this paper, we will discuss the charge strategy which takes into consideration of both total charge time and mechanical safety. Based on the pulsed currents charging method reported by Purushothaman et al. [6,17], three-stage charge methods which includes two connective galvanostatic stages followed by a potentiostatic stage will be evaluated. Analytical models will be developed to simulate the evolutions of Li-ion concentration and DISes, with the aim to achieve a good balance between total charge time and mechanical stress. Our work will be able to provide a general solution for the Li-ion concentration and stress profile under the described combinational operations, and optimize the charge procedure by considering both total charge time and DISes.

2. Analysis

Consider a general charge procedure which combines multiple galvanostatic and potentiostatic operations with arbitrary time sequence. In order to analyze Li-ion concentration distribution in battery at the present time, the present single elementary (galvanostatic or potentiostatic) operation in the charge procedure will be focused and the concentration accumulated during the past charge history is assumed as the initial condition.

2.1. Concentration profile with general initial condition

A spherical active particle of radius R in electrodes is considered, within which the diffusion of Li-ions is assumed to be governed by Fick's law [4,18]:

$$D \frac{1}{r} \frac{\partial^2 (rc)}{\partial r^2} = \frac{\partial c}{\partial t}, \quad (1)$$

where c is the molar concentration of lithium, D is the diffusion coefficient of lithium in the particle, t stands for time in a single elementary operation. The boundary conditions are

$$D \frac{\partial c}{\partial r} = \frac{i_n}{F} \quad \text{for } r = R \quad (2)$$

for galvanostatic operation, where $F = 96485.3C/mol$ is Faraday's constant, i_n is the surface current density, $i_n > 0$ represents lithiation and $i_n < 0$ indicates delithiation; and

$$c = c_{\text{surf}} \quad \text{for } r = R \quad (3)$$

for potentiostatic operation, where c_{surf} is the surface concentration.

A lot of literatures have investigated the concentration profile with a uniform initial solute concentration [4,7,9,19]. However, when operation switches, the initial concentration of the present operation is the final state of the previous one, usually not uniform. In this case, the initial condition of concentration profile is in a general form of

$$c = c_0(r) \quad \text{for } t = 0. \quad (4)$$

If the present operation is galvanostatic, by solving equations (1-2) and (4) we have the evolution of concentration follows:

$$\bar{c} = I \cdot f(\bar{r}, \tau) + g(\bar{r}, \tau), \quad (5a)$$

$$\text{with } f(\bar{r}, \tau) = 3\tau + \frac{1}{2}\bar{r}^2 - \frac{3}{10} - \frac{2}{\bar{r}} \sum_{n=1}^{\infty} e^{-\lambda_n^2 \tau} \frac{\sin(\lambda_n \bar{r})}{\lambda_n^2 \sin(\lambda_n)}, \quad (5b)$$

$$g(\bar{r}, \tau) = Q_0 + \frac{2}{r} \sum_{n=1}^{\infty} e^{-\lambda_n^2 \tau} \frac{\sin(\lambda_n \bar{r})}{\sin^2(\lambda_n)} \int_0^1 \sin(\lambda_n \bar{\zeta}) \bar{\zeta} \bar{c}_0(\bar{\zeta}) d\bar{\zeta}, \quad (5c)$$

where $\bar{c} = c / c_{\max}$, $\bar{c}_0 = c_0 / c_{\max}$, $\bar{r} = r / R$, $\bar{\zeta} = \zeta / R$, $\tau = Dt / R^2$, λ_n are the solutions of $\lambda_n \cot \lambda_n = 1$, $c_{\max}$ is the saturation concentration, $I = i_n R / (FDc_{\max})$ is the dimensionless charge current density, $Q_0 = 3 \int_0^1 \bar{\zeta}^2 \bar{c}_0(\bar{\zeta}) d\bar{\zeta}$ is the normalized amount of lithium has been inserted into the particle in the past operations. The first term of the right-hand side of equation (5a) represents the contribution of the present operation to the concentration which is proportional to the charge current density. The second term of the right-hand side of equation (5a) denotes the contribution of past operations to the concentration at the present time. The spatial distribution of this part evolves with time but the total amount of lithium is unchanged during the present operation, i.e., $3 \int_0^1 \bar{r}^2 g(\bar{r}, \tau) d\bar{r} = Q_0$.

If the present operation is potentiostatic, the concentration at the present time can be obtained by solving equations (1, 3-4), i.e.

$$\begin{aligned} \bar{c}(\bar{c}_{\text{surf}}, \tau, \bar{r}) = & \bar{c}_{\text{surf}} \left[1 + 2 \sum_{m=1}^{\infty} e^{-(m\pi)^2 \tau} \frac{(-1)^m}{m\pi \bar{r}} \sin(m\pi \bar{r}) \right] \\ & + \frac{2}{r} \sum_{m=1}^{\infty} e^{-(m\pi)^2 \tau} \sin(m\pi \bar{r}) \int_0^1 \bar{c}_0(\bar{\zeta}) \bar{\zeta} \sin(m\pi \bar{\zeta}) d\bar{\zeta} \end{aligned} \quad (6)$$

where $\bar{c}_{\text{surf}} = c_{\text{surf}} / c_{\max}$. Again, the first term in the equation represents the contribution of the present operation while the second term gives the contribution of the past operations to the concentration at the present time.

If the initial concentration $\bar{c}_0$ is constant and does not vary spatially, Eq. 5a and 6 will degenerate to

$$\bar{c} = \bar{c}_0 + I \left[3\tau + \frac{1}{2} \bar{r}^2 - \frac{3}{10} - \frac{2}{r} \sum_{n=1}^{\infty} e^{-\lambda_n^2 \tau} \frac{\sin(\lambda_n \bar{r})}{\lambda_n^2 \sin(\lambda_n)} \right] \quad (7)$$

for galvanostatic cases, and

$$\bar{c} = \bar{c}_{\text{surf}} + 2(\bar{c}_{\text{surf}} - \bar{c}_0) \sum_{m=1}^{\infty} e^{-(m\pi)^2 \tau} \frac{(-1)^m}{m\pi r} \sin(m\pi \bar{r}) \quad (8)$$

for potentiostatic cases. These two expressions are in consistent with the report by Cheng et al. [4].

Note that the series terms in above solutions will approach to zero once the operation time τ is large enough. Thus, Eqs. 5 and 7 will approach to the same expression:

$$\bar{c} = 3I\tau + \frac{1}{2} I \bar{r}^2 - \frac{3}{10} I + Q_0. \quad (9)$$

This means that, after certain operation time, the concentration profile under galvanostatic operation depends only on dimensionless charge current I and initial amount of lithium Q_0 , but is not influenced by the initial distribution.

2.2. Diffusion induced stress

It is assumed that the active particle undergoes elastic deformation during lithiation and delithiation. The isotropic elastic constitutive equation reads as

$$\sigma_{ij} = \frac{E}{1+\nu} \varepsilon_{ij} + \frac{E\nu}{(1+\nu)(1-2\nu)} \varepsilon_{\alpha\alpha} \delta_{ij} - \frac{E}{1-2\nu} \frac{\Omega c}{3} \delta_{ij}, \quad (10)$$

where ν , E and Ω are Poisson's ratio, Young's modulus and partial molar volume of active material, respectively. With satisfying the mechanical boundary condition $\sigma_r(R)=0$, the diffusion induced stresses in radial and hoop directions are

provided by Cheng et al. [4]:

$$\sigma_r = \frac{2E\Omega c_{\max}}{9(1-\nu)} \left[Q - \bar{c}_{ave}(\bar{r}) \right], \quad (11)$$

$$\sigma_\theta = \frac{E\Omega c_{\max}}{9(1-\nu)} \left[2Q + \bar{c}_{ave}(\bar{r}) - 3\bar{c}(\bar{r}) \right], \quad (12)$$

where $\bar{c}_{ave}(\bar{r}) = \left(3/\bar{r}^3 \right) \int_0^{\bar{r}} \bar{\xi}^2 \bar{c}(\bar{\xi}) d\bar{\xi}$ is the dimensionless average concentration in the spherical volume of radius r within the active particle, and $Q = \bar{c}_{ave}(1) = 3 \int_0^1 \bar{\xi}^2 \bar{c}(\bar{\xi}) d\bar{\xi}$ represents the normalized amount of lithium in the active particle, or called the normalized capacity. The above derived equations are valid for constant material parameters which do not vary with concentration. Young's modulus E [20,21] and partial molar volume Ω [22] may not be constant. The effect of concentration-dependent elastic modulus has been discussed in Ref. [23]. The solutions for the cases where Ω is not constant can be found in the Appendix.

The maximum stresses commonly appear at the center of particle or the surface [4], which are respectively given by:

$$\bar{\sigma}_0 = \frac{(1-\nu)\sigma_r(0)}{E} = \frac{(1-\nu)\sigma_\theta(0)}{E} = \frac{2\Omega c_{\max}}{9} \left[Q - \bar{c}(0) \right], \quad (13)$$

$$\bar{\sigma}_1 = \frac{(1-\nu)\sigma_\theta(1)}{E} = \frac{\Omega c_{\max}}{3} \left[Q - \bar{c}(1) \right], \quad (14)$$

where $\bar{c}(0)$ and $\bar{c}(1)$ denote the concentrations at the center and surface, respectively. It is suggested that the center of delithiated particles is compressed hydrostatically and the surface is stretched bi-axially.

If the present operation is galvanostatic, substituting the solution for concentration into equations (13) and (14) we get the DISes at the center and surface

of particle as follows

$$\bar{\sigma}_0 = \bar{i} \left[\frac{1}{15} + \frac{4}{9} \sum_{n=1}^{\infty} \frac{1}{\lambda_n \sin(\lambda_n)} e^{-\lambda_n^2 \tau} \right] - \frac{4}{9} \Omega c_{\max} \sum_{n=1}^{\infty} e^{-\lambda_n^2 \tau} \frac{\lambda_n}{\sin^2(\lambda_n)} \int_0^1 \sin(\lambda_n \bar{\zeta}) \bar{\zeta} \bar{c}_0(\bar{\zeta}) d\bar{\zeta}, \quad (15)$$

$$\bar{\sigma}_1 = \bar{i} \left[-\frac{1}{15} + \frac{2}{3} \sum_{n=1}^{\infty} \frac{1}{\lambda_n^2} e^{-\lambda_n^2 \tau} \right] - \frac{2}{3} \Omega c_{\max} \sum_{n=1}^{\infty} e^{-\lambda_n^2 \tau} \frac{1}{\sin(\lambda_n)} \int_0^1 \sin(\lambda_n \bar{\zeta}) \bar{\zeta} \bar{c}_0(\bar{\zeta}) d\bar{\zeta}, \quad (16)$$

where $\bar{i} = I \Omega c_{\max} = (i_n R \Omega) / FD$ called the electrochemical load factor which is introduced by Ref. [13,15], and the normalized capacity is given by

$$Q = Q_0 + 3\tau I \quad (17)$$

Letting the galvanostatic operation time τ be long enough in equations (15-16), the steady-state stresses $\bar{\sigma}_0$ at the center and $\bar{\sigma}_1$ at the surface arrive at:

$$\bar{\sigma}_0 = -\bar{\sigma}_1 = \frac{1}{15} \bar{i} \quad (18)$$

which is proportional to the electrochemical load factor but independent on the initial solute concentration $\bar{c}_0$. This steady-state stress for galvanostatic operation was also reported in Ref. [4].

If the present operation is potentiostatic the stresses at the center and surface of particle can written as

$$\sigma_0 = \frac{2E\Omega c_{\max}}{9(1-\nu)} [Q - \bar{c}(0)], \quad (19)$$

$$\sigma_1 = \frac{E\Omega c_{\max}}{3(1-\nu)} [Q - \bar{c}_{\text{surf}}], \quad (20)$$

where

$$\bar{c}(0) = \bar{c}_{\text{surf}} + 2\bar{c}_{\text{surf}} \sum_{m=1}^{\infty} (-1)^m e^{-(m\pi)^2 \tau} + 2 \sum_{m=1}^{\infty} m\pi e^{-(m\pi)^2 \tau} \int_0^1 \bar{c}_0(\bar{\zeta}) \bar{\zeta} \sin(m\pi \bar{\zeta}) d\bar{\zeta}, \quad (21a)$$

$$Q = \bar{c}_{\text{surf}} - \bar{c}_{\text{surf}} \frac{6}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} e^{-(m\pi)^2 \tau} + 6 \sum_{m=1}^{\infty} e^{-(m\pi)^2 \tau} \int_0^1 \sin(m\pi \bar{r}) \bar{r} \int_0^1 \bar{c}_0(\bar{\zeta}) \bar{\zeta} \sin(m\pi \bar{\zeta}) d\bar{\zeta} d\bar{r}. \quad (21b)$$

Since $\bar{c}_{\text{surf}}$ is constant, the stress at the surface changes linearly with the capacity.

3. Selection of a charge method

Here we suggest that the optimal selection of a charge method is based on the criteria considering both mechanical stress and total charge time. For demonstrating methodology we will focus on the positive electrode in which particles are delithiated and the surface is bi-axially stretched when the cell is charging. Considering that tensile stress at surface might induce surface crack, the peak value of $\bar{\sigma}_1$, denoted by $\bar{\sigma}_{\text{max}}$, will be considered as the stress parameter for selection of a charge method. The evolution of stress $\bar{\sigma}_1$ with the normalized capacity and its peak value $\bar{\sigma}_{\text{max}}$ for each charge method will be obtained by using the expressions of $\bar{\sigma}_1$ given by Eqs.16 and 20 in section 2. The initial concentration $\bar{c} = 1$ for each charge process is assumed.

3.1 Two-stage charge methods

In this section we consider such a kind of two-stage charge methods in which the first galvanostatic operation is followed by a potentiostatic operation, shown in figure 1a. The blue solid line illustrates a particular two-stage charge method in which the

Fig.1 Illustration of two-stage charge methods: (a) current density, (b) surface concentration and (c) surface stress, evolve with normalized capacity.

galvanostatic operation is switched to the potentiostatic one when the decreasing concentration at the surface of particles, shown in **Figure 1b**, reaches the limit $\bar{c}_{\text{surf}} = 0$. This particular two-stage method is taken as the reference charge method, and called the normal switch method, which is most commonly used at present.

Another possible two-stage charge method denoted by the red dash line in figure 1a,

is realized by choosing some earlier switch time, characterized by capacity difference ΔQ relative with the normal switch method. When the operation switch turns on in this earlier switch method the concentration at the surface is assumed to jump to zero $\bar{c}_{\text{surf}} = 0$, figure 1b, in order to make the lithium ions delithiated out of the particles as many as possible. For comparison the dimensionless charge currents I for all two-stage charge methods are identical.

Since the current density decreases with charge time for two-stage charge methods, the charge process is assumed to be terminated by a cut-off electrical current in potentiostatic stage, with 3% of the current density in the galvanostatic stage. The total charge time is evaluated by using the cut-off current and denoted by $\bar{t}_{\text{end}}$.

Figure 1c shows evolution of the stress at surface, which increases with the normalized capacity in galvanostatic stage monotonically, arrives at its peak value when the operation switch turns on, then decreases linearly in potentiostatic stage, and finally approaches to zero. For the earlier switch, because the sudden drop for the surface concentration $\bar{c}_{\text{surf}}$ is enforced at the time moment of operation switch, a significant jump of the stress occurs at the particle surface. It is observed that the peak stress for the earlier switch method is higher than that for the normal switch method. This is always true, shown in figure 2, for any current density I applied in the galvanostatic stage, indicating the normal switch method is the best charge method for mechanical integrity among the two-stage charge methods.

In figure 2 the total charge time $\bar{t}_{\text{end}}$ (solid lines) is also plotted as a function of the dimensionless charge current I for three different ΔQ . A larger ΔQ means

Fig.2 Variation of charge time $\bar{t}_{\text{end}}$ and maximum stress $\bar{\sigma}_{\text{max}}$ with respect to dimensionless current density I .

earlier operation switch, while $\Delta Q = 0$ stands for the normal switch. Reduction of total charge time by shifting the switch time earlier is invisibly small. Therefore, the normal switch method is the best of two-stage charge methods by considering both mechanical integrity and charge speed, and the early operation switch is not suggested.

It is seen from **figure 2** that employing a larger charge current I can reduce, indeed, the total charge time $\bar{t}_{\text{end}}$ significantly within a certain range of current, however, further increasing current only gain a marginal reduction of the charge time but have to pay the price of rising in mechanical stress.

3.2 Three-stage charge methods

In this section, inspired by the pulsed current charging method [6,17], three-stage charge methods which include two connective galvanostatic stages with different

Fig.3 Illustration of three-stage charge methods: (a) current density and (b) surface concentration, evolve with normalized capacity. Reference method: a normal switch two-stage process. Method *a*: an initial low current stage followed by a high current stage; method *b*: an initial high current stage followed by a low current stage. Both methods *a* and *b* end by potentiostatic stages.

currents followed by a potentiostatic stage will be discussed. Two different three-stage charge methods are considered and schematically shown in figure 3. Method *a* includes an initial galvanostatic stage of low current followed by a galvanostatic stage of high current while method *b* starts with an initial galvanostatic stage of high current

followed by a galvanostatic stage of low current. I_{high} and Q_{high} denote the higher current density and the duration of the high current stage, respectively, while I_{low} denotes the lower. For both three-stage charge methods the third stage is a potentiostatic stage which starts with the surface concentration $\bar{c}_{\text{surf}} = 0$ and terminates when the current reaches 3% of the higher current.

In order to quantitatively evaluate the charge acceleration for the three-stage charge methods, a normal switch two-stage charge process is chosen as the reference in which the current density is identical to I_{low} , shown in figure 3.

Figure 4 shows evolution of the stress at surface for the charge method a .

Fig.4 Evolution of surface stress in three-stage charge method a with respect to normalized capacity.

Employing the higher current in the second stage leads to faster rising of stress, which reaches its peak value when the operation switches to potentiostatic. It is observed that the peak stress for method *a* is higher than the stress for the reference two-stage method. This is always true, shown in figure 5, for any current density I_{high} applied in the second galvanostatic stage. This suggests that the three-stage charge method *a* would increase the risk of mechanical failure for active particles, compared with the normal two-stage charge method.

Fig.5 Variation of charge time $\bar{t}_{\text{end}}$ and maximum stress $\bar{\sigma}_{\text{max}}$ with respect to dimensionless current density I_{high} in method *a*.

However, introducing a high current stage can reduce the total charge time $\bar{t}_{\text{end}}$ (solid lines in figure 5) significantly. Besides, the total charge time $\bar{t}_{\text{end}}$ is also

Fig.6 Evolution of surface stress for three-stage charge method b with respect to normalized capacity: (a) constant partial molar volume; (b) linear variation of the

partial molar volume with concentration, $\frac{\Omega}{\Omega_0} = k\bar{c} + 1$

plotted for three different Q_{high} . The larger Q_{high} means that the galvanostatic stage of high current is longer. It is seen from figure 5 that reduction of charge time by increasing the duration of the high current stage is considerable.

The evolution of the stress at surface for method *b* is demonstrated in figure 6a. The stress increases rapidly in the first stage due to the high current density, and arrives at its first peak value when first stage ends. In the second stage in which the current is lower, the sudden drop in the current leads to a rapid decreasing of the stress. With further charge, the stress increases again and arrives at its second peak value when the operation switches to potentiostatic.

For active materials with a non-constant partial molar volume Ω [22], which is assumed to be a linear function of lithium-ion concentration, the stress evolution is calculated by using the solutions listed in the Appendix and is illustrated in figure 6b. Comparing figure 6a with figure 6b, it is seen that the qualitative trends of stress for both the constant Ω and the concentration-dependent Ω are the same.

The heights of the two peak values are current dependent as shown in figure 6a and b. The second peak value is almost identical to the peak value of the reference two-stage method. Meanwhile, the larger high current density I_{high} leads to higher first peak value which could be lower or higher than the reference value, indicating I_{high} in a certain range could avoid the rising of stress.

Indeed, shown in figure 7, when I_{high} is smaller than a critical value, the maximum stress does not increase and is identical to the reference value. Similar to the method *a*, the total charge time $\bar{t}_{\text{end}}$ can be significantly reduced by employing

the high current stage, shown in figure 7. Therefore, the method *b* is a promising way to accelerate the charge process without raising the risk of mechanical failure. Since method *a* has an obvious disadvantage for stress increasing which can be avoided by method *b*, it is suggested that method *b* is the best one among the three-stage charge methods.

Fig.7 Variation of charge time $\bar{t}_{end}$ and maximum stress $\bar{\sigma}_{max}$ with respect to dimensionless current density I_{b1} for the first stage in method *b*.

It is also seen from figure 7 that the critical value of I_{high} depends upon the duration of the high current stage Q_{high} . The longer the Q_{high} is, the smaller the critical value of I_{high} is. This suggests one can draw a $Q_{high} - I_{high}$ map for optimal design of method *b*, as shown in figure 8. In the area below the red solid line the

reduction of total charge time can be achieved without rising of the maximum stress

$\bar{\sigma}_{\max}$.

Fig.8 $Q_{\text{high}} - I_{\text{high}}$ map showing area where the maximum stress would not be

increased in the three-stage charge method *b*.

It has to be pointed out that our conclusions obtained for charge method selection are based on theoretical results. However, it is found that our theoretical predictions are supported, to some extents, by the experiment work conducted by Li et al [24]. In the experiments they compared a pulse charging protocol, which involves multi-pulse currents and relaxation periods, with the galvanostatic charging method in terms of dischargeable capacity and microstructural changes. It was found that the

dischargeable capacity of the batteries charged by the pulse charging protocol is higher than that by the galvanostatic charge method, indicating that the introduction of pulse current can improve battery performance. This experimental results back up our suggested charge method *b* which employs the initial galvanostatic stage of high current. Furthermore, more severe microcracking and microstructural changes in the electrodes were observed for the galvanostatic charge method than for the pulse charging protocol. It was convinced that such microcracking had been caused by the diffusion induced stress. Our theoretical predictions have indicated that the introduction of an initial galvanostatic stage of high current can reduce the diffusion induced stress. Therefore, this experimental microstructural observation again supports, to some extents, our theoretical results for charge method selection.

4. Concluding remarks

In this paper, two charge strategies have been evaluated based on peak stresses and charge duration. One is a two-stage method which includes a connective galvanostatic-potentiostatic operation. The other one is a three-stage method which has one more galvanostatic stage of high current.

In order to analyze the concentration profile under alterable operations, analytic expressions of both the concentration profile with general initial condition and the diffusion induced stress within a spherical active electrode particle under either galvanostatic or potentiostatic operation have been developed in Section 2. Simulations found that although the initial distribution of concentration $\bar{c}_0$

influences the subsequent lithium concentration and stress profiles, the effects gradually vanish with respect to increase of charge time. For galvanostatic operation after enough long time, the concentration distribution depends only on dimensionless charge current I and initial amount of lithium Q_0 . As consequences, the stresses at the center and surface of the particle are also independent of the initial solute concentration. It has also been found that the stress at the surface varies linearly with the capacity in potentiostatic operation.

Two-stage charge methods have been evaluated by discussing the switch time from galvanostatic to potentiostatic operation in Section 3.1. Compared with the normal switch operation, in which the galvanostatic-potentiostatic switching takes place when the decreasing concentration at the surface of particles in the positive electrode reaches the limit $\bar{c}_{\text{surf}} = 0$, another possible two-stage charge method considers earlier switching. It is found earlier switching leads to sudden drop of the surface concentration, as well as sudden jumps of current density and stress at surface. This charge method negligibly reduces the total charge time but significantly increases the stress, indicating that the normal switch operation is the best for mechanical integrity among the two-stage charge methods.

Then, two kinds of three-stage charge methods have been discussed in Section 3.2: method *a*, an initial galvanostatic stage of low current followed by a galvanostatic stage of high current; and method *b*, in which the two galvanostatic stages are connected in a reverse sequence.

Both methods are capable of accelerating the charge process due to introduction

of a high current stage. In addition, the high current stage in both methods induces a stress peak. For method *a*, the stress peak is highest in the whole duration. However, for method *b*, the peak stress is tunable by controlling the current density and stage duration. In some circumstances, the peak stress is even lower than that in subsequent low current stage. Therefore, it is suggested that method *b* is the best choice as it can accelerate charge process without rising maximum stress. Furthermore, a map based on the current density and duration of the high current stage has been prepared. According to the $Q_{\text{high}} - I_{\text{high}}$ map, one can design charge strategy for optimized balance between charge time and stress.

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Appendix. Solutions for concentration-dependent partial molar volume Ω

Substituting the constitutive equation Eq. 10 into the balance equation,

$$\frac{dS_r}{dr} + \frac{2}{r}(S_r - S_q) = 0, \quad (\text{A.1})$$

and then employing strain-displacement relations,

$$e_r = \frac{du_r}{dr}, \quad e_q = \frac{u_r}{r}, \quad (\text{A.2a,b})$$

where u_r is the radial displacement, we have the equation

$$\frac{du_r^2}{d^2r} + \frac{2}{r} \frac{du_r}{dr} - \frac{2u_r}{r^2} - \frac{1+u}{1-u} \frac{d(Wk)}{3dr} = 0 \quad (\text{A.3})$$

The solution reads as follows

$$u_r = \frac{1+u}{1-u} \frac{1}{3r^2} \dot{\mathcal{O}}_0^r Wk r^2 dr + C_1 r + \frac{C_2}{r^2}, \quad (\text{A.4})$$

where C_1 and C_2 are unknown constant. Using the boundary condition $s_r(R) = 0$

along with the condition that $u_r(0)$ is finite, C_1 and C_2 must be zero. The

expression of stresses can be found as

$$\sigma_r = \frac{2E}{9(1-\nu)} \left[\bar{Q} - \bar{\varepsilon}_{ave}(\bar{r}) \right], \quad (\text{A.5})$$

$$\sigma_\theta = \frac{E}{9(1-\nu)} \left[2\bar{Q} + \bar{\varepsilon}_{ave}(\bar{r}) - 3\bar{\varepsilon}(\bar{r}) \right], \quad (\text{A.6})$$

where $\bar{\varepsilon} = \Omega c$, $\bar{\varepsilon}_{ave}(\bar{r}) = \left(3/\bar{r}^3 \right) \int_0^{\bar{r}} \bar{\zeta}^2 \bar{\varepsilon}(\bar{\zeta}) d\bar{\zeta}$ and $\bar{Q} = \bar{\varepsilon}_{ave}(1) = 3 \int_0^1 \bar{\zeta}^2 \bar{\varepsilon}(\bar{\zeta}) d\bar{\zeta}$.

The maximum stresses commonly appear at the center of particle or the surface,

which are respectively given by:

$$\bar{\sigma}_0 = \frac{2}{9} \left[\bar{Q} - \bar{\varepsilon}(0) \right], \quad (\text{A.7})$$

$$\bar{\sigma}_1 = \frac{1}{3} \left[\bar{Q} - \bar{\varepsilon}(1) \right]. \quad (\text{A.8})$$

Eqs. 13-14 are the special cases of Eqs. A7-A8 when Ω is constant.

Specifically, we may assume that Ω is a linear function of lithium-ion concentration

$$\frac{\Omega}{\Omega_0} = k\bar{c} + 1, \quad (\text{A.9})$$

where Ω_0 is the partial molar volume for $\bar{c}=0$ and k is a free material parameter.

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