RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Interaction between dislocation mechanics on diffusion induced stress and electrochemical reaction in a spherical Lithium ion battery electrode

Zhijun Liu[a], Jianqiu Zhou [a,b,*], Bingbing Chen[a], Jianwei Zhu[a]

[a] Department of Mechanical and Power Engineering, Nanjing Tech University, Nanjing, Jiangsu Province 210009, China.

[b] Department of Mechanical Engineering, Wuhan Institute of Technology, Wuhan, Hubei Province 430070, China.

*Corresponding author. Tel: +86-25-83588706; Fax: +86-25-83374190.

E-Mail addresses: zhouj@njut.edu.cn; liuzhijun@njut.edu.cn.com

Abstract

The effect of coupling dislocation induced stress with electrochemical reaction in a spherical battery electrode is investigated in this paper. A new coupled model among diffusion, dislocation, reversible electrochemical reaction is established by combining diffusion induced stress (DIS), dislocation induced stress and the forward reaction induced stress in the spherical electrode. The results of our model show that the interaction between dislocation induced stress and the forward reaction induced stress plays a significant role in decreasing the tensile stress and even the tensile state can be turned into the compressive stress, which may become a resistance to fracture and decrepitation due to DIS. However, the electrochemical reaction will result in the surface tangential stresses sharply increase with a larger relative rate of reaction and diffusion. Therefore, we provide a new theoretical method to explain the volume change and understand the stress evolution in the electrode.

Keywords: Li-ion battery; stress; electrochemical reaction; dislocation; diffusion

1. Introduction

Lithium ion batteries (LIBs) have been considered as the most promising alternative and green technology for energy storage applied in portable electronic devices, hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and other electric utilities because of their low weight, non-toxicity, high capacity storage and high energy density compared to conventional batteries.[1, 2] Recent research on anodes for LIBs has been mainly focused on electrode materials and material structure design in terms of their morphologies. Because there have been some success in addressing material stability issues by designing nanostructured silicon materials including nanowires, nanotubes, nanoporous films and silicon nanoparticle carbon composites.[3] This nanostructuring strategy has greatly increased the cycle life of anodes to up to a few hundred cycles with 80% capacity retention.[3] But there still have much challenge works needing to be done for materials undergoing large volume changes. Silicon has a large charge storage capacity, low voltage plateau, low cost and this makes it an attractive anode material.[4, 5] However, Si suffers from large volume variation (+270%)[5] during lithiation which causes particle pulverization and amorphization, loss of electrical contact, and early cycling capacity fading.[6] Owing to volume variation during Li inserted into or extracted from the active material of electrode in LIBs, there are different stresses such as DIS, reaction stress, dislocation induced stress which may cause fracture, and possibly cause irreversible capacity loss of the electrode.[6-8] It is urgent to study the stress in the electrode to increase the mechanical durability.

Kalnaus et al. analyzed the crack of silicon particles during Li intercalation by using the theory of DIS.[9] Verbrugge and co-workers suggested that the tendency for fracture and decrepitation could be reduced or avoided by reducing the material size to the nanometer range.[10-12] Chen et al. analyzed fracture damage of nanowire lithium-ion battery electrode affect by DIS.[13] Wei et al. took into account dislocation mechanics on the DIS within a spherical particle.[14] Cheng et al. provided a detailed description of the effect of operating conditions, electrode particle size, particle shape, and phase transformation on DISs in electrodes.[10] Yang et al. studied the coupled problem of interactions of stress and diffusion.[15] R.M. McMeeking et al. analyzed the role of solid mechanics in electrochemical energy systems within lithium-ion batteries.[16] Verbrugge et al. studied battery cycle life prediction with coupled chemical degradation and fatigue mechanics.[17] Cui et al developed a mathematical framework to investigate the interaction between bulk diffusion and interfacial chemical reaction in binary systems.[18] Chakraborty et al. studied the mechanical and chemical effects in the deformation and failure of a cylindrical electrode particle in a Li-ion battery.[19] Zhang et al. analyzed the effect of reversible electrochemical reaction on Li diffusion and stresses in cylindrical Li-ion battery electrodes.[7] Larche and Cahn considered the effect of stresses on local diffusion in a solid, where the coupling between diffusion and chemical stresses was addressed.[20] Sanboh Lee et al. studied DIS in a hollow cylinder.[21] Hao et al. studied that DIS of core-shell nanotube electrodes in lithium-ion batteries.[22] Bucci et al. analyzed two separate electrochemical reactions at the Si/electrolyte interface to characterize the mechanical

and electrochemical response of thin film amorphous Si electrodes during cyclic lithiation.[23] Wu et al. presented a coupled thermal-electrochemical modeling of uneven heat generation in lithium-ion battery packs.[24] Yang et al. studied the insertion-induced expansion of a thin film on a rigid substrate.[25] Li et al. provided an analytical modeling of dislocation effect on DIS in a cylindrical lithium ion battery electrode.[26] Chen et al.[27, 28] analyzed the distribution of dislocation in nanostructured thin film electrode and the effect of misfit dislocation on Li-ion diffusion and stress in spherical electrode. Cheng et al used a thermal stress analysis approach to investigate DIS evolution at the two-phase boundary during the lithiation process.[29] Tavassol et al studied the electrochemical surface stress changes during Li deposition in a model system for Li-ion battery anodes.[30]

Most of above mentioned analyses and studies have respectively studied the effect of DIS affected by various influence factors based on dislocation mechanics, solid mechanics, electrochemical theory and establishment of the theoretical model. However, few works have considered the importance of the coupling between dislocation mechanics and electrochemical reaction in Li-ion battery electrodes.

In this paper, the influence of DIS and the reaction induced stress in a spherical Li-ion battery electrode is studied by studying dislocation mechanics and the reversible electrochemical reaction. Some new relations between electrochemical stresses and DIS are formulated, from which an analytical dislocation mechanics and electrochemical reaction are obtained. In this paper, we aim to study the following three questions.

5

(i)   Calculating and studying the DIS, dislocation-induced stress and electrochemical reaction induced stress on potentiostatic charging operation.

(ii)   Providing a coupled model for explaining stresses in Li-ion battery spherical electrode by studying the interactional effects of dislocation mechanics and electrochemical reaction.

(iii)   Providing a new theoretical way to understand the volume changes and stress evolution in the electrode. .

2. Analysis and Methods

2.1. Diffusion-induced stresses in the spherical electrode

In this paper, consider a spherical silicon negative electrode in the range of $0 < r < R$, where R is the radius of spherical electrode. Figure 1 is a schematic of the lithium-ion battery showing the two electrodes, the positive and the negative, separator and current collectors. The electrodes are consisted of active storage particles and Li-ions flow through the separator from the positive electrode to the negative during charge and vice-versa during the discharging process. Figure 2a shows the schematic illustration of the storage particles inserted Li-ion which is subjected to diffusion stresses, chemical stresses and dislocation-induced stress. During charging, Li-ion migrates along radial direction through the surface of electrode simultaneously and inward to the center of electrode. The process of inserting Li-ion into the storage particles causes a change in volume which leads to diffusion, stress and dislocation. During diffusion process, the reversible reaction

occurs on the electrode/electrolyte interfaces. The DIS arising from the lithium ion insertion or extraction from the electrode is similar to the thermal stresses arising from the heat transfer, whereas the thermal diffusivity mimics the lithium-ion diffusivity, and the temperature gradient represents the lithium-ion concentration gradient.[24] So we introduce DIS by analogy to thermal stress.[31, 32] We assume that the electrode is an isotropic, linearly elastic solid. Therefore, the constitutive equations associated with lithium ion concentration in the solid spherical coordinate can be given by

$$\varepsilon_{rr} = \frac{1}{E}\left(\sigma_{rr} - 2\nu\sigma_{\theta\theta}\right) + \frac{1}{3}\Omega c \tag{1}$$

$$\varepsilon_{\theta\theta} = \frac{1}{E}\left[(1-\nu)\sigma_{\theta\theta} - \nu\sigma_{rr}\right] + \frac{1}{3}\Omega c \tag{2}$$

where ε_{rr} and $\varepsilon_{\theta\theta}$ are strain components along radial and tangential direction, respectively. σ_{rr} and $\sigma_{\theta\theta}$ are stress components along radial and tangential direction, respectively. E is the Young's modulus, ν is Poisson's ratio, c is the molar concentration of solute, and Ω is the partial molar volume of solute.

Because of the symmetry of sphere, the radial and tangential strains in the infinitesimal formulation of deformation can be expressed as functions of radial displacement, u, as:

$$\varepsilon_{rr} = \frac{du}{dr} \quad \text{and} \quad \varepsilon_{\theta\theta} = \frac{u}{r} \tag{3}$$

Considering that lithium ion diffusion in electrode material is much slower than elastic deformation and the mechanical equilibrium is proved much faster than the diffusion equilibrium [33], so we treat the mechanical equilibrium as a static equilibrium

problem. Therefore, the force equilibrium in axisymmetrics case is

$$\frac{d\sigma_{rr}}{dr} + \frac{2}{r}\left(\sigma_{rr} - \sigma_{\theta\theta}\right) = 0 \tag{4}$$

The stress boundary conditions for the spherical model can be expressed as follows:

$$\sigma_{rr}/_{r=R} = 0, \sigma_{rr}/_{r=0} = finite \tag{5}$$

Regardless of the dislocation mechanism, basing on equations (1)-(5), the expressions of radial and tangential stresses can be written as:

$$\sigma_{rr} = \frac{2\Omega E}{3(1-v)}\left[\frac{1}{R^3}\int_0^R c(r,t)r^2 dr - \frac{1}{r^3}\int_0^r c(r,t)r^2\,dr\right] \tag{6}$$

$$\sigma_{\theta\theta} = \frac{2\Omega E}{3(1-v)}\left[\frac{1}{R^3}\int_0^R c(r,t)r^2 dr + \frac{1}{2r^3}\int_0^r c(r,t)r^2\,dr - \frac{1}{2}c(r,t)\right] \tag{7}$$

2.2 Dislocation model in the spherical electrode

According to the work of Prussin[34], An arbitrary radial infinitesimal element surface layer with the thickness of dr is shown in Figure 2b. The solute concentration at the bottom of the diffused layer is assumed as c(r, t) in radii r position. Then the concentration on the upper surface $r + \triangle r$ becomes c(r, t) + $\frac{\partial C(r,t)}{\partial r}$dr. By exerting the solute concentration gradient, the expression of dislocation density is written as: [14]

$$\rho(r,t) = \frac{\varphi}{b}\frac{\partial C(r,t)}{\partial r} \tag{8}$$

where $\rho(r,t)$ is dislocation density, φ is a solute lattice contraction coefficient that can be related to the partial molar volume of the solute, which is $\Omega/3$.

Wei et al. studied dislocation density in terms of the solute concentration gradient.[14] Prussin[34] found that when this surface stress exceeds the stress, σ_g, necessary to generate dislocation, the generated dislocations lie in the surface and their Burgers vectors have a positive edge component in the surface. However, they
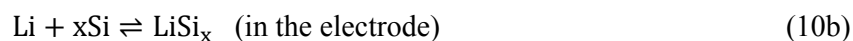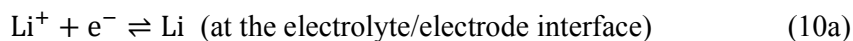
did not further study the relation between the stress and dislocation. So we assumed that dominating effect on the interaction between dislocations and diffusing solutes is the contribution to the long-range term. The relation between the stress and dislocation density can be achieved from the work of Estrin:[35]

$$\sigma_{\zeta} = M\chi\mu b\sqrt{\rho} \tag{9}$$

where M is the Taylor orientation factor, χ is the empirical constant and μ is the shear modulus.

2.3 Electrochemical reaction induced stresses in spherical electrode

It is known that Li-ion inserted into or extracted from electrode can cause the volume change. The electrochemical reaction can also create volume change due to the atomic volume of reactants being different from that of the reaction product. But the insertion of Li-ion into electrode is a complicated process, which involves diffusion of Li-ion in electrolyte, migration of Li-ion through solid electrolyte interphase (SEI), charge transfer at SEI-electrode interface, and diffusion/reaction in the electrode.[36] So the following reversible reactions occur during the insertion of Li-ion in the electrode.

$$Li^+ + e^- \rightleftharpoons Li \quad \text{(at the electrolyte/electrode interface)} \tag{10a}$$

$$Li + xSi \rightleftharpoons LiSi_x \quad \text{(in the electrode)} \tag{10b}$$

The forward reaction can make the electrode expand and the backward reaction will make it shrink, so they can create the pressure and tension respectively. The volumetric strain $\varepsilon_{\text{diffusion}}$ created by Li diffusion is [34, 37]

$$\varepsilon_{\text{diffusion}} = c\Omega \tag{11}$$

The volumetric strain $\varepsilon_{reaction}$ created by formation of the reaction products is

$$\varepsilon_{reaction} = \psi(w_1 - w_2) \tag{12}$$

where ψ is the difference of atomic volume between reactants and the reaction product. $w_1(LiB_X)$ is the fractions of forward reaction product, w_2 is the backward reaction products.

In this paper, we will neglect the presence of a sharp interface between lithiated and unlithiated domains in the electrode for Li insertion. According to "The Law of Mass Action" of Devereux [8] and the work of Yang[38], we considered a reversible electrochemical reaction of first order in the electrode. So w_1 and w_2 can be written as [38]

$$w_1 = \alpha_1 \int_0^t v_1 \, dt = \alpha_1 \psi \int_0^t k_1 c \, dt \tag{13}$$

$$w_2 = \alpha_2 \int_0^t v_2 \, dt = \alpha_2 \psi \int_0^t k_2 w_1 \, dt \tag{14}$$

where v_1 is the forward reaction rate, v_2 is the backward reaction rate, α_1 and α_2 are the proportional constants.

Considering the isotropic deformation due to Li diffusion and electrochemical reaction, we can obtain the resultant volumetric strain created by the Li diffusion and electrochemical reaction can be obtained by using the Eqs. (11)-(14) as follows:

$$\phi = c\Omega + \alpha_1 \psi \int_0^t k_1 c \, dt - \alpha_2 \psi \int_0^t k_2 w_1 \, dt \tag{15}$$

Under the generalized plane strain condition and following the linear theory of thermoelasticity in deriving the Duhamel-Neumann equations[39], the diffusion-reaction- induced stress in spherical electrode can be obtained

$$\sigma_r = \frac{E\nu(\varepsilon_r + \varepsilon_\theta)}{(1+\nu)(1-2\nu)} + \frac{E\varepsilon_r}{(1+\nu)} - \frac{E}{3(1-2\nu)}\left(c\Omega + \alpha_1 \psi \int_0^t k_1 c \, dt - \alpha_2 \psi \int_0^t k_2 w_1 \, dt\right) \tag{16}$$

10

$$\sigma_\theta = \frac{Ev(\varepsilon_r+\varepsilon_\theta)}{(1+v)(1-2v)} + \frac{E\varepsilon_\theta}{(1+v)} - \frac{E}{3(1-2v)}\left(c\Omega + \alpha_1\psi\int_0^t k_1 c\,dt - \alpha_2\psi\int_0^t k_2 w_1\,dt\right) \quad (17)$$

The items related to concentration c represents the stress induced by Li diffusion and connected to α_1 , α_2 represent the stress induced by the forward reaction and the backward reaction, respectively. If ignore the effect of electrochemical reaction, i.e., $\alpha_1=\alpha_2=0$, Eqs. (16) and (17) reduce to the constitutive relations for DIS. Besides, the forward reaction can make the electrode expand and the backward reaction will make it shrink, so they can create the pressure and tension respectively. The compressive stress induced by forward reaction σ_1 and tension stress induced by backward reaction σ_2 can be obtained

$$\sigma_1 = \frac{-E\alpha_1\psi\int_0^t k_1 c\,dt}{3(1-2v)} \quad (18)$$

$$\sigma_2 = \frac{E\alpha_2\psi\int_0^t k_2 w_1\,dt}{3(1-2v)} \quad (19)$$

It is obvious that dislocation-induced stress σ_ζ and the forward reaction induced stress σ_1 can act as a resistance to the process of diffusion during lithium-ion insertion and extraction and the backward reaction σ_2 enhance the process of diffusion. Here, a coupled model interacted with dislocation-induced stress, electrochemical reaction stress and diffusion-induced stress will be firstly proposed. It has been found that the backward reaction can be ignored for both galvanostatic and potentiostatic charging.[7] So the diffusion-reaction-dislocation-induced stresses in spherical electrode at any location and time can be expressed as

$$\sigma_r(r,t) = \sigma_{rr} + \sigma_1 - \sigma_\zeta$$

$$= \frac{2\Omega E}{3(1-v)}\left[\frac{1}{R^3}\int_0^R c(r,t)r^2 dr - \frac{1}{r^3}\int_0^r c(r,t)r^2\,dr\right] - \frac{E\alpha_1\psi\int_0^t k_1 c\,dt}{3(1-2v)} - M\chi\mu b\sqrt{\rho} \quad (20)$$

$$\sigma_\theta(r,t) = \sigma_{\theta\theta} + \sigma_1 - \sigma_\zeta$$

11

$$= \frac{2\Omega E}{3(1-\nu)} \left[\frac{1}{R^3} \int_0^R c(r,t)r^2 dr + \frac{1}{2r^3} \int_0^r c(r,t)r^2\, dr - \frac{c(r,t)}{2} \right]$$

$$-\frac{E\alpha_1\psi \int_0^t k_1 c dt}{3(1-2\nu)} - M\chi\mu b\sqrt{\rho} \tag{21}$$

Therefore, DIS at any time and location of the spherical electrode, with the resistance of dislocation and the forward reaction, can be obtained if the composition profile is known. For illustration these purposes, we choose corresponding parameters in recent literatures for a Li-ion battery electrode material which are listed in Table 1. In spherical electrode, consider the transport of the solute from outer surfaces into inner along the radial direction of the electrode. We assume the diffusion of Si is a single-phase process and the deformation of electrode with linear elastically isotropic solid which is quasi-static process. The diffusion equation can be written as [40]

$$\frac{\partial c}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \tag{22}$$

where D is the diffusion coefficient of Li-ions.

In the paper, we merely study the interaction between dislocation effect on DIS and electrochemical reaction stress to explain the volume change and stress evolution in the electrode. As the electrochemical reaction is reversible, the respective roles between forward and backward reaction should be identified. Under potentiostatic operation, the boundary conditions and the initial solute concentration for the spherical electrode are given by

$$c|_{r=0} = \text{finite} \tag{23}$$

$$c|_{r=R} = c_R \tag{24}$$

$$c|_{0\le r\le R} = c_0 \tag{25}$$

With the consideration of the diffusion equation and the boundary conditions in

Eqs. (5) and (6), the solute concentration during insertion for potentiostatic operation can be expressed as [40]

$$\frac{c(r,t)-c_0}{c_R-c_0}=1+2\sum_{n=1}^{\infty}\frac{(-1)^n}{n\pi\eta}\sin(n\pi\eta)\exp(-n^2\pi^2\beta)\tag{26}$$

Where radical position is $\eta=r/R$ and dimensionless time is $\beta=Dt/R^2$.

The solute concentration is correspondingly varying with the change of time and location. Figure 3a shows the solute concentration increases with time, and reduce continuously from the surface to the center of the spherical electrode during the charging process for potentiostatic control.

Regardless of dislocation and electrochemical reaction effect, substituting Eqs. (26) into Eqs. (6) and (7), the associated radial and tangential stresses are

$$\frac{\sigma_r(r,t)}{\left[E\Omega(c_R-c_0)/(3(1-\upsilon))\right]}$$
$$=-4\sum_{n=1}^{\infty}\exp(-n^2\pi^2\beta)\times\left(\frac{1}{(n\pi)^2}+(-1)^n\left(\frac{\sin(n\pi\eta)-n\pi\eta\cos(n\pi\eta)}{(n\pi\eta)^3}\right)\right)\tag{27}$$

$$\frac{\sigma_\theta(r,t)}{\left[E\Omega(c_R-c_0)/(3(1-\upsilon))\right]}$$
$$=-2\sum_{n=1}^{\infty}\exp(-n^2\pi^2\beta)\tag{28}$$
$$\times\left(\frac{2}{(n\pi)^2}+\frac{(-1)^n}{n\pi\eta}\sin(n\pi\eta)-(-1)^n\left(\frac{\sin(n\pi\eta)-n\pi\eta\cos(n\pi\eta)}{(n\pi\eta)^3}\right)\right)$$

3. Results and discussion

Figure 3b shows the radial stresses as a function of time and position during potentiostatic charging. The radial stresses are tensile in the spherical electrode and the surface radial stress is zero. The tensile radial stress decreases monotonically from

the center of the electrode to surface and the highest stress occurs in the center. Then the radial stress at the center reduces continuously with increasing concentration. The tangential stress is compressive at the surface and tensile at center of the sphere electrode is shown in Figure 3c. The maximum tangential stress occurs at the surface at time zero. The tangential stress varies from compressive at the surface to tensile in the center is resulted from the expansion of outer region is restrained by the inner region.

Taking account of dislocation effects, we take Eqs. (8) and (26) into Eqs.(9) to obtain the solution for dislocation induced stress:

$$\frac{\sigma_\zeta}{M\,\chi\mu b\sqrt{2\varphi\left(c_R-c_0\right)/bR}} = \left[\sum_{n=1}^{\infty}\exp\left(-n^2\pi^2\beta\right)\times\left(\frac{(-1)^n}{\eta}\cos\left(n\pi\eta\right)-\frac{(-1)^n}{n\pi\eta^2}\sin\left(n\pi\eta\right)\right)\right]^{\frac{1}{2}} \tag{29}$$

Figure 3d illustrates the dislocation induced stress generated by solute diffusion during potentiostatic charging under different time and location. The dislocation induced stresses are tensile in the spherical electrode and the dislocation induced stress in the center is zero. The maximum dislocation induced stress is at the surface of sphere, which has the peak value at the beginning of charging as a result of the maximum solute concentration gradient, and reduces as charging goes on.

With the consideration of electrochemical reaction effects, we define a parameter $\tau = \alpha_1 \psi k_1$ as the forward reaction factors. Here the relative rate of forward reaction and diffusion $\varpi = \tau/\Omega$ vary from 0 to 1.[7] The time, we can substitute Eqs. (26) into Eqs. (18) to obtain the solution for the forward reaction induced stress:

$$\frac{\sigma_1}{\varpi E\Omega(c_R-c_0)/3(1-2\mathrm{v})} = \frac{c_R t}{c_R-c_0} + 2\sum_{n=1}^{\infty}\frac{(-1)^n R^2}{\eta D n^3 \pi^3}\sin(n\pi\eta)\left(-\exp(-n^2\pi^2\beta)+1\right) \quad (30)$$

Figure 4 shows the forward reaction induced stress in the spherical electrode during potentiostatic charging under different relative rates of reaction and diffusion ϖ. The relative rates of reaction and diffusion plays an important role in determining the electrochemical reaction. Compare Figure 4a with Figure 4b, the reaction induced stress with ϖ =0.5 is about five times than that with ϖ =0.1, indicating that reaction induced stress is much larger than DIS. The forward reaction induced stress begins to increase as the process of charging goes on while Li-ion enters the electrode from the outer region. The forward reaction induced stress is the compressive in the spherical electrode. The forward reaction induced stress gradually increase from the center to the surface of the electrode and the maximum reaction induced stress occurs at the surface. It can be found that the electrochemical reaction mechanism has a significant effect on distribution of all kinds of stresses. Meanwhile, the forward reaction will enhance compressive stress and decrease DIS at some extent. But the tangential stress increase significantly while the electrochemical reaction is very rapid compared with the diffusion, which will accelerate structural cracking or capacity loss of the electrode. Therefore, the reaction induced stress is similar to double-edge sword, when it is properly used, we will benefit from it.

The radial stress and tangential stress with the influence of dislocation during potentiostatic charge are illustrated in Figure 5a and b. The dash lines in Figure 5 denote the DIS with the influence of dislocation and vice-versa the solid lines. By comparing the dash lines with the solid lines, it can be found that the radial stresses

and tangential stresses with the influence of dislocation are decreased significantly. It is interesting to manifest that the tensile stresses are convert to compressive stresses, which will decrease the propagation of crack induced by tensile stress in the electrode. By comparing Figure 4 with Figure 5, we find that the influence of electrochemical reaction is stronger than that of dislocation.

The corresponding radial, tangential stresses in ϖ =0.5 and radial, tangential stresses in ϖ =0.1 are shown in figure 6 with the influence of the forward reaction without the dislocation effect during potentiostatic charge under different radial position and different dimensionless time. The dash lines in Figure 6 denote the DIS with the influence of electrochemical reaction and vice-versa the solid lines. It can be found that the radial stresses and tangential stresses in the outer region are decreased significantly and radial stresses are even converted to compressive stresses. Compared the Figure 6b with Figure 6d, DIS is decreased more with a larger relative rate of reaction and diffusion.

Figure 7 shows the radial, tangential stresses in ϖ =0.5 and radial, tangential stresses in ϖ =0.1 combining the forward reaction and the dislocation during potentiostatic charge under different position and time. Coupling the forward reaction with the dislocation, DIS will be decreased at some extent, which is helpful in prolonging the cycle life of spherical electrode and decreasing the propagation of crack induced by tensile stress in the electrode. But under the condition of a larger relative of reaction and diffusion, the electrochemical reaction will play a dominant role in impacting the mechanical properties of spherical electrode and even in turn

make the electrode more prone to cracking. These numerical results account for electrochemical reaction and dislocation interaction. It is found that the coupled effect plays a significant role in determining the process of stress evolution. Furthermore, we found that, for a lower ϖ, the forward electrochemical reaction is helpful to relax the tensile stress and inhibit bulk diffusion, which is consistent to the results found by Cui[18].

4. Summary and conclusions

In this paper, the interaction between dislocation effect on DIS and electrochemical reaction mechanism has been investigated by providing a coupled model considering the influence of coupling the dislocation induced stress with the forward reaction induced stresses in the spherical electrode during potentiostatic charging. Following the model used in diffusion equation and the theory of linear elasticity, it has been found that electrochemical reaction and dislocation mechanism have more significant effect on DIS. With the coupled effect, the radial and tangential tensile stresses are decreased sharply and radial stresses are even converted to compressive stresses. The crack generation and propagation caused by tensile stresses will be decreased at some extent. However, the electrochemical reaction will result in the surface tangential stresses increase sharply with a larger relative of rate of reaction and diffusion. It is noteworthy that the outer region in electrode tends to have a larger relative density of fractures, which makes it easier to crack. From these mechanical theories, the spherical electrode materials with lower relative rate of reaction and diffusion ϖ and high dislocation density are expected to be able to inhibit DIS and

optimize their stability and cycling capacity. Our theoretical model based on the coupled effect in a spherical electrode, show that the lithiation process and stress evolution are impacted by interaction between dislocation mechanics on DIS and electrochemical reaction. Our numerical results suggest a strategy to relax tensile stress quickly by increase the electrochemical reaction and dislocation density, which are similar with recent real experimental observations[2, 41-45] and mathematical frameworks[14, 18]. By building the new relationship of dislocation and electrochemical reaction in spherical electrode, this paper presents a new theoretical method to optimize the mechanical properties of electrode materials and lead to environmental and economic benefits.

References

1. X. Su, Q. Wu, X. Zhan, J. Wu, S. Wei and Z. Guo, J Mater Sci., 47, 2519 (2012).

2. X. H. Liu and J. Y. Huang, Energy Environ. Sci., 4, 3844 (2011).

3. H. Wu, G. Chan, J. W. Choi, I. Ryu, Y. Yao, M. T. McDowell, S. W. Lee, A. Jackson, Y. Yang, L. Hu and Y. Cui, Nature Nanotech., 7, 310 (2012).

4. N. Liu, Z. Lu, J. Zhao, M. T. McDowell, H. W. Lee, W. Zhao and Y. Cui, Nature Nanotech., 9, 187 (2014).

5. C. Pereira-Nabais, J. Światowska, A. Chagnes, A. Gohier, S. Zanna, A. Seyeux, P. Tran-Van, C.-S. Cojocaru, M. Cassir and P. Marcus, J. Phys. Chem. C., 118, 2919 (2014).

6. X. Xiao, P. Liu, M. W. Verbrugge, H. Haftbaradaran and H. Gao, J. Power Sources, 196, 1409 (2011).

7. T. Zhang, Z. Guo, Y. Wang and J. Zhu, J. Appl. Phys., 115, 083504 (2014).

8. F. D. O., Topics in Metallurgical Thermodynamics, Wiley, New York (1983).

9. S. Kalnaus, K. Rhodes and C. Daniel, J. Power Sources, 196, 8116 (2011).

10. R. Deshpande, Y.-T. Cheng and M. W. Verbrugge, J. Power Sources, 195, 5081

(2010).

11. Y.-T. Cheng and M. W. Verbrugge, J. Appl. Phys., 104, 083521 (2008).

12. M. W. Verbrugge and Y.-T. Cheng, J. Electrochem. Soc., 156, A927 (2009).

13. B. Chen, J. Zhou, X. Pang, P. Wei, Y. Wu and K. Deng, RSC Adv., 4, 21072 (2014).

14. P. Wei, J. Zhou, X. Pang, H. Liu, K. Deng, G. Wang, Y. Wu and B. Chen, J. Mate. Chem. A, 2, 1128 (2014).

15. F. Yang, Mater. Sci. Eng., A, 409, 153 (2005).

16. R. M. McMeeking and R. Purkayastha, Procedia IUTAM, 10, 294 (2014).

17. R. Deshpande, M. Verbrugge, Y.-T. Cheng, J. Wang and P. Liu, J. Electrochem. Soc., 159, A1730 (2012).

18. Z. Cui, F. Gao and J. Qu, J. Mech. Phys. Solids., 61, 293 (2013).

19. J. Chakraborty, C. P. Please, A. Goriely and S. J. Chapman, Int. J. Solids Struct., 54, 66 (2015).

20. F. C. Larché and J. W. Cahn, Acta Metallurgica et Materialia, 40, 947 (1992).

21. S. Lee, W. L. Wang and J. R. Chen, Mater. Sci. Eng., A, 285, 186 (2000).

22. F. Hao and D. Fang, J. Appl. Phys., 113, 013507 (2013).

23. G. Bucci, S. P. V. Nadimpalli, V. A. Sethuraman, A. F. Bower and P. R. Guduru, J. Mech. Phys. Solids., 62, 276 (2014).

24. B. Wu, V. Yufit, M. Marinescu, G. J. Offer, R. F. Martinez-Botas and N. P. Brandon, J. Power Sources, 243, 544 (2013).

25. F. Yang, J. Power Sources, 241, 146 (2013).

26. J. Li, Q. Fang, F. Liu and Y. Liu, J. Power Sources, 272, 121 (2014).

27. B. Chen, J. Zhou, J. Zhu and Z. Liu, RSC Adv., 4, 64216 (2014).

28. B. Chen, J. Zhou, J. Zhu, T. Liu and Z. Liu, J. Electrochem. Soc., 162, H493 (2015).

29. C.-K. ChiuHuang and H.-Y. Shadow Huang, J. Electrochem. Soc., 160, A2184 (2013).

30. H. Tavassol, M. K. Y. Chan, M. G. Catarello, J. Greeley, D. G. Cahill and A. A. Gewirth, J. Electrochem. Soc., 160, A888 (2013).

31. S. P. T. a. J. N. Goodier, Theory of Elasticity, McGraw-Hill, New York (1970).

32. J. C. J. H.S. Carslaw, Conduction of Heat in Solids, Clarendon, Oxford (1959).

33. Y.-T. Cheng and M. W. Verbrugge, J. Power Sources, 190, 453 (2009).

34. S. Prussin, J. Appl. Phys., 32, 1876 (1961).

35. Y. Estrin, J. Mater. Process. Technol., 80–81, 33 (1998).

36. M. M. Kamisah, H. Siti Munirah and M. S. Mansor, Ionics, 13, 223 (2007).

37. J. C.-M. Li, Metall. Trans. A, 9 (1353 (1978)).

38. F. Yang, J. Appl. Phys., 107, 103516 (2010).

39. B. A. B. a. J. H. Weiner, Theory of Thermal Stress, Dover Publications, Mineola, New York (1997).

40. J. Crank, The Mathematics of Diffusion, Oxford University, England (1998).

41. S. W. Lee, M. T. McDowell, J. W. Choi and Y. Cui, Nano Lett., 11, 3034 (2011).

42. M. J. Chon, V. A. Sethuraman, A. McCormick, V. Srinivasan and P. R. Guduru, PhRvL, 107, 045503 (2011).

43. L.-F. Cui, R. Ruffo, C. K. Chan, H. Peng and Y. Cui, Nano Lett., 9, 491 (2009).

44. C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins and Y. Cui, Nat Nano, 3, 31 (2008).

45. S. W. Lee, M. T. McDowell, L. A. Berla, W. D. Nix and Y. Cui, Proceedings of the National Academy of Sciences, 109, 4080 (2012).

Table 1 Material properties and operating parameters

Parameter	Symbol	Value
Young's modulus of Lithiated Si	E	30-80 Gpa
Poisson's ratio	v	0.22
Burgers vector	b	2.532 Å
Maximum stoichiometric Li concentration	$c_{s\,max}$	$2\times10^{-5}m^3s^{-1}$
Diffusion coefficient	D	$2\times10 m^3 mol^{-1}$
Partial molar volume of solute	Ω	$2.0152\times10^4 mol\,m^{-3}$
Taylor orientation factor	M	1.732-3.06
Empirical constant	χ	0.33
Lattice constant of Si	a	5.431 Å
The relative rate of reaction and diffusion	ϖ	0-1
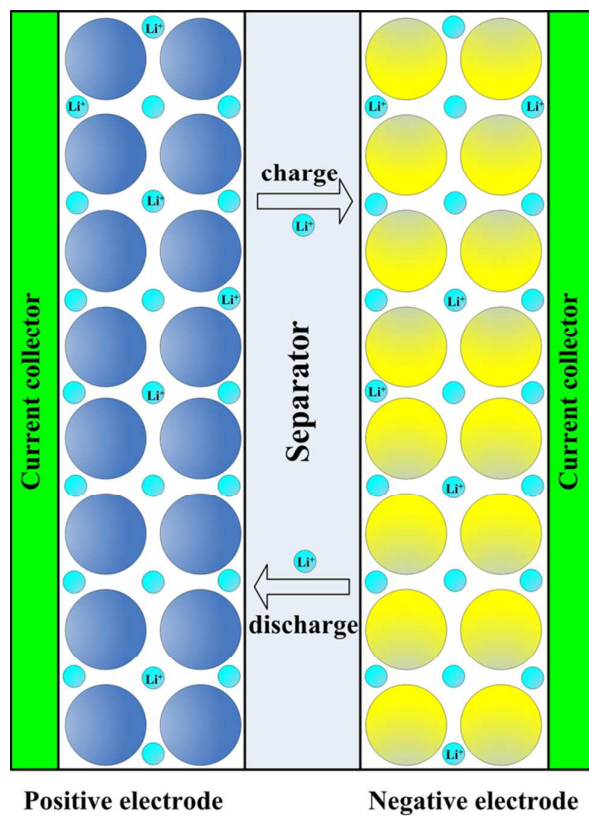
Fig. 1 A schematic of the composition of the Li-ion battery. The main components are the current collectors, the electrodes, the positive and negative and separator. The electrodes are consisted of active storage particles and Li-ions flow through the separator from the positive electrode to the negative during charge and vice-versa during the discharging process.
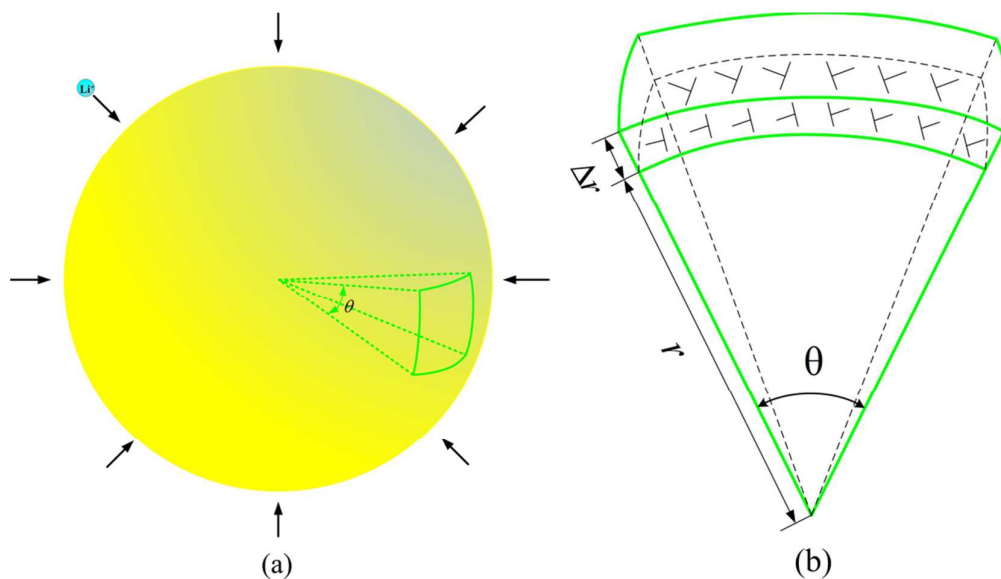
(a)   (b)

Fig. 2 Schematic illustration of the storage particles inserted Li-ion (a) is subjected to diffusion stresses, chemical stresses and dislocation-induced stress. The process of inserting Li-ion into the storage particles causes a change in volume which leads to diffusion, dislocation (b) and stress.
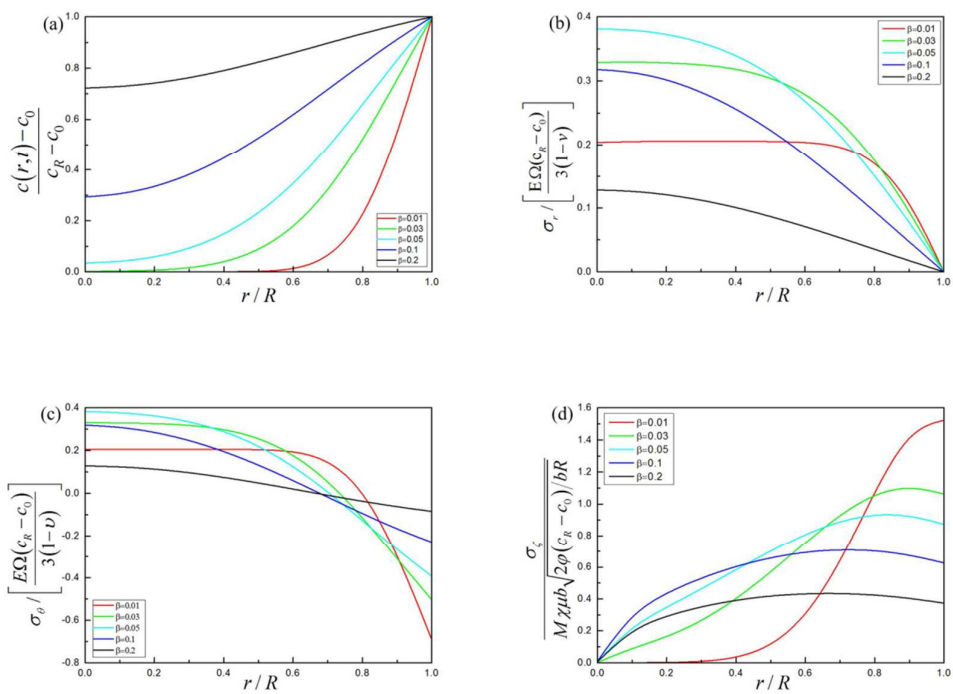
Fig.3. The profile of solute concentration (a) and the corresponding radial stress (b), tangential stress (c) without the influence of dislocation and dislocation-induced stress (d) during potentiostatic charging under different radial position for different dimensionless time.
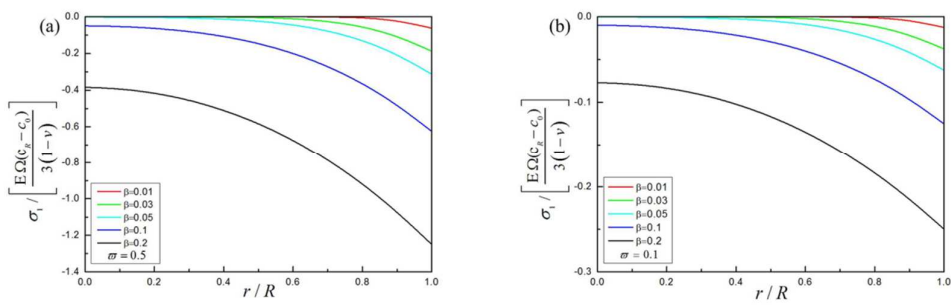
Fig.4 For different radial position and different dimensionless time, the reaction induced stress in the electrode during potentiostatic charge under different relative rates of reaction and diffusion ϖ .
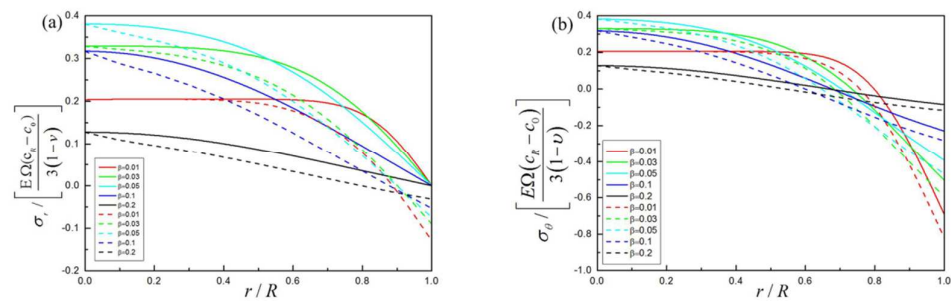
Fig. 5 The corresponding radial stress (a) and tangential stress (b) with the influence of dislocation during potentiostatic charge under different radial position and different dimensionless time of radii 5 nm spherical particle electrode.
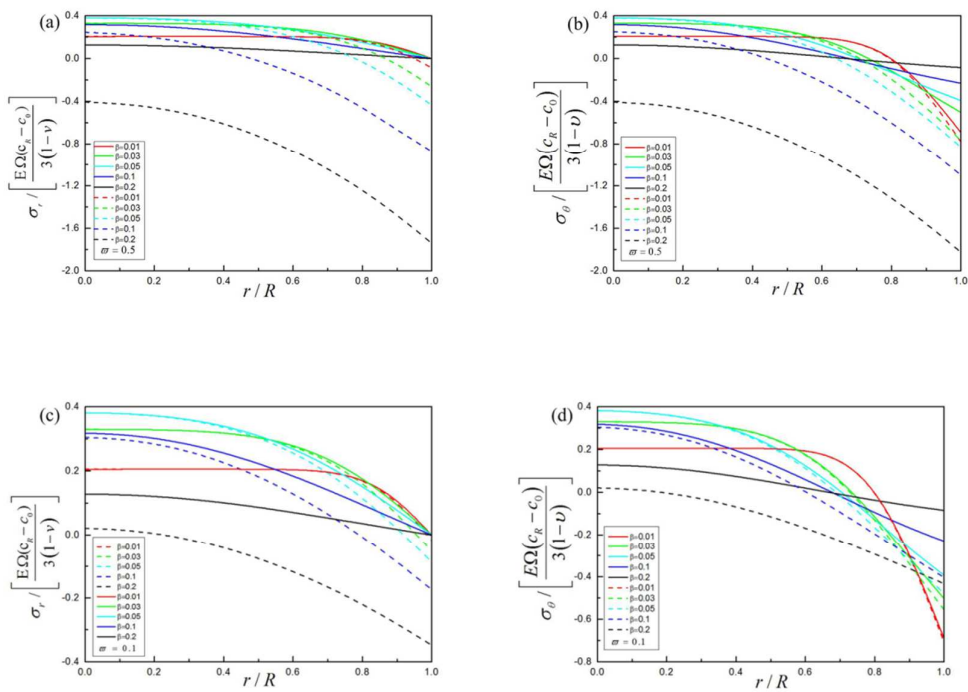
Fig. 6 The corresponding radial (a), tangential (b) stresses in ϖ =0.5 and radial (c), tangential (d) stresses in ϖ =0.1 with the influence of the forward reaction without the dislocation effect during potentiostatic charge under different radial position and different dimensionless time of radii 5 nm spherical particle electrode.
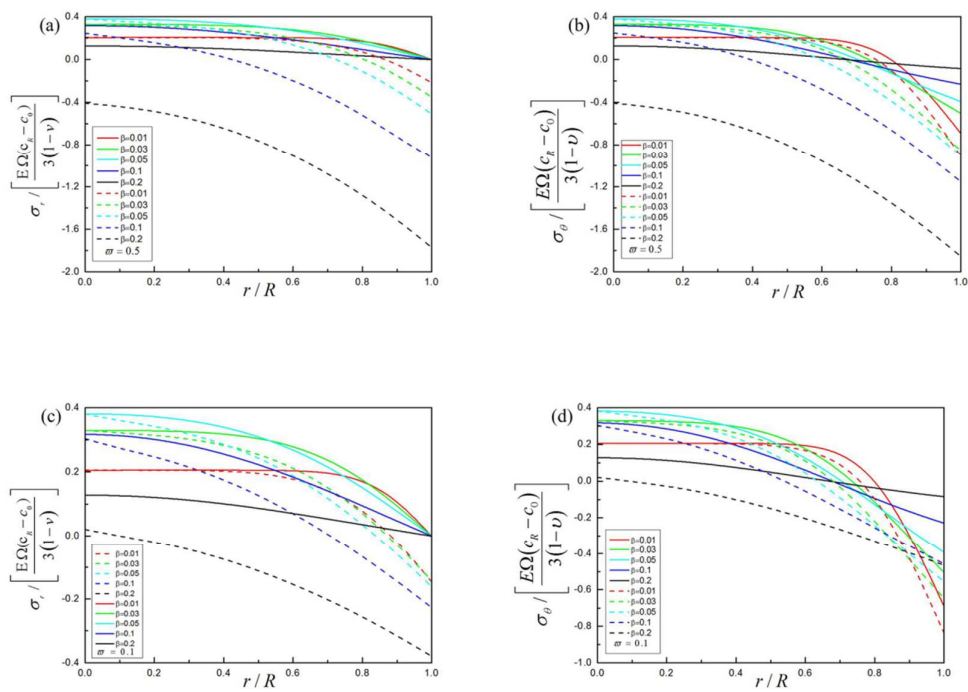
Fig. 7 The corresponding radial (a), tangential (b) stresses in ϖ =0.5 and radial (c),

tangential (d) stresses in ϖ =0.1 with the influence of coupling the forward reaction

with the dislocation during potentiostatic charge under different radial position and

different dimensionless time of radii 5 nm spherical particle electrode.