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Diffusion induced stress and distribution of dislocation in nanostructured thin film electrode during lithiation

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Abstract

Li-ion battery electrode materials with huge volume changes are calling for studies on fracture during lithiation. By analyzing the process of lithiation, the new model is established with dislocation mechanisms of the nanostructured thin film electrode materials on diffusion induced stress for improving Li-ion battery life undergoing potentiostatic or galvanostatic charging. In present work, the interaction between diffusion and dislocation induced stress or strain energy is demonstrated under potentiostatic and galvanostatic charging. The stress and strain energy can evolve quite differently under potentiostatic or galvanostatic charging. At the same time, we observe that the magnitude of stress and strain energy is influenced by the dislocation. What's more, the total strain energy or maximum stress affected by the dislocation is larger under the potentiostatic charging than that under the galvanostatic charging at the beginning of charging. However, total strain energy or maximum stress under galvanostatic charging is larger than potentiostatic charging in the later lithiation process. The influence of mechanical behaviour with the dislocation effect which is more significant about the distribution of the stress and strain energy in the nanostructured thin film electrode is specified. These results also show that it is possible to control dislocation density with the methods of nanotechnology to improve Li-ion battery life.

Key words: Li-ion battery, diffusion induced stress, dislocation strain energy, Nanostructured electrode

1 Introduction

Due to their high energy storage density,¹⁻³ Li-ion battery is used in many commercial electronic appliances. To achieve a higher energy density, new anode materials and different anode shapes are being intensively studied in the Li-ion battery. For example, Si is one of the most promising anode materials used in Li-ion battery electrode because of a theoretical capacity of 4200mAhg⁻¹.⁴⁻⁶ However, owing to volume change,⁷⁻⁹ there is a large stress led to irreversible capacity loss and poor cyclability in the electrode during lithiation.¹⁰ Recent experiments show that mechanical failure of the electrode can be mitigated by using different nanostructured anode shapes, such as nanowires,¹¹ thin films,^{12,13} and hollow nanoparticles¹⁴. These structures can reduce the stress by managing the deformation through shape optimization and geometric restrictions.

A number of theoretical models had been performed on analyzing the mechanical failure of the electrode owing to Li⁺ diffusion. Prussin¹⁵ made an analogy between thermal stress and diffusion induced stress (DIS) in a thin plate. Li¹⁶ analyzed a number of analytical solutions to DIS problems in spherical, cylindrical, and thin plate geometry. Huggins et al.¹⁷ utilized Griffith's criteria to expound fracture phenomenon in rechargeable electrochemical systems. To avoid pre-existing crack, Bhandakkar and Gao¹⁸ developed a cohesive model to suggest a critical characteristic dimension. Qiu¹⁹ developed a novel water-soluble Li-ion binder to enhance the cyclability of c/Li-ion phosphate cathodes, Recently, Wei. et.al.²⁰ had established the dislocation model to analyze the diffusion induced stresses in a spherical particle. At

the same time, Chen.et.al.²¹ had also analyzed the fracture damage of the nanowire electrode in Li-ion battery. The stress induced by Li⁺ diffusion can lead to fracture of the electrode, which has been confirmed through many experiments. A recent design of electrodes involves nanostructures thin film, which can enhance the mechanical and chemical stability of anodes simultaneously. For example, nanostructured Si thin film exhibited superior performance during charge cycling.¹² Thus, we consider the nanostructured thin film electrodes. It is necessary to clarify the phenomena of mechanical properties in nanostructured thin film electrode during lithiation.

The charging nanoparticle electrode with one face of the nanoparticle touching the electrolyte in liquid electrolytes and a reaction front propagates progressively along the r-direction of the nanoparticle causes the nanoparticle to swell by the transmission electron microscope (TEM) observation.²² The process of the Li⁺ intercalation has a “Medusa zone” containing a high density of dislocations. It will go on nucleation at the moving front and absorbed from behind. Huang²³ also found there is a high density of dislocation in a single SnO₂ nanowire electrode. Few reports specifically considered the dislocation effect induced by Li⁺ diffusion in nanostructured thin film electrode. Thus, we aim to develop an analytical model with dislocation effect to analyze the mechanical behavior in nanostructured thin film electrode. For this purpose, the analytical model will be explored to explain the diffusion process by finite elasticity-plasticity theory²⁴⁻²⁶ and dislocation theory²⁷ under potentiostatic and galvanostatic operation. In addition, dislocation induced strain energy is predicted to affect the magnitude distribution of the total strain

energy. Finally, we will provide a theoretical method for prolonging Li-ion battery life in the nanostructured thin film electrode by taking into account the dislocation effect.

2 Analytical model in nanostructured thin film electrode

2.1 stress and distribution of dislocation by solute diffusion

The insertion of Li^+ into electrode is a diffusion process, which involves the diffusion of Li^+ in electrolyte, migration of Li^+ through solid electrolyte interphase(SEI), charge transfer at the electrode interface, and diffusion in the electrode. So the reversible reactions will occur during lithiation in the nanostructured thin film electrode. Lithium diffusion may depend on the different crystal structures (layered, spinel, olivine). In this paper, these different crystal structures are manifested through some parameters, such as, Young's modulus of material, Molar volume, Maximum concentration, lattice constant of material, Burgers vector, etc. Fig.1 shows a thin film electrode with width $2h$ submitted to insertion of Li^+ . The electrode material is regarded as an isotropic linear elastic solid and the deformation is assumed as quasi-static. According to the solute diffusion theory, the transport of solute is modeled as a concentration driven diffusion process along the thickness direction of the electrode. The diffusion equation in the thin film can be expressed as²⁸

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 C}{\partial y^2} \quad (1)$$

Where D is the diffusion coefficient which can be considered as constant and C is the

molar concentration of solute. The Li^+ into host causes a swelling transformation strain β , which can be defined as $\Omega/3$. Ω is the partial molar volume of solute in the electrode. It is worth noting that this model may work for the “half-cell” and the effect of SEI layer will be ignored because the SEI layer is weakly formed “half-cell” as compared to “full-cell”. The stress caused by concentration gradients is similar to those caused by temperature gradients. For the concentration gradients, we have the relation.

$$\varepsilon_x = -\beta C \quad (2)$$

Where the ε_x is a component of strain. Timoshenko and Goodier²⁶ has derived an expression for the stress in a thin plate when the temperature distribution is independent of the x and z coordinates. By analogy the thermal stresses, the diffusion induced stress will be developed in a thin film electrode.

$$\sigma(y,t) = \frac{\beta CE}{1-\mu} - \frac{\beta E}{2h(1-\mu)} \int_{-h}^h C dy - \frac{3\beta E y}{2(1-\mu)h^3} \int_{-h}^h C y dy \quad (3)$$

Where E is Young’s modulus of electrode material and μ is Poisson’s ratio. Eq. (3) gives the DIS in the electrode during lithiation. Thus, DIS distribution can be identical to the concentration profile from which it was derived. It is clear that there is a datum stress $\sigma_u=0$ induced by an arbitrary solute distribution. It satisfies the condition that the sum of the tensile stress is equivalent to the sum of the compressive stress.

Pearson et al.²⁹ appear that the stress distribution by solute lattice contraction is sufficient to induce plastic deformation and dislocations in dislocation-free silicon.

What's more, Prussin¹⁵ proposed that the diffusion of solute atoms can lead to the generation of dislocations. Therefore, we will consider the dislocations effect due to the diffusion of Li^+ in the nanostructured thin film electrode. As has been reported, the highest stress is found at the surface at the very beginning of the diffusion process. According to the Prussin¹⁵, the initial stress exceeds the stress σ_g which necessary to induce dislocation, the dislocations generated must lie in the surface and their Burgers vectors must have a positive edge component in the surface. It is obvious that dislocations induced stress can act as a resistance to the process of diffusion during lithiation. Thus, the tensile stress will be reduced when the dislocation is considered in the electrode. The new datum, $\sigma u=0$, is determined by the requirement that the sum of the compressive stress equals the sum of the tensile forces will be reformed. As a result of stress reducing, the neutral planes will be moved farther from the surfaces of the diffused lattice. The greater the stress decreased, the closer the neutral planes approach the depth of solute penetration.

In Fig.2, we assume the initial stress exceeds the stress σ_g and the volume of the diffused layer lying between the planes $y=a$ and $y=h$. Let C be the solute concentration at the bottom surface y and the concentration at the upper surface then becomes $C + (\partial C/\partial y)dy$. Thus, the evolution of plastic strain tensor during lithiation is dependent on the dislocation density (ρ), According to result given by Prussin, the expression for the dislocation density in terms of the Li^+ concentration gradient:

$$\rho = \frac{\beta}{b_y} \frac{\partial C}{\partial y} \quad a < |y| < h \quad (4)$$

$$\rho = 0 \quad 0 < |y| < a \quad (5)$$

Where b_y is the magnitude of the edge component of the Burgers vector of the dislocation in the y direction. With increasing diffusion, the stress imposed by lattice contraction decreases at the surface. The dislocation will move into the interior.

According to the theory of Estrin,³⁰ the diffusion induced dislocation stress can be

express by

$$\sigma^1 = M\varphi Gb_y \sqrt{\rho} \quad 0 < |y| < b \quad (6)$$

$$\sigma^1 = 0 \quad b < |y| < a \quad (7)$$

where M is the average Taylor factor. The variation of M can be included in the model. However, in what follows, M will be considered constant for simplicity, G is the shear modulus and φ is a numerical constant. It is very difficult if not impossible to obtain the exact solution of the resultant stress distribution of the electrode when the dislocation is considered. Thus, the resultant stress at the electrode can be approximately as

$$\sigma^1(y,t) = \frac{\beta CE}{1-\mu} - \frac{\beta E}{2h(1-\mu)} \int_{-h}^h C dy - \frac{3\beta E y}{2(1-\mu)h^3} \int_{-h}^h C y dy - M\varphi Gb_y \sqrt{\rho} \quad 0 < |y| < b \quad (8)$$

$$\sigma^1(y,t) = \frac{\beta CE}{1-\mu} - \frac{\beta E}{2h(1-\mu)} \int_{-h}^h C dy - \frac{3\beta E y}{2(1-\mu)h^3} \int_{-h}^h C y dy \quad b < |y| < a \quad (9)$$

Hence, the distribution of stress with the dislocation effect will be obtained if the composition profile is known.

2.2 Diffusion and dislocation under galvanostatic and galvanostatic charging

In this paper, the charging conditions of potentiostatic and galvanostatic will be considered. Under the potentiostatic conditions, Li-ion battery is charged with the

constant voltage. The initial and boundary conditions can be expressed as

$$C(h, 0) = C_h, \quad C(0, t) = \text{finite} \quad (10)$$

The initial Li^+ concentration in the electrode is denoted as zero. The analytic solution is well known about the diffusion problem and the expression during charging could be expressed by[28]

$$\frac{C(y, t)}{C_h} = 1 + 2 \sum_{n=0}^{\infty} \frac{(-1)^n}{n} \exp[-Dn^2\pi^2 t/4h^2] \sin \frac{n\pi y}{h} \quad (11)$$

So the stress without considering the dislocation effect can be obtained by substituting it into Eq. (3)

$$\sigma(y, t) = \frac{E\beta C_h}{D(1-\mu)} \left[\sum_{n=1}^{\infty} \left(\frac{2(-1)^n}{(\pi n)^2} \left(\frac{2}{n^2\pi^2} \right) + \frac{(-1)^n}{n\pi y/h} \sin(n\pi y/h) - (-1)^n \left(\frac{\sin(n\pi y/h) - n\pi y/h \cos(n\pi y/h)}{(n\pi y/h)^3} \right) \right) \right] \exp(-Dn^2\pi^2 t/h^2) \quad (12)$$

The variations of solute concentration profiles can be sketched out by using of Eq. 8 in the Fig. 3(a) during the first charging cycle. Due to the symmetry of the problem, the results are plotted only over half of the thin film width. Concentration continuously rises with charging time at the same location during insertion. Corresponding to the condition shown, DIS distribution will be showed in Fig. 3(b) without considering the dislocation effect. From the Fig. 3(b), the stress is tensile near the center and compressive near the free surface of the electrode. In addition, the tensile stress at the center appears before the solute reaches there. At the center, the stress always have the same magnitude so that the stress at the center is purely hydrostatic in tension Especially, the maximum stress, which is compressive, occurs at the surface.

$$\sigma_x \max = -\frac{EC_1}{3(1-\mu)} \quad (13)$$

At any location, the stress first increases, reaches a maximum, then decreases with charging time and tends to a steady-state in the Fig.3(c). There are some dislocations in the electrode during diffusion process. According to the theory of the dislocation in this paper, the dislocation induced stress can be written as

$$\sigma_x^1 = M\phi G \left[\beta b_y C_h \sum_{n=1}^{\infty} \left((-1)^n \left(\frac{\sin(n\pi y/h) - nn\pi y/h \cos(n\pi y/h)}{(n\pi y/h)^3} \right) \right) \exp(-Dn^2\pi^2 t/h^2) \right]^{1/2} \quad (14)$$

$$a < |y| < h$$

$$\sigma_x^1 = 0 \quad 0 < |y| < a \quad (15)$$

For the purpose of accounting for the dislocation effect, the parameters of Li-ion battery electrode materials under potentiostatic operation, which are listed in Table 1, are cited from references.^{18, 32-33} For simplicity, we assume the a is about the half of width ($a=h/2$) of the electrode. From the Fig. 4, normalized dislocation induced stress always maintains the tensile stress state with different locations and charging time during insertion. At any location, the dislocation induced stress will first increases, reaches a maximum, and then decreases with the charging time. What's more, the maximum dislocation induced stress nearby the surface of electrode will reduce with time increases. This is due to the reason that the constant surface concentration suppresses dislocation nucleation over time. Fig. 5 shows the coupling stress between diffusion and dislocation induced stress on the mechanical behavior of electrode during potentiostatic charging. The dot lines represent the stresses considering the dislocation effect and the solid lines represent the stresses without considering the

dislocation effect. If the dislocation effect exists, there is a significant decrease in tensile stress at nanoscale, and even it can make the tensile stress becoming compressive stress by comparing different time. Through comparative analysis, the magnitude of stresses is significantly decreasing at any given time when the dislocation is considered.

Under galvanostatic charging, the charging rate is assumed as 1C. To comprehend the stress due to the diffusion, the boundary conditions under galvanostatic can be found as

$$D \frac{\partial c}{\partial r} \Big|_{r=0} = 0 \quad (16)$$

$$-D \frac{\partial c}{\partial r} \Big|_{r=R} = -\frac{I}{F} \quad (17)$$

Where I is a constant current density and $F = 96486.7 \text{ C mol}^{-1}$ is the Faraday's constant. The analytic solution is well known about the diffusion problem and the expression during the insertion can be expressed by²⁸

$$C(r, t) = \frac{Ih}{FD} \left[\frac{Dt}{h^2} + \frac{3y^2 - h^2}{6h^2} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \cos\left(\frac{n\pi y}{h}\right) \exp(-Dn^2\pi^2 t/h^2) \right] \quad (18)$$

So the DIS can be given by

$$\sigma(y, t) = \frac{E\beta}{1-\mu} \frac{Ih}{FD} \left[\frac{h^2 - 3y^2}{6h^2} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \cos\left(\frac{n\pi y}{h}\right) \exp(-Dn^2\pi^2 t/h^2) \right] \quad (19)$$

The result for insertion normalized concentration is shown in the Fig. 6(a) under the galvanostatic charging. The concentration continuously rises with charging time and different locations. Normalized stress making it straightforward to compare in the thin film electrode is illustrated in Fig. 6(b). The DIS is tensile at the center and

compressive at the surface in the Fig. 6(b) without considering the dislocation effect.

At the center, the tensile stress occurs before the solute reaches the center, and the maximum stress is tensile when the stress is compressive at the surface with the same magnitude. At any location, the stress increase in magnitude with charging time and will tend to a steady-state. The peak stress occurs at the surface after reaching the steady state

$$\sigma_{\max} = \frac{E\beta I h}{3(1-\mu)FD} \quad (20)$$

During the galvanostatic charging, there are also some dislocations in the electrode because of solute diffusion. According to the theory of the dislocation in this paper, the dislocation induced stress can be written as

$$\sigma^1(y,t) = MG\phi \left[\frac{\beta I}{FD} b_y C_h \left(\frac{y}{h} + \frac{h^2 \pi}{y^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \sin\left(\frac{n\pi y}{h}\right) \exp(-Dn^2 \pi^2 t/h^2) - \frac{h}{y} \sum_{n=0}^{\infty} \frac{(-1)^n \cos(n\pi y/h)}{n^2} \exp(-Dn^2 \pi^2 t/h^2) \right) \right]^{1/2} \quad (21)$$

$$a < |y| < h \quad (21)$$

$$\sigma^1(y,t) = 0 \quad 0 < |y| < a \quad (22)$$

During the charging process, dislocation effect can contribute to stress distribution because of Li^+ diffusion under the galvanostatic charging. The dislocation at the surface moves into the interior. Normalized dislocation induced stress increases monotonically to a steady state with charging time during lithiation in the Fig.7. For insertion, the dislocation induced stress is tensile in the electrode. The maximum dislocation induced stress occurs at the surface of the electrode and can be given in $\sigma^1_{\max} = MG\phi(\beta I/b_y FD)^{1/2}$. Here, we will consider the coupling stress between the DIS and the dislocation induced stress in the thin film electrode. The dot lines

represent the stress considering the dislocation effect and the solid lines represent the stress without considering the dislocation effect. The Fig. 8 shows the effect of dislocation on stress for the Si electrode with variations of time. It is obvious that the magnitude of tensile stress may be significantly and even be reverted to a state of compressive stress from the Fig. 8. Significantly, there is an evident decreasing tensile stress at the nanoscale level.

2.3 The maximum stress in the nanostructured thin film electrode

Above this, the dislocation effect should be considered in the nanostructured thin film electrode. Under the charging conditions of potentiostatic and galvanostatic, the different maximum principal stresses are tensile, occurs at the center or surface of the electrode during steady insertion starting from uniform lithium concentration. The maximum stress considering the dislocation effect in the nanostructured electrode can be expressed as

$$\sigma_{\max} = \sigma_x \max - \sigma_x^1 \max \quad (23)$$

During the process of potentiostatic and galvanostatic, the maximum stress will be proposed from this paper. The Fig.9 shows the normalized center stress and maximum stress σ_{\max} with considering the dislocation stress in the electrode during the potentiostatic and galvanostatic charging. What's more, normalized center stress or maximum stress under galvanostatic charging is weaker under potentiostatic charging. The main reason is that the gradient of Li^+ concentration under galvanostatic charging is lower than that under potentiostatic charging. Significantly, the normalized maximum stress is greater than that for galvanostatic charging in the

potentiostatic charging at the beginning of charging. However, normalized maximum stress for the galvanostatic charging is greater than that of potentiostatic charging at the later lithiation process in the Fig.9. Therefore, it is obvious that we will first use the galvanostatic charging operation followed by the potentiostatic charging to reduce the stress in the Li-ion battery. This dislocation induced stress maybe one of factors responsible for the observed behaviour to the fracture of nanoparticle used in Li-ion battery under the two charging operations. Furthermore, the stress analysis can estimate remedies for avoiding fracture because of Li^+ diffusion in the nanostructured electrode.

3 strain energy of the nanostructured thin film electrode

To estimate the fracture resistance, we can also discuss the the strain energy in the electrode. For nanoscale film, the total strain energy contains the bulk energy and dislocation strain energy. Depending on the theory of the linear incremental constitutive relation³¹, we assume the incremental deformation is infinitesimal. When small deformations are supposed, the strain energy release rates will be linearly with the size. The bulk strain energy density can be calculated accumulated as a result of the deformation for the isotropically deformed film.

$$e(y) = \frac{\sigma(y,t)^2}{2E} \quad (24)$$

Bulk strain energy which is stored in the electrode because of the elastic deformation and the Bulk strain energy can be obtained by integrating the strain energy density over the entire volume of the thin film

$$G_T = 2 \int_0^h e(y) y dy \quad (25)$$

From above we can define strain energy with dimensionless form as $G = G_T / 2Eh^3 (\beta C_h / (1 - \mu))^2$. Fig. 10(a) shows that variation of bulk strain energy for representative values of Poisson's ratio under the potentiostatic charging without considering the dislocation induced strain energy. The difference in the strain energy profiles in the four cases owes to the different Poisson's ratio. In case of the plane stress condition, the total strain energy first increases, reaches a maximum, and then decrease because of the transient nature of the stresses. Under the galvanostatic charging, similar to the potentiostatic case, Poisson's ratio effects stored energy significantly. However, bulk strain energy is increasing monotonously initially and reaches a peak values with the charging time. In addition, the bulk strain energy will increase monotonically to a steady-state consistent with charging time in Fig. 10(b).

The dislocation energy will be considered in the electrode. In the case of a dislocation, this means making a cut in the medium to the dislocation line and displacing the faces of the cut relatively by a Burgers vector. For a single Volterra dislocation in a strained body, the elastic energy per unit length evaluates to²⁷

$$G = \frac{ub^2}{4\pi(1-u)} \log \frac{h}{y} \quad (26)$$

When diffusion proceeds under conditions of constant surface concentration, the total number of dislocation N per unit length of diffused layer, which can be determined as follows

$$N = \int_a^h \rho dy \quad (27)$$

The strain energy due to dislocation can be expressed by

$$\begin{aligned}
 G &= N \frac{ub^2}{4\pi(1-u)} \log \frac{h}{y} \\
 &= \int_a^h \rho dy \frac{ub^2}{4\pi(1-u)} \log \frac{h}{y}
 \end{aligned}
 \tag{28}$$

when the dislocation considered, the strain energy will be plotted at the 200nm width of thin film electrode in the Fig.11. Under the potentiostatic charging, the Fig. 11(a) shows dislocation strain energy initially increases, reaches a peak value, and then decreases for the nanostructured thin film electrode. During galvanostatic charging, the dislocation strain energy is increasing initially and reaches a peak values with the charging time. The dislocation induced deformation has a great impact on total strain energy of the electrode in the Fig. 11(b). It is shown that the dislocation induced strain energy has a comparable magnitude to the bulk strain energy for the nanostructured electrode. In addition, dislocation effect under galvanostatic charging is greater than that under potentiostatic charging in Fig.11. This is because galvanostatic charging need more charging time potentiostatic charging. As a result, the dislocation effect would induced more strain energy at the galvanostatic charging than that at the potentiostatic charging. Finally, the normalized total strain energy of two charging condition is compared. Significantly, the normalized total strain energy is greater than that for galvanostatic charging in the potentiostatic operation at the beginning of charging. However, total strain energy for the galvanostatic charging is greater than that of potentiostatic charging at the later lithiation process in the Fig.12. Therefore, it is obvious that we will first use the galvanostatic charging operation

followed by the potentiostatic charging operation to avoiding fracture in the Li-ion battery. These results also show that it is possible to control dislocation density for improve Li-ion battery life.

4 Conclusions

An analytical model has been developed to analyze diffusion induced stress and distribution of dislocation in the nanostructured electrode undergoing potentiostatic and galvanostatic charging by using a combination of diffusion kinetics and dislocation theory. The conventional theoretical study the only diffusion induced stress during charging. When using the nanostructured thin film electrode, dislocation induced stress plays an important role in a Li-ion battery during lithiation. A new model is established with dislocation mechanisms of the electrode. With the dislocation effect, the magnitude of tensile stresses significantly is decreasing at any given time for the both galvanostatic and potentiostatic charging. It is shown that the dislocation effect would induce more stress at the galvanostatic charging than that at the potentiostatic charging. Finally, the maximum stress and strain energy affected by dislocation has been established undergoing the galvanostatic or potentiostatic charging. In addition, the maximum stress and the strain energy affected by the dislocation is greater under the potentiostatic operation than under the galvanostatic operation at the beginning of charging. However, maximum stress and strain energy under potentiostatic charging is lower than galvanostatic charging in the later lithiation process. These results shows that the method considering the galvanostatic charging operation firstly followed by then potentiostatic charging operation and

dislocation density is constructed to mitigate the stress of the nanostructured thin film electrode. This can provide a strategy to prolong the Li-ion battery life.

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Table 1. Nanostructured electrode Si material properties and operating parameters

Parameter	symbol	value
Diffusion coefficient	D	$1.2 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$ ^a
Young's modulus of lithiated Si	E	90.13 GPa
molar volume of Si	Ω	$1.2052 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ ^a
maximum concentration	C_{max}	$2.0152104 \times 10^4 \text{ m}^3 \text{ mol}^{-1}$ ^a
Poisson's ratio of Si electrode	μ	0.22 ^a
Taylor orientation factor	M	1.732-3.06 ^b
Empirical constant	ϕ	0.33 ^b
Burgers vector	b_y	2.532 \AA ^c
Current density	I	0.11 Am^{-2}

^a Ref. 18

^b Ref. 32

^c Ref.33

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Figure

Fig 1. Schematic of Li-ion diffusion in a thin film electrode width $2h$ which is modeled as diffusion along the thickness during insertion

Fig 2. An element of a diffused layer of nanostructured thin film electrode which affected by distribution of dislocation

Fig 3. The concentration solute distribution and variations of stress at the dimensionless under potentiostatic charging. (a) Concentration during lithiation, (b)DIS versus the locations, (c) DIS versus dimensionless time. The concentration is normalized by C_h , while the stresses are normalized by $E\beta C_h/1-\mu$.

Fig 4. Variations of dislocation induced stress at different charging time and width

locations during insertion under the potentiostatic charging. The stresses are normalized by $M\phi G\sqrt{\beta C_h b_y/h}$

Fig 5. Variations of stresses owing to the solute stress at the dimensionless time under potentiostatic charging. The stresses are normalized by $E\beta C_h/1-\mu$. The dot lines represent the stresses considering the dislocation effect and the solid lines represent the stresses without considering the dislocation effect.

Fig 6. Distribution of solute concentration solute and diffusion induced stress under galvanostatic charging. (a) Solute concentration during lithiation, (b) DIS during lithiation. The concentration is normalized by $C_h FD/Ih$, while the stress is normalized by $E\beta FD/Ih(1-\mu)$

Fig 7. Snapshot variations of dislocation induced stress at different charging time and locations under the galvanostatic charging. The stresses are normalized by $M\phi G\sqrt{\beta b_y I/h FD}$

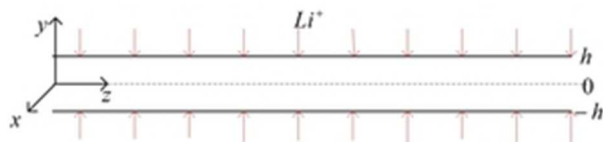
Fig 8. Variations of the coupling stress in a thin film electrode under galvanostatic charging. The stresses are normalized by $E\beta FD/Ih(1-\mu)$. The dot lines represent the stresses considering the dislocation effect and the solid lines represent the stresses without considering the dislocation effect

Fig 9. Normalized maximum stress considered the dislocation effect under the potentiostatic charging and the galvanostatic charging.

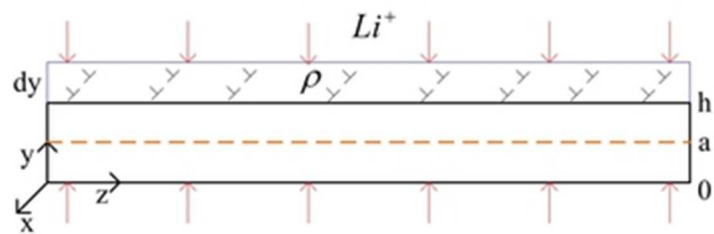
Fig 10. Strain energy versus time without considered the dislocation effect for potentiostatic and galvanostatic charging. (a)Under potentiostatic charging, (b)Under galvanostatic charging.

Fig 11. Normalized bulk strain energy, dislocation strain energy, total strain energy with time for a 200nm electrode at $\mu=0.3$.(a)Under potentiostatic charging, (b)Under galvanostatic charging

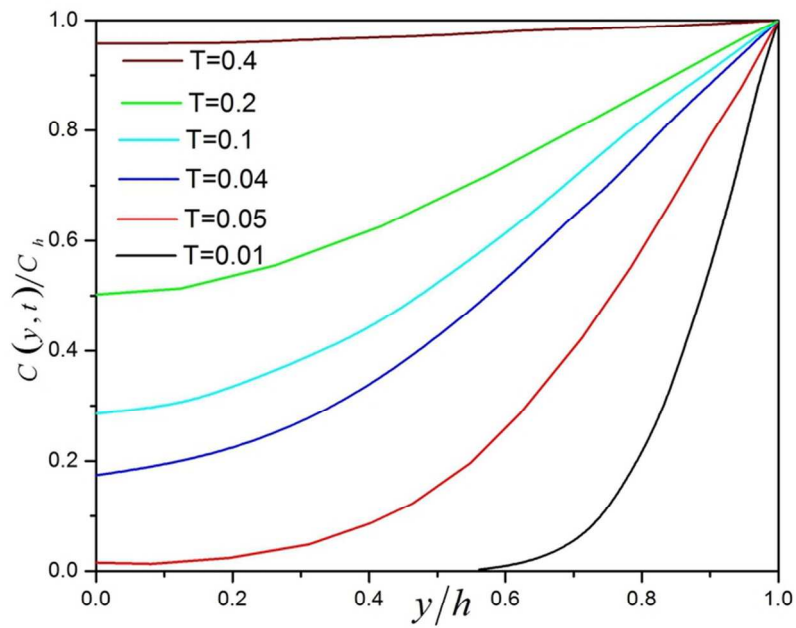
Fig 12. Normalized total strain energy versus time under the potentiostatic and galvanostatic charging when the dislocation strain energy is considered.



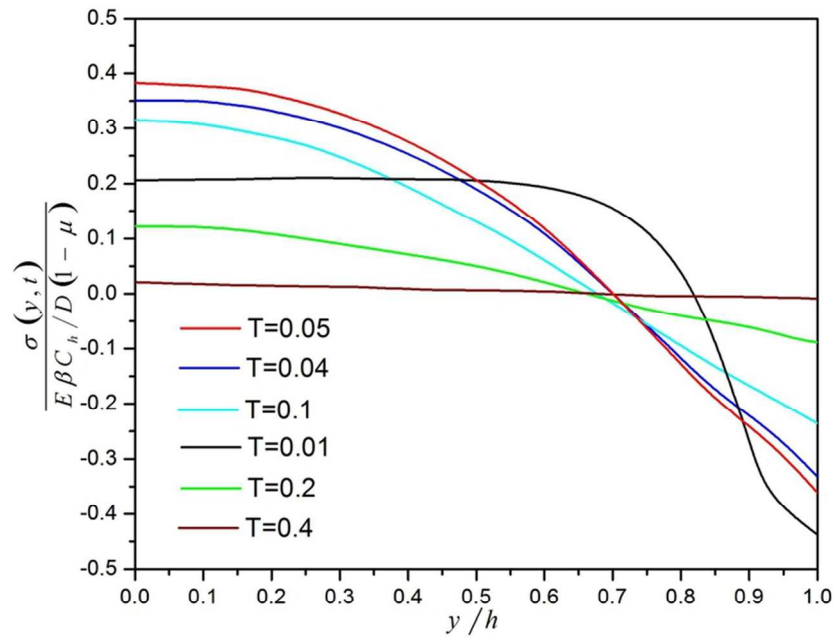
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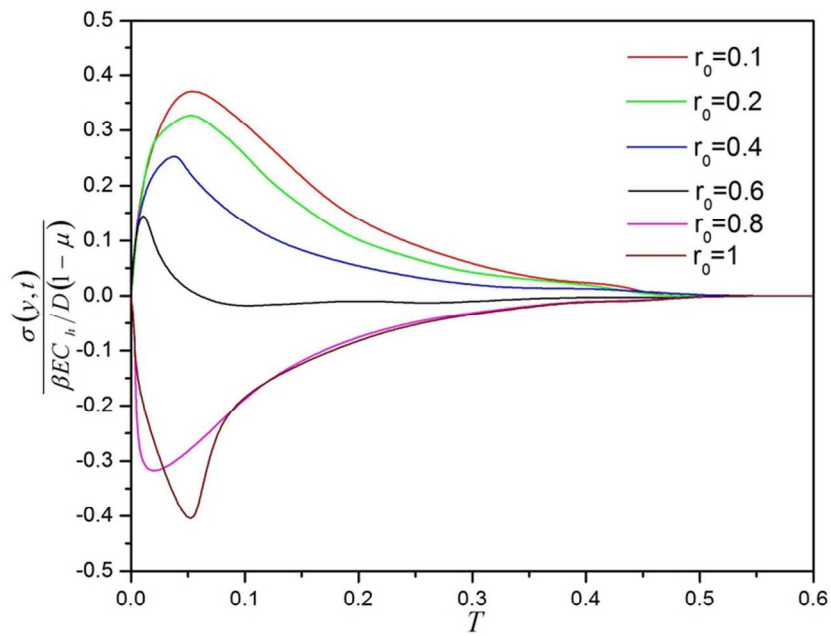
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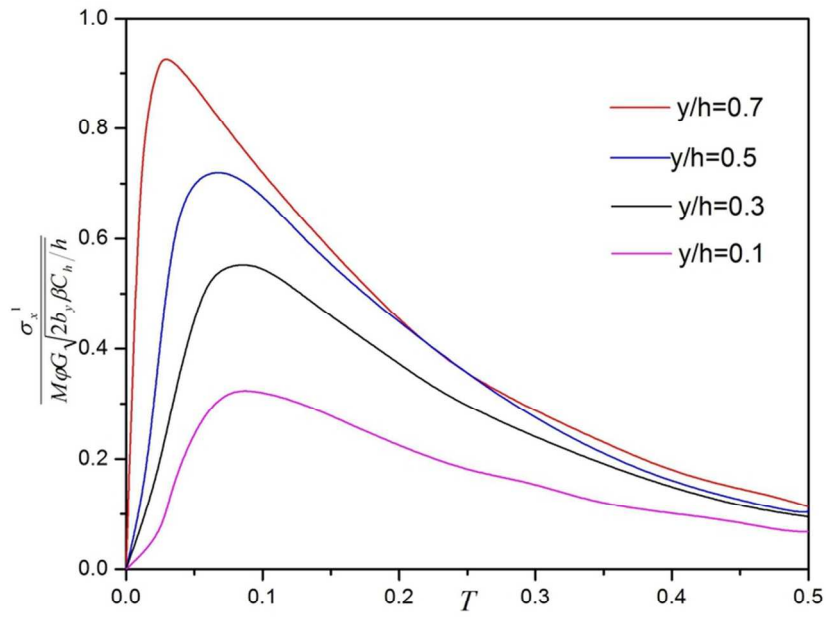
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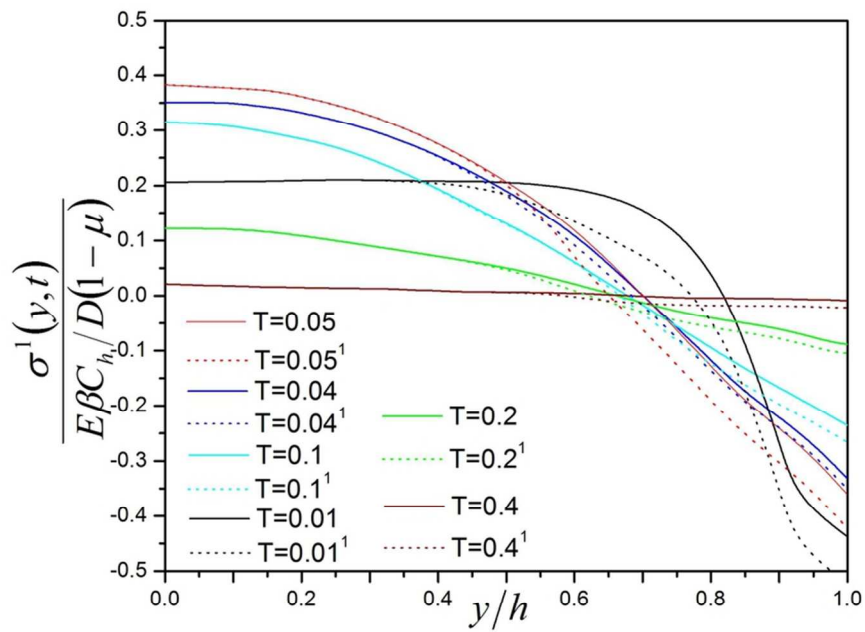
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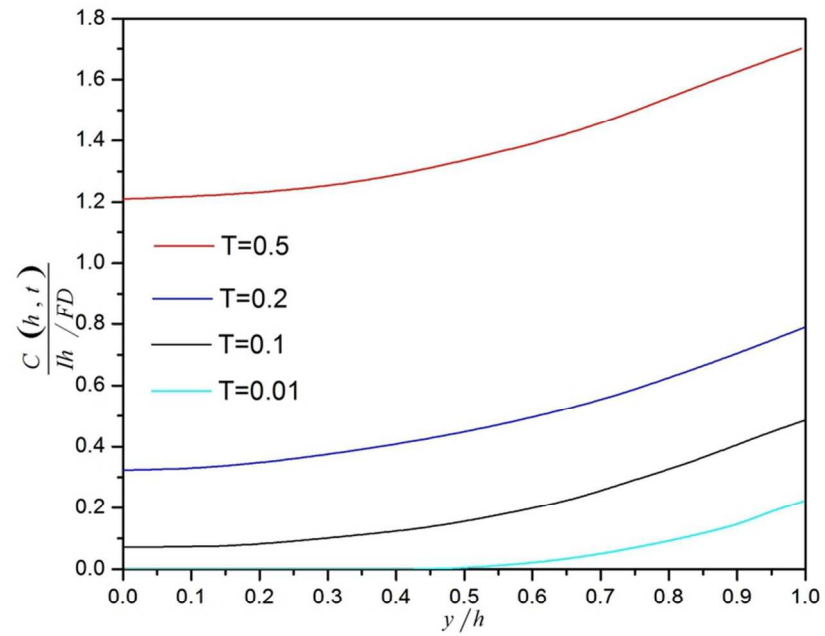
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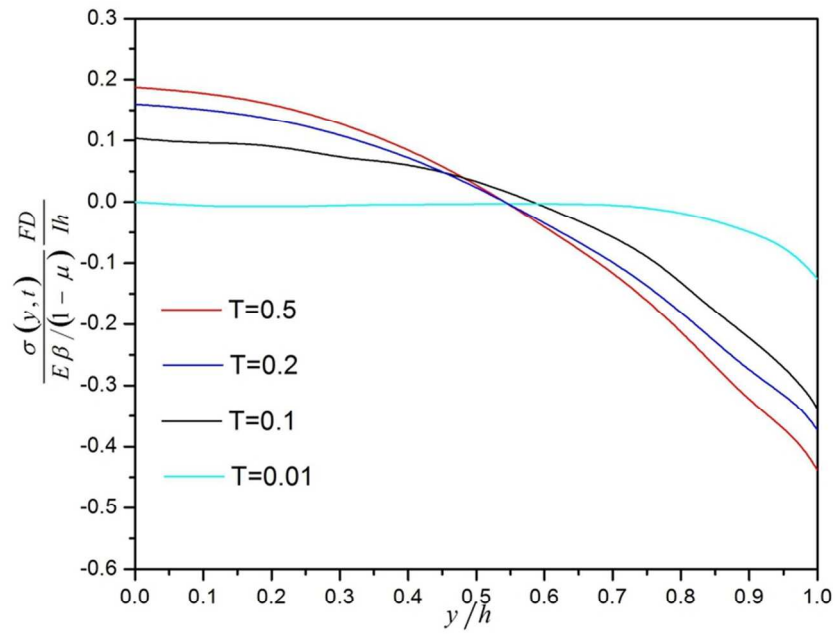
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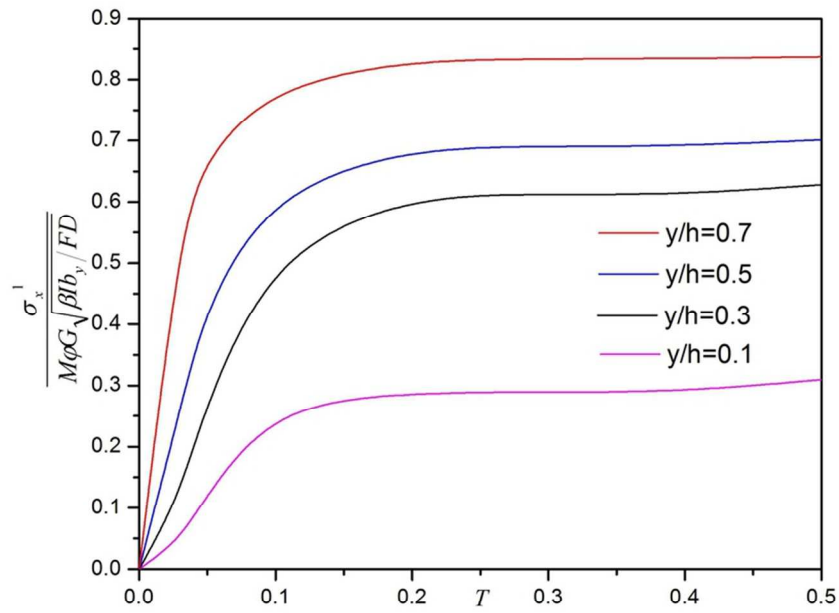
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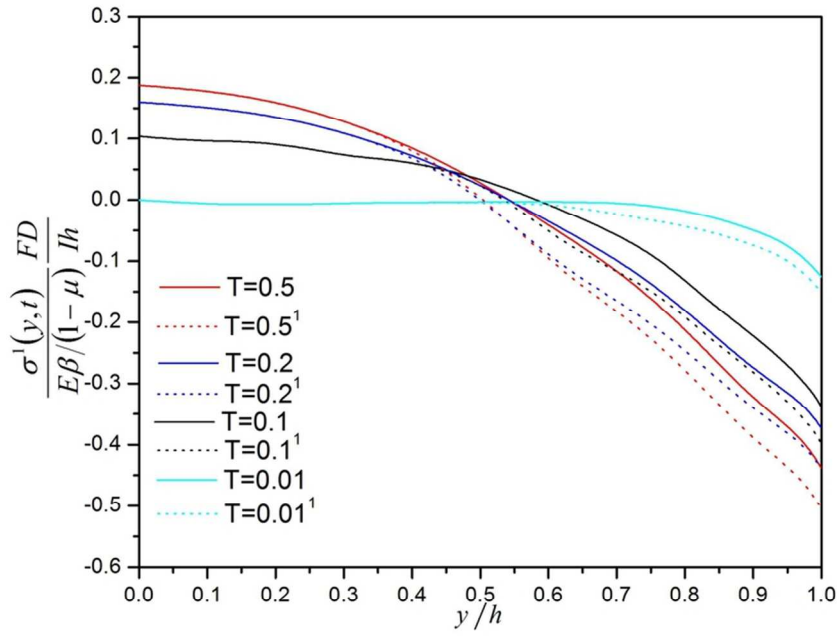
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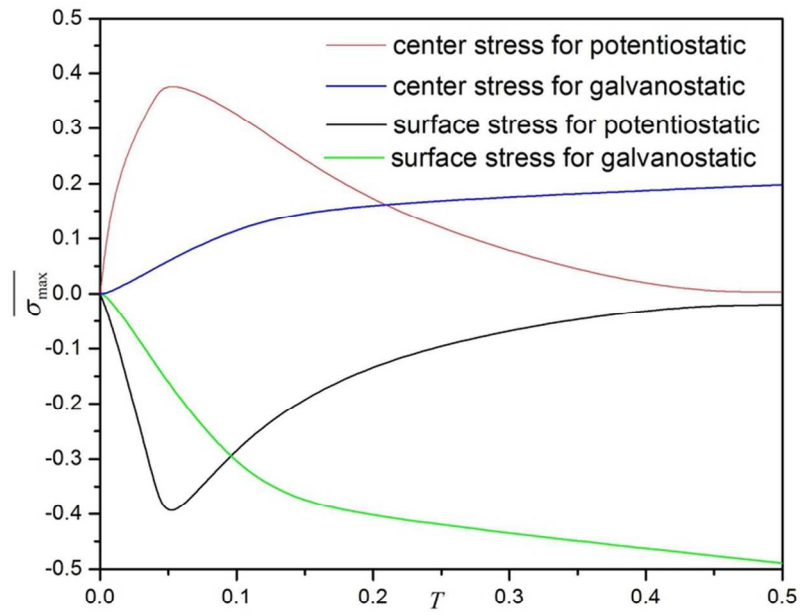
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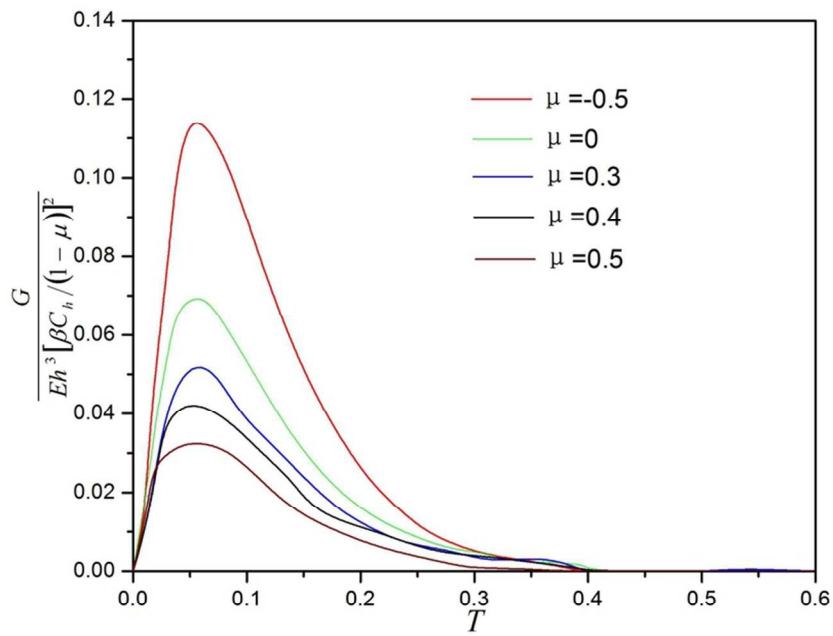
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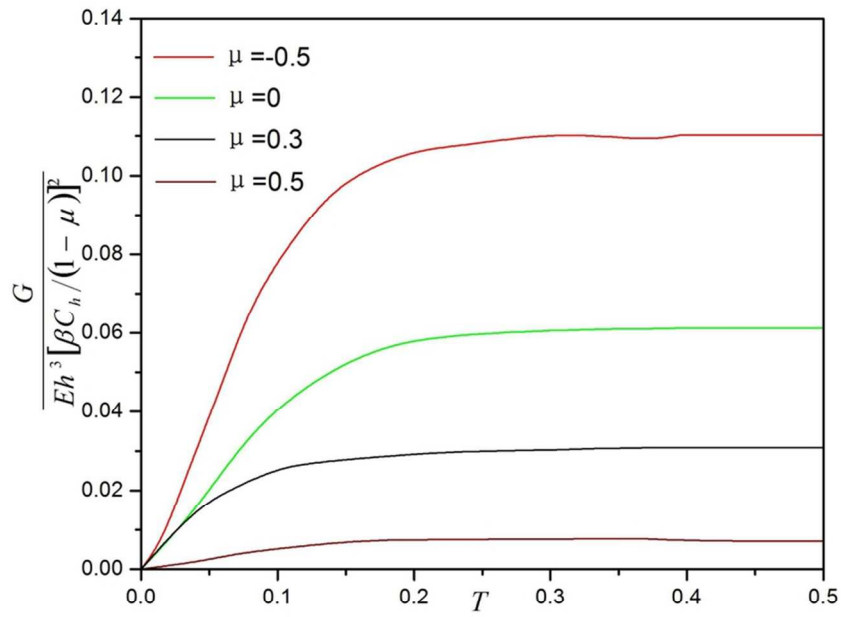
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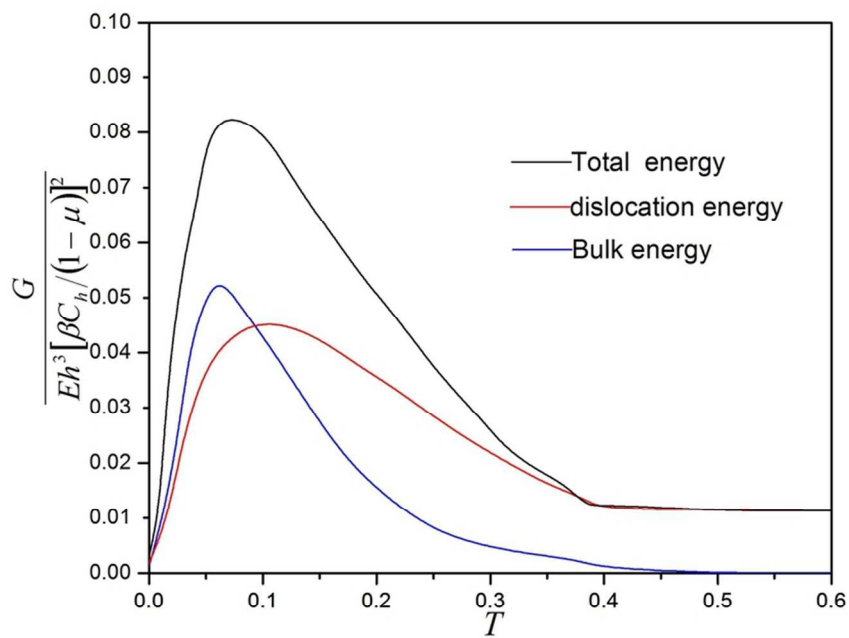
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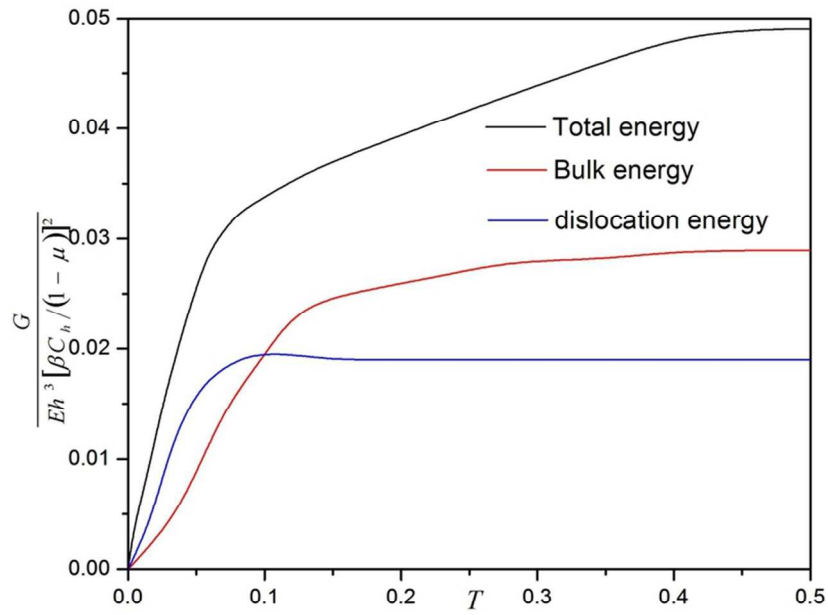
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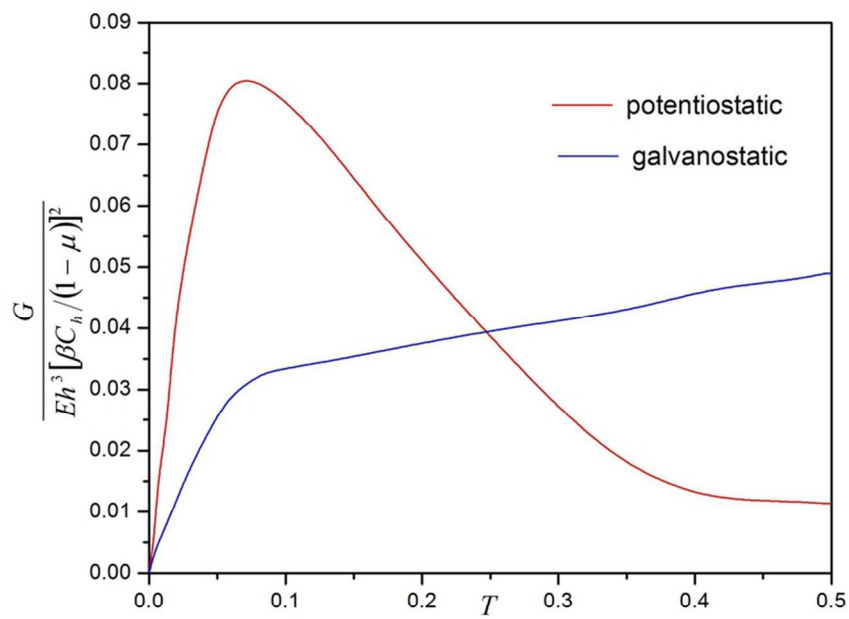
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82x63mm (300 x 300 DPI)

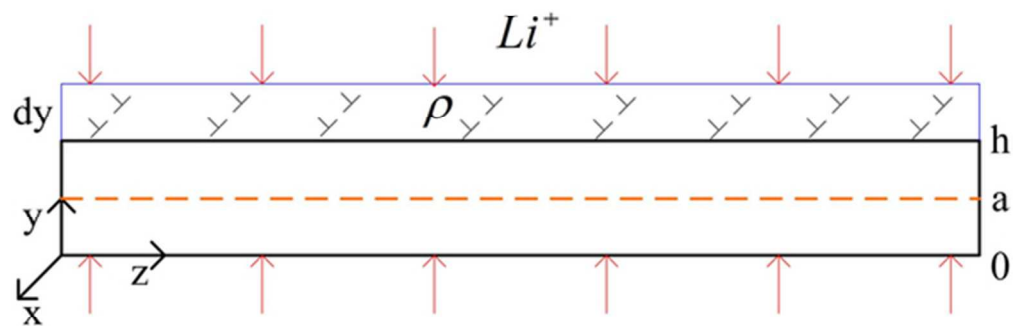


82x63mm (300 x 300 DPI)



82x63mm (300 x 300 DPI)

An analytical model of dislocation mechanical distribution for improving Li-ion battery life



50x25mm (300 x 300 DPI)