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# A chemo-mechanical damage model at large deformation: numerical and experimental studies on polycrystalline energy materials



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## ABSTRACT

The unique mechanical properties and transport features of grain boundaries (GBs) in polycrystalline materials have been widely investigated. However, studies which focus on the unique chemomechanics phenomena resulting from GBs' are exceedingly sparse. In this work, a thermodynamically consistent framework has been developed to explore the multi-physics coupling between mechanics and species diffusion. Constitutive laws for the bulk and the across-GB interaction laws have been derived for large deformations from the system free energies. A chemo-mechanically coupled cohesive zone model is developed which takes into account mode-dependent fracture properties in the presence of GBs. Polycrystalline LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub> (NMC) particles and Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> nanowires haveüeen selected to demonstrate the impact of GBs on the modeled and observed chemo-mechanics. The model has been implemented in the open-source finite element (FE) package MOOSE. Simulation results indicate that the chemical process and the mechanical degradation go hand-in-hand, where enhanced intergranular chemical inhomogeneities weaken the mechanical strength of the GBs, while damage to the GBs affects or even block transport across the GB. Furthermore, experimentally observed characteristics of chemomechanical degradation, e.g., chemical "hot-spots" and surface layer delamination can be accurately predicted by the model.

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#### 1. Introduction

Energy materials such as cathodes and solid-state electrolytes (SE) in lithium-ion batteries (LIBs) are often comprised of singlecrystalline or polycrystalline particles which interconnect to form networks. These materials have been thoroughly investigated due to the rising interest of LIBs and the high demand for energy storage systems and electric vehicles. For example, the polycrystalline LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub> (NMC) material has become a promising choice for LIBs due to its high capacity, electrochemical stability, and costeffectiveness (Whittingham, 2004, 2008; Andre et al., 2015). It is well-known that Co can contribute to the rate capability, and that Ni content can increase the capacity, while Mn can improve the thermal stability (Bak et al., 2014). Thus the improved electrochemical performance of NMC materials can be achieved by par-

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tially replacing Co in  $LiCoO_2$  by Ni and Mn, and the material cost can also be reduced in this way. Motivated by a similar focus to improve electrochemical performance various, polymorphs of vanadium pentoxide ( $V_2O_5$ ) have been considered as cathode materials owing to the abundance of crystallographic sites for hosting guest species and the large thermodynamic driving force for intercalation reactions (Horrocks et al., 2013).

While significant promise has been shown in these materials, a host of fundamental questions remain unanswered. For instance, the improved NMC particle exhibits a hierarchical meatball structure, where a secondary spherical particle with the size around 10 mm is formed by small primary particles or small grains of submicron size aggregate through van der Waals interactions (Miller et al., 2013; Harlow et al., 2019). Consequently, the mechanical strength of the secondary particle is much lower than the typical structure of the single-particle embedded in the conductive matrix. The key contributor to the mechanical degradation of NMC materials is therefore the decohesion of primary particles or the grain boundary (GBs) cracking. In the thermodynamically stable  $\alpha$ -V<sub>2</sub>O<sub>5</sub> structure, considerable lithiation heterogeneity has been observed within single particles as well as across particles embed-

ded in an interconnected network i.e., GB interfaces. Li-ion transport and phase nucleation could be strongly influenced by defects and structural distortions induced by this heterogeneity, which can further change the phase heterogeneity and induce phase separation between the Li-rich and Li-poor regions (De Jesus et al., 2017).

Therefore, the structural and mechanical stability of GBs and their interfaces in polycrystalline materials and interconnected particle network materials play an important role in determining the electrochemical performance of the battery. The unique mechanical and chemical properties of the GBs in these materials have long been recognized, for instance, the intergranular cleavage under cyclic lithiation/de-lithiation process has been widely reported in cathode polycrystalline materials. Moreover, GBs also influence the transport path of ions. Therefore, a full understanding of the mechanically-driven degradation of these materials requires a close-look at the interplay between chemistry and mechanics.

A few recent experimental studies have been presented to investigate the fracture of polycrystalline materials. A new coating method for the surface between primary particles in NMC materials has been introduced by Kim et al. (2015), which can suppress GB microcracks during cycling, improve structural stability and electrochemical performance. Later, this type of coating was extended to the secondary particle surface (Kim et al., 2016a). Results show that the discontinuity of particle contact in NMC particles between the anisotropically oriented grains will reduce the electronic conductivity and mechanical strength of NMC materials. Furthermore, the cracks at the GBs can lead to newly opened surfaces, deteriorate the layer-to-cubic phase transformation during cycling, thus the capacity decreases further (Kim et al., 2016b; Sun and Manthiram, 2017). Significant efforts have been made to alleviate the GB cracking behavior, such as applying gluenanofiller (Kim et al., 2015) and inserting phase-coherent coating materials between primary particles or GBs (Min et al., 2018). Meanwhile, during the lithiation process of V<sub>2</sub>O<sub>5</sub> interconnected particle networks, hot spots of lithium content can be captured at the interconnected section between each particle, which is contrasted by the typical intraparticle heterogeneity observed in this system (De Jesus et al., 2017). Moreover, the anisotropic lattice "breathing" of primary particles can result in the GB cracking (Gent et al., 2016). The NMC secondary particle therefore exhibits the state-of-charge (SOC) heterogeneity due to the anisotropic volume change induced stresses, where several chemical hot spots are observed inside the particle. While these studies have shown probable solutions, a comprehensive mechanism for fracture at and across GBs is still lacking. As such, there exists a need for thermodynamically consistent models which account for the multiphysical phenomena present in materials used for energy applications.

Motivated by this situation, several numerical attempts have been made to provide fundamental insight into the mechanism of the intergranular cracking and the across-GB interaction. The lithiation process of cathode materials involves the interaction between lithium diffusion and mechanics. On the one hand, lithium intercalation into the host material can cause significant lattice expansion, resulting in substantial large volumetric strains (Beaulieu et al., 2001). On the other hand, mechanical stresses can contribute to the driving force for diffusion (Christensen and Newman, 2006; Stein and Xu, 2014). In addition, considerable strain derived from lattice mismatch at phase boundaries can result in high stresses that play a role in cracking and mechanical fatigue in these characteristically brittle ceramic materials (Gabrisch et al., 2008). To investigate this interplay, the mechanically coupled Cahn-Hilliard type diffusion model has been presented to account for the phase separation and lithium insertion induced large deformation of cathode materials (Zhao et al., 2019; Bai et al., 2019, 2020; Santos et al., 2020; Bai, 2021). The isogeometric analysis (IGA) (Hughes et al., 2005), which is a popular choice in finite element method (FEM) and boundary element method (BEM) community (Bai et al., 2015; Qu et al., 2018; Gong et al., 2017; Liu et al., 2015), has been used to solve the fourth-order Cahn–Hilliard equation in Zhao's work (Zhao et al., 2015; Zhao et al., 2019). Later, this model has been extended to combine the pseudo-2D model (P2D) (Doyle et al., 1993) to study the impact of cathode particle's shapes and phase separation behaviors on the cell performance, where the mixed formula has been introduced to split the fourth-order equation into two second-order equations (Bai et al., 2019).

A practical approach to model GB behavior in FEM is based on the use of an initially zero thickness element, which is also known as cohesive zone element (Scheider and Brocks, 2003; Park and Paulino, 2012; Rezaei et al., 2017). For a summary of the available interface models and recent updates, see also Rezaei et al. (2020) and references therein. In such models, the idea is to formulate a relationship between interface traction and the displacement jump which is also known as the traction-separation law. Additionally, interface models have to be thermodynamically consistent for an arbitrary mode-dependent opening (Rezaei et al., 2019). In chemo-mechanically coupled problems, cohesive zone models (CZMs) are also applied. Bucci et al. (2017), using the cohesive technique, studied electro-chemo-mechanical fracture in solid electrolytes. del Busto et al. (2017) presented a CZM to study hydrogen assisted fatigue where the traction-separation law is hydrogen dependent. The electro-chemo-mechanically coupled model was proposed by Wu and Lu (2016) for the fracture of polycrystalline materials such as NMC. Their findings indicate that the fracture is caused by the separations between primary grains. In the stress calculation, however, the secondary particle is viewed as a continuum, which is distinct from the grain boundary problems as described above. This conclusion has also been confirmed by Sun et al. (2016), where the discrete element method (DEM) with the CZM is implemented to simulate the crack initiation and propagation at the GBs (interface) between primary grains. Their results indicate that the diffusion of lithium can cause lattice expansion and contraction, leading to crack formation. Furthermore, the damage accumulation at the interface can involve a high concentration gradient, which can accelerate crack propagation. However, the concentration field in this work is introduced as prescribed field quantities and only one-way coupling is considered i.e., the influence of stress in altering diffusion is ignored. Such a one-way coupling strategy has also been pursued by Zhang et al. (2019), where the finite element method (FEM) with the cohesive zone model (CZM) is employed to simulate the intergranular fracture within the NMC particle. However, the impact of stresses on the transport of lithium is still missing. Furthermore, the evolution of Li concentration and stresses have been studied by Xu et al. (2018) based on FEM and CZM, where the diffusion of lithium and the stress evolution are fully coupled via a chemomechanical model. Simulation results indicate the slow charging rate can result in severe disintegration of the secondary particle while fast charging leads to less damage. Accordingly, this model has been extended to model the corrosive fracture of NMC particles under large deformation, where the competition between energy release rate and fracture resistance during lithium insertion and extraction have been examined in detail (Xu and Zhao, 2018). However, the impact of the GBs between primary particles has not been studied deeply. Moreover, Zhao et al. (2017) presented a chemo-mechanical model that accounts for the lithium transport and also the interface reactions across the particle network (grains). The results indicate the lithium content hot spots can be attributed to the interaction between grains where the transgrain phase separation happens. Singh and Pal (2020) proposed a chemo-mechanical GB model in more recent work. However, the

GB transport is formulated concerning the concentration jump across GBs. The presented two-dimensional results of multigrains do not show the prominent chemical inhomogeneity observed in experiments, which indicates the improvement of a more general GB kinetics. An understanding of these inhomogeneities across GBs and the crack propagation along the GBs is fundamental for accurate predictions of the degradation in polycrystalline materials. Though fundamental chemo-mechanical principles addressed in this work are broadly applicable to polycrystalline ion conductors and interconnected particle networks in general, we have focused on two exemplary cathode materials namely, LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub> (NMC) and V<sub>2</sub>O<sub>5</sub>. To this end, a thermodynamically consistent multiphysics framework for the polycrystalline materials is presented. In particular, the model takes into account the finite strain regime. Moreover, both mechanically coupled diffusion processes in the bulk and the across-GB interaction for the lithium diffusion across the GBs as well as the mechanical failure at the GBs have been derived from this framework. The across-GB transport concerns the continuity of ion flux as well as the presence of concentration jumps and also the chemical potential jumps across GBs. Moreover, the mechanical failure considers both the isotropic elastic properties and the chemically induced volume expansion of adjacent primary particles or grains.

The article is organized as follows: In Section 2, the general thermodynamic framework for the diffusion and fracture of polycrystalline material is presented, with details of the free energy contributions from the lithium diffusion and finite strain deformation. In Section 2.4, the Holmheltz free energy and the dissipation potentials for the bulk and interface will be presented. Section 2.4.2 details the across-GB interactions. Section 3 demonstrates the impact of the GBs on the crack patterns of polycrystalline materials. Finally, concluding remarks are given.

## 2. Model

## 2.1. Problem description

During the (de-) lithiation process of polycrystalline energy materials, the insertion/extraction of lithium into the host material can involve both the transport of species as well as mechanical stresses. Consequently, the chemical process and mechanical degradation are inextricably linked: the enhanced intergranular chemical inhomogeneity challenges the mechanical strength of GBs, while the damage of GBs can further influence or even block across-grain transport. Therefore, it is important to develop a thermodynamically consistent modeling framework to elucidate the interplay between the chemical and mechanical processes. Polycrystalline materials typically exhibit grains, and therefore grain boundaries (GBs), along several orientations. During the (de-) lithiation process of the polycrystalline materials, the lithium can diffuse through the grains and across GBs. Therefore, to reveal the mechanism of stresses generation and interfacial debonding along the GBs, the development of a general continuum theory for the transport of lithium through all the grains and also the interface (GBs) between grains is extremely important.

#### 2.2. Kinetics of grains and grain boundaries

Considering the macroscopically homogeneous body  $\mathscr{B}$  with the region of the occupied electrode space in a fixed reference configuration at time t, which contains n non-overlapped subdomains to account the arbitrary individual grains of the reference body  $\mathscr{B}$ , i.e.  $\mathscr{B}_i$  and  $\mathscr{B}_j$  in Fig. 1, expressed as  $\mathscr{B} = \bigcup_{i=1}^n \mathscr{B}_i$ . The external boundary of the whole domain is denoted by  $\partial \mathscr{B}$  with  $\vec{\mathbf{n}}$  represents the outward unit normal on the boundary  $\partial \mathscr{B}$  of body  $\mathscr{B}$ . By denoting  $\mathbf{X}$  an



**Fig. 1.** (Left) The schematic illustration of the NMC particle with multiple grains and GBs. (Right) The representing subdomain  $\mathscr{B}_1$  and  $\mathscr{B}_2$  with a common interface  $\Gamma_i$ , where  $\mathbf{n}_i$  indicates the normal vector of the interface, while the GBs on each side are respectively denoted by (+) and (-).

arbitrary material point of body  $\mathscr{D}$ , the motion of the body can be described by a smooth one-to-one mapping  $\mathbf{x} = \boldsymbol{\chi}(\mathbf{X}, t) = \mathbf{X} + \mathbf{U}$ , where  $\mathbf{U}$  and  $\boldsymbol{\chi}$  denote the displacement vector and the motion, respectively. Then the *deformation gradient* and *velocity* can be written out as follows:

$$\mathbf{F} = \nabla \boldsymbol{\chi}, \qquad \mathbf{v} = \dot{\boldsymbol{\chi}}, \tag{1}$$

where  $\nabla$  denotes the gradient operator in the reference configuration or the material configuration. Thus, the deformation gradient tensor **F** can be expressed as:

$$\mathbf{F} = \nabla \boldsymbol{\chi} = \mathbf{I} + \nabla \boldsymbol{U}. \tag{2}$$

As mentioned in Section 1, during the charge and discharge process, the insertion/extraction of lithium into the host material can create stress due to the changes in lattice dimensions and crystal structures, which are associated with the overall volume changes and phase transformation, respectively. Based on the multiplicative decomposition theory, the deformation gradient at any material point **X** can thereby be decomposed into the elastic distortion part **F**<sub>e</sub> and the (de-) intercalation-induced swelling part **F**<sub>c</sub> as follows:

$$\mathbf{F} = \mathbf{F}_e \mathbf{F}_c \text{ with } J = \det \mathbf{F} = J_e J_c, \tag{3}$$

and

$$\mathbf{F}_c = (J_c)^{\frac{1}{3}} \text{I with } J_c = \det \mathbf{F}_c = 1 + \Omega C, \tag{4}$$

where  $C(\mathbf{X}, t)$  is the concentration of lithium per unit volume in the reference configuration, and where  $\Omega$  is the partial molar volume.  $J = \det \mathbf{F}, J_e = \det \mathbf{F}_e$  and  $J_c = \det \mathbf{F}_c$  are the determinants of related deformation gradient tensor, respectively. The right Cauchy-Green deformation tensor and the Green–Lagrange strain tensor are then defined as:

$$\mathbf{C} = \mathbf{F}^{\mathrm{T}}\mathbf{F}, \mathbf{E} = \frac{1}{2} \left( \mathbf{F}^{\mathrm{T}}\mathbf{F} - \mathbf{I} \right) = \frac{1}{2} (\mathbf{C} - \mathbf{I}),$$
(5)

moreover, we can have:

$$\mathbf{C}_{e} = \mathbf{F}_{e}^{\mathsf{T}} \mathbf{F}_{e}, \qquad \mathbf{E}_{e} = \frac{1}{2} \left( \mathbf{F}_{e}^{\mathsf{T}} \mathbf{F}_{e} - \mathbf{I} \right) = \frac{1}{2} (\mathbf{C}_{e} - \mathbf{I}). \tag{6}$$

The true concentration  $c(\mathbf{x}, t)$  in the current configuration can thus be obtained as c = C/J. Meanwhile, the chemical potential in the reference body  $\mathscr{B}$  is described by  $\mu(\mathbf{X}, t)$ .

Similarly, the motion of the interface (GBs) can be described by the two neighboring domains, i.e.  $\mathscr{B}_1$  and  $\mathscr{B}_2$ , separated by the common interface  $\Gamma_l$  in the reference configuration, as shown in Fig. 1. Let  $U^{\pm}$  denote the displacement fields on the two sides of the interface, the motion of the GBs can thus be characterized as follows:

$$\mathbf{x}^{\pm} = \mathbf{\chi}^{\pm} = \mathbf{X} + \mathbf{U}^{\pm} \quad \text{on} \quad \Gamma_{I}^{\pm}, \tag{7}$$

where  $\mathbf{x}^{\pm}$  denote the spatial position of the upper and lower GB, namely  $\Gamma_I^{\pm}$  in Fig. 1, on the two sides of the deformed interface.  $\chi^{\pm}$  denotes the motion of the two GBs. Thereby, the displacement jump vector  $\Delta$  of the interface can be written out as follows:

$$\Delta = \mathbf{X}^{+} - \mathbf{X}^{-} = \boldsymbol{\chi}^{+} - \boldsymbol{\chi}^{-} = (\mathbf{X} + \boldsymbol{U}^{+}) - (\mathbf{X} + \boldsymbol{U}^{-}) = \llbracket \boldsymbol{U} \rrbracket.$$
(8)

Similarly, the concentration  $C_I^+ \in \Gamma_I^+$  and  $C_I^- \in \Gamma_I^-$ , and the chemical potentials  $\mu_I^+ \in \Gamma_I^+$  and  $\mu_I^- \in \Gamma_I^-$  on the two sides of the interface follow the same notation. Moreover, the relation  $\vec{\mathbf{n}}_I^+ = -\vec{\mathbf{n}}_I^- = \vec{\mathbf{n}}_I$  should be considered at the interface.

## 2.3. Governing equations and boundary conditions

Since the time scales associated with the wave propagation are comparatively smaller than the diffusion process, we neglect all the inertial effects. Therefore, without the consideration of body forces, the mechanical equilibrium equation of  $\mathscr{B}$  can be expressed as:

$$\nabla \cdot \mathbf{P} = 0in \quad \mathscr{B} \times (0, \mathscr{T}), \tag{9}$$

where **P** is the first Piola–Kirchhoff stress tensor, and  $\mathcal{T}$  denotes the current time. Then the traction on the surface  $\Gamma_t$  can be given by:

$$\mathbf{t}^{p}(\vec{\mathbf{n}}) = \mathbf{P} \cdot \vec{\mathbf{n}} \text{ on } \Gamma_{t} \times (0, \mathscr{T}).$$
(10)

The related boundary conditions are listed below:

$$\boldsymbol{U} = \boldsymbol{U}^{p} \text{on} \quad \Gamma_{u} \times (\boldsymbol{0}, \mathcal{F}), \tag{11}$$

$$\mathbf{P} \cdot \vec{\mathbf{n}} = \mathbf{t}^{p} \mathbf{on} \quad \Gamma_{t} \times (\mathbf{0}, \mathscr{T}), \tag{12}$$

$$\mathbf{P} \cdot \vec{\mathbf{n}}_{l} = \mathbf{t}_{l}^{+} = -\mathbf{t}_{l}^{-} = \mathbf{t}_{l} \text{ on } \Gamma_{l} \times (\mathbf{0}, \mathscr{T})$$
(13)

fns are specified by the displacement  $U^p$  on  $\Gamma_u$  and the traction  $t^p$  on  $\Gamma_t$ , respectively. In Eq. (13),  $t_l^+$  and  $t_l^-$  are the tractions on the two GBs, namely  $\Gamma_l^+$  and  $\Gamma_l^-$ , respectively.  $t_l$  represents the traction at the interface  $\Gamma_l$ .

Without the consideration of chemical reaction, the mass conservation of lithium in domain  $\mathcal{B}$  can be written out as follows:

$$\int_{\mathscr{B}} \dot{C} dV = -\int_{\partial \mathscr{B}} \mathbf{J} \cdot \mathbf{\vec{n}} dSin \quad \mathscr{B} \times (\mathbf{0}, \mathscr{T}),$$
(14)

where **J** is the diffusion flux defined as the number of moles of Li measured per unit reference area per unit time, which will be discussed in the following section. Thereby, the local form of the mass balance can be given as:

$$C + \nabla \cdot \mathbf{J} = 0 \text{in} \quad \mathscr{B} \times (0, \mathscr{T}). \tag{15}$$

The initial conditions and related boundary conditions for the diffusion process are listed as below:

$$C = C^{p} \text{on} \quad \Gamma_{c} \times (0, \mathcal{T}), \tag{16}$$

$$\boldsymbol{J} \cdot \boldsymbol{\vec{n}} = \boldsymbol{J}^{p} \mathbf{on} \quad \boldsymbol{\Gamma}_{I} \times (\mathbf{0}, \mathcal{T}), \tag{17}$$

$$C(\mathbf{X}, \mathbf{0}) = C^{0}(\mathbf{X}) \text{in} \quad \mathscr{B} \times (\mathbf{0}, \mathscr{F}), \tag{18}$$

$$\boldsymbol{J} \cdot \boldsymbol{\tilde{n}}_{l} = J_{l} \text{on} \quad \Gamma_{l} \times (\boldsymbol{0}, \mathcal{T}), \tag{19}$$

where the chemical boundary conditions are respectively prescribed by the applied flux  $J^p$  on  $\Gamma_J$  and the concentration  $C^p$  on  $\Gamma_c$ . The initial concentration of Li is represented by  $C^0$  and  $J_I$  is the flux vector across the GB. The calculation of  $J_I$  depends on the flux  $J_I^+$  and  $J_I^-$  on the two sides of the GB, which will be introduced in details in the following section. It should be mentioned that, here we only focus on the across-GB diffusion, the GB diffusion is beyond the scope of this work and will be discussed in future work.

## 2.4. Thermodynamics

In this work, the chemo-mechanical interplay in both the grains and GBs is involved. Therefore, we treat the bulk domain (grains)  $\mathscr{B}$  and the interface (GBs)  $\Gamma_I$  as two independent thermodynamics systems. For the consideration of quasi-static condition, the total kinetic energy can take the form as:  $\mathscr{K} = \int_{\mathscr{B}} \frac{1}{2}\rho \dot{\chi} \cdot \dot{\chi} dV \equiv 0$ . Following the work of Anand (2012) and Di Leo et al. (2014), we introduce the microforce balance theory for the system. Furthermore, the contribution of species is thought to be the energy transport caused by species flux (Sain et al., 2018). Thus, the external expenditure of power for our polycrystalline particle can be written out as follows:

$$\mathscr{W}_{\text{ext}} = \int_{\partial\mathscr{R}} (\mathbf{P} \cdot \vec{\mathbf{n}}) \cdot \dot{\mathbf{\chi}} dS + \int_{\partial\mathscr{R}} \boldsymbol{\xi} \cdot \dot{\mathbf{C}} dS - \int_{\partial\mathscr{R}} \mu \mathbf{J} \cdot \vec{\mathbf{n}} dS,$$
(20)

where the scalar microscopic traction  $\xi = \xi \cdot \vec{\mathbf{n}}$  is introduced to account for the power over  $\dot{C}$  on the boundary of the particle, and  $\xi$  denotes the microscopic traction vector that expends power over the gradient  $\nabla \dot{C}$ .  $\mu$  denotes the chemical potential of Li inside the particle.

Next, we introduce the stress tensor  $S_e$ , which is powerconjugate to  $\dot{F}$ , defined as follows (Di Leo et al., 2014; Anand, 2012):

$$\mathbf{S}_{e} = \mathbf{P}\mathbf{F}_{c}^{T} = \boldsymbol{J}\boldsymbol{\sigma}\mathbf{F}_{e}^{-T}, \qquad \mathbf{P} = \mathbf{S}_{e}\mathbf{F}_{c}^{-T}, \tag{21}$$

where  $\sigma$  is the Cauch stress tensor, and the relation between  $S_e$  and the second Piola–Kirchhoff **S** (Anand, 2012) is written as:

$$J_{c}\mathbf{S} = \mathbf{F}_{e}^{-1}\mathbf{S}_{e}, \qquad \mathbf{S}_{e} : \dot{\mathbf{F}}_{e} = (J_{c}\mathbf{S}) : \left(\mathbf{F}_{e}^{T}\dot{\mathbf{F}}_{e}\right) = \frac{1}{2}(J_{c}\mathbf{S}) : \dot{\mathbf{C}}_{e},$$

$$\mathbf{S} = J_{e}\mathbf{F}_{e}^{-1}\boldsymbol{\sigma}\mathbf{F}_{e}^{T}.$$
(22)

Moreover, we can have the Mandel stress tensor  $\mathbf{M}_{e}$  as follows:

$$\mathbf{M}_{e} = \mathbf{C}_{e}\mathbf{S} = J_{e}\mathbf{F}_{e}^{T}\boldsymbol{\sigma}\mathbf{F}_{e}^{-T}, \qquad \mathbf{F}_{e}^{T}\mathbf{S}_{e} = J_{c}\mathbf{M}_{e}.$$
(23)

Considering that  $\mathscr{W}_{int} = \mathscr{W}_{ext}$  must be held for an arbitrary part of the body  $\mathscr{B}$ , thereby, the corresponding internal expenditure of power with the mechanical contribution of GBs can be expressed as:

$$\mathcal{W}_{int} = \mathcal{W}_{ext} = \int_{\partial\mathcal{B}} (\mathbf{P} \cdot \vec{\mathbf{n}}) \cdot \dot{\mathbf{\chi}} dS + \int_{\partial\mathcal{B}} (\boldsymbol{\xi} \cdot \vec{\mathbf{n}}) \cdot \dot{C} dS - \int_{\partial\mathcal{B}} \mu \mathbf{J} \cdot \vec{\mathbf{n}} dS$$

$$= \int_{\mathcal{B}} \nabla \cdot (\mathbf{P} \cdot \dot{\mathbf{\chi}}) dV + \int_{\mathcal{B}} \nabla \cdot (\boldsymbol{\xi} \dot{C}) dV - \int_{\mathcal{B}} \nabla \cdot (\mu \mathbf{J}) dV$$

$$+ \int_{\Gamma_{1}^{+}} (\mathbf{P} \cdot \vec{\mathbf{n}}) \cdot \dot{\mathbf{\chi}} dS + \int_{\Gamma_{1}^{-}} (\mathbf{P} \cdot \vec{\mathbf{n}}) \cdot \dot{\mathbf{\chi}} dS - \int_{\Gamma_{1}^{+}} \mu \mathbf{J} \cdot \vec{\mathbf{n}} dS - \int_{\Gamma_{1}^{-}} \mu \mathbf{J} \cdot \vec{\mathbf{n}} dS$$

$$= \int_{\mathcal{B}} \mathbf{P} : \nabla \dot{\mathbf{\chi}} dV + \int_{\mathcal{B}} \nabla \boldsymbol{\xi} \cdot \dot{C} dV + \int_{\mathcal{B}} \boldsymbol{\xi} \cdot \nabla \dot{C} dV - \int_{\mathcal{B}} \nabla \mu \cdot \mathbf{J} dV$$

$$- \int_{\mathcal{B}} \mu \cdot \nabla \mathbf{J} dV + \int_{\Gamma_{I}} \mathbf{t}_{I} \cdot \dot{\Delta} d\Gamma - \int_{\Gamma_{I}} \mu_{I} \mathbf{J}_{I} \cdot \vec{\mathbf{n}}_{I} d\Gamma$$

$$= \int_{\mathcal{B}} \mathbf{P} : \left( \dot{\mathbf{F}}_{e} \mathbf{F}_{c} + \mathbf{F}_{e} \dot{\mathbf{F}}_{c} \right) dV + \int_{\mathcal{B}} \nabla \boldsymbol{\xi} \cdot \dot{C} dV + \int_{\mathcal{B}} \boldsymbol{\xi} \cdot \nabla \dot{C} dV$$

$$- \int_{\mathcal{B}} \nabla \mu \cdot \mathbf{J} dV - \int_{\mathcal{B}} \mu \cdot \nabla \mathbf{J} dV + \int_{\Gamma_{I}} \mathbf{t}_{I} \cdot \dot{\Delta} d\Gamma - \int_{\Gamma_{I}} \mu_{I} \mathbf{J}_{I} \cdot \vec{\mathbf{n}}_{I} d\Gamma,$$
(24)

where  $\mu_I$  denotes the chemical potential at the GBs, and **J**<sub>I</sub> denotes the flux at the interface. A represents the time derivative of the displacement jump. Substituting Eq. (21)<sub>2</sub> and Eq. (22)<sub>2</sub> into Eq. (24) with the relationship  $\mathbf{A} : \mathbf{BC} = (\mathbf{B}^T \mathbf{A}) : \mathbf{C} = (\mathbf{AC}^T) : \mathbf{B} (\mathbf{A}, \mathbf{B} \text{ and } \mathbf{C} \text{ are the second order tensors}), one can have:$ 

$$\mathcal{W}_{int} = \int_{\mathscr{R}} \frac{1}{2} (J_{c}\mathbf{S}) : \dot{\mathbf{C}}_{e} dV + \int_{\mathscr{R}} \frac{\Omega}{3} \operatorname{tr}(\mathbf{M}_{e}) \dot{C} dV + \int_{\mathscr{R}} \nabla \boldsymbol{\xi} \cdot \dot{C} dV + \int_{\mathscr{R}} \boldsymbol{\xi} \cdot \nabla \dot{C} dV - \int_{\mathscr{R}} \nabla \mu \cdot \mathbf{J} dV - \int_{\mathscr{R}} \mu \cdot \nabla \mathbf{J} dV + \int_{\Gamma_{I}} \mathbf{t}_{I} \cdot \dot{\Delta} d\Gamma - \int_{\Gamma_{I}} \mu_{I} \mathbf{J}_{I} \cdot \vec{\mathbf{n}}_{I} d\Gamma = \int_{\mathscr{R}} \frac{1}{2} (J_{c}\mathbf{S}) : \dot{\mathbf{C}}_{e} dV + \int_{\mathscr{R}} \bar{\omega} \dot{C} dV + \int_{\mathscr{R}} \boldsymbol{\xi} \cdot \nabla \dot{C} dV - \int_{\mathscr{R}} \nabla \mu \cdot \mathbf{J} dV - \int_{\mathscr{R}} \mu \cdot \nabla \mathbf{J} dV + \int_{\Gamma_{I}} \mathbf{t}_{I} \cdot \dot{\Delta} d\Gamma - \int_{\Gamma_{I}} \mu_{I} \mathbf{J}_{I} \cdot \vec{\mathbf{n}}_{I} d\Gamma,$$
(25)

where  $\bar{\omega}$  represents the scalar microscopic stress that expends power over the rate  $\dot{C}$ , defined as follows:

$$\bar{\omega} = \frac{\Omega}{3} \operatorname{tr}(\mathbf{M}_{e}) + \nabla \cdot \boldsymbol{\xi}.$$
<sup>(26)</sup>

Considering that, the Helmholtz free energy  $\Psi$  of the system in the reference body can be split into the bulk part  $\Psi_b$  and the interface part  $\Psi_l$ :

$$\int_{\mathscr{B}} \Psi dV = \int_{\mathscr{B}} \Psi_b dV + \int_{\Gamma_l} \Psi_l d\Gamma.$$
(27)

By assuming the isothermal condition as mentioned in Anand (2012), the free energy imbalance for the system with both grains and GBs can be written out as follows:

$$\int_{\mathscr{B}} \Psi_b dV + \int_{\Gamma_l} \Psi_l d\Gamma \leqslant \mathscr{W}_{\text{ext}} = \mathscr{W}_{\text{int}},$$
(28)

Then by using Eq. (25), we can thus rewrite Eq. (28) as follows:

$$\int_{\mathscr{B}} \left[ \frac{1}{2} (I_{c} \mathbf{S}) : \dot{\mathbf{C}}_{e} + \bar{\omega} \dot{C} + \boldsymbol{\xi} \cdot \nabla \dot{C} - \dot{\Psi}_{b} - \nabla \mu \cdot \mathbf{J} - \mu \cdot \nabla \mathbf{J} \right] dV + \int_{\Gamma_{l}} \left[ \mathbf{t}_{l} \cdot \dot{\Delta} - \mu_{l} \mathbf{J}_{l} \cdot \vec{\mathbf{n}}_{l} - \dot{\Psi}_{l} \right] d\Gamma \ge 0$$
(29)

Next, we assume the GB with an infinite small width *w*. Thus, we can have  $\int_{\mathscr{B}_l} (\mathrm{ffl}) = w \int_{\Gamma_l} (\mathrm{ffl})$ , where  $\mathscr{B}_l$  denotes the "volume" of the interface. Then, by applying mass conservation relationships  $\dot{C} + \nabla \cdot \mathbf{J} = 0$  for the bulk and  $\dot{C}_l + \nabla \cdot \mathbf{J}_l = 0$  for the interface, as well as the divergence theorem to Eq. (29), the dissipation inequality for the described system is obtained:

$$\mathscr{D} = \int_{\mathscr{R}} \left[ \frac{1}{2} (J_{c} \mathbf{S}) : \dot{\mathbf{C}}_{e} + \bar{\omega} \dot{C} + \boldsymbol{\xi} \cdot \nabla \dot{C} + \mu \dot{C} - \nabla \mu \cdot \mathbf{J} - \dot{\Psi}_{b} \right] dV + \int_{\Gamma_{I}} \left[ \mathbf{t}_{I} \cdot \dot{\Delta} + w \left( \mu_{I} \dot{C}_{I} - \mathbf{J}_{I} \cdot \nabla \mu_{I} \right) - \dot{\Psi}_{I} \right] d\Gamma \ge 0.$$
(30)

Furthermore, Eq. (30) must hold for all parts of  $\mathscr{B}$ , we can thereby remove the integration operator, and split the total dissipation into the bulk one:

$$\mathcal{D}_{b} = \frac{1}{2} (J_{c} \mathbf{S}) : \dot{\mathbf{C}}_{e} + \bar{\omega} \dot{C} + \boldsymbol{\xi} \cdot \nabla \dot{C} + \mu \dot{C} - \nabla \mu \cdot \mathbf{J} - \dot{\Psi}_{b} = \frac{1}{2} (J_{c} \mathbf{S}) : \dot{\mathbf{C}}_{e} + \mu_{\text{net}} \dot{C} + \boldsymbol{\xi} \cdot \nabla \dot{C} - \nabla \mu \cdot \mathbf{J} - \dot{\Psi}_{b} \ge 0,$$
(31)

and the interfacial one:

$$\mathscr{D}_{I} = \mathbf{t}_{I} \cdot \dot{\Delta} + w \Big( \mu_{I} \dot{C}_{I} - \mathbf{J}_{I} \cdot \nabla \mu_{I} \Big) - \dot{\Psi}_{I} \ge 0.$$
(32)

In Eq. (31), the net chemical potential  $\mu_{\rm net}$  is defined as:

$$\mu_{\rm net} = \mu + \bar{\omega}. \tag{33}$$

2.4.1. Helmholtz free energies and dissipation potentials for grains

For the fully coupled multiphysics process, the bulk free energy contains the contribution from the deformation as well as the species diffusion. Therefore, the bulk free energy per unit reference volume takes a form  $\Psi_b = \Psi_b(\mathbf{C}_e, C, \nabla C)$ . To this end, the time derivative of  $\Psi_b$  can be determined by the chain rule as follows:

$$\dot{\Psi}_{b} = \frac{\partial \Psi_{b}}{\partial \mathbf{C}_{e}} : \dot{\mathbf{C}}_{e} + \frac{\partial \Psi_{b}}{\partial \mathbf{C}} \dot{\mathbf{C}} + \frac{\partial \Psi_{b}}{\partial \nabla \mathbf{C}} \cdot \nabla \dot{\mathbf{C}}.$$
(34)

Substituting Eq. (34) into bulk dissipation inequality, namely Eq. (31), we have:

$$\mathscr{D}_{b} = \left(\frac{1}{2}J_{c}\mathbf{S} - \frac{\partial\Psi_{b}}{\partial\mathbf{C}_{e}}\right) : \dot{\mathbf{C}}_{e} + \left(\mu_{\text{net}} - \frac{\partial\Psi_{b}}{\partial C}\right)\dot{\mathbf{C}} - \left(\boldsymbol{\xi} - \frac{\partial\Psi_{b}}{\partial\nabla C}\right)\nabla\dot{\mathbf{C}} - \mathbf{J}\cdot\nabla\mu \ge 0.$$
(35)

By employing the Coleman-Noll procedure, the second Piola–Kirchhoff stress tensor **S**, the net chemical potential  $\mu_{net}$ , and the microstress  $\xi$  vector can be expressed as follows:

$$\mathbf{S} = \frac{1}{J_c} \frac{2\partial \Psi_b}{\partial \mathbf{C}_e},\tag{36}$$

$$\mu_{\rm net} = \frac{\partial \Psi_b}{\partial C},\tag{37}$$

$$\boldsymbol{\xi} = \frac{\partial \boldsymbol{\Psi}_b}{\partial \nabla \boldsymbol{C}}.$$
(38)

Therefore, the bulk dissipation in (35) is further reduced to

$$\mathscr{D}_{b} = -\mathbf{J} \cdot \nabla \mu \ge \mathbf{0}. \tag{39}$$

The positiveness of Eq. (39) can be ensured by assuming a convex dissipation potential  $\Phi_b$  of the bulk such that:

$$\mathbf{J} = -\frac{\partial \Phi_b}{\partial \nabla \mu}.\tag{40}$$

Recalling the definition of  $\mu_{net}$  in Eq. (33), and combining Eqs (37) and (38) as well as the second microforce balance in Eq. (26), we write the final expression of the chemical potential as follows:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_{\text{net}} - \bar{\boldsymbol{\omega}} = \frac{\partial \Psi_b}{\partial C} - \nabla \cdot \frac{\partial \Psi_b}{\partial \nabla C} - \frac{\Omega}{3} \text{tr}(\mathbf{M}_e). \tag{41}$$

According to Zhao et al. (2015) and Bai et al. (2019), the total bulk Helmholtz free energy  $\Psi_b$  per unit reference volume for phaseseparating materials with mechanical coupling can be split into three parts:

$$\Psi_b = \Psi_b^c + \Psi_b^i + \Psi_b^e, \tag{42}$$

where  $\Psi_b^c(C)$ ,  $\Psi_b^i(\nabla C)$  and  $\Psi_b^e(C, \mathbf{C}_e)$  denote the chemical free energy, the interfacial free energy, and the mechanical free energy, respectively. The superindex *i* indicates the interphase between phases, instead of the GB. These three different contributions of free energies are listed below:

$$\Psi_b^c = RTC_{\max} \Big[ \overline{C} \ln \overline{C} + \left(1 - \overline{C}\right) \ln \left(1 - \overline{C}\right) + \chi \overline{C} \left(1 - \overline{C}\right) \Big], \tag{43}$$

$$\Psi_b^i(\nabla C) = \frac{1}{2} C_{\max} \kappa |\nabla \overline{C}|^2, \tag{44}$$

$$\Psi_b^e(C, \mathbf{C}_e) = J_c \left[ \frac{K}{2} (J_e - 1)^2 + \frac{G}{2} (\bar{I}_1 - 3) \right], \tag{45}$$

where  $\overline{C} = C/C_{max}$  is the normalized concentration of Li per unit reference volume,  $C_{max}$  denotes the maximum concentration of lithium that the host material can hold. One can investigate the single-phase system by setting  $\chi < 2$ , while  $\chi > 2$  is adopted for the coexistence of the two-phase system. The scalar parameter  $\kappa$  denotes the interface energy parameter. The neo–Hookean model is employed in Eq. (45) for the particle under large deformation, which can be easily extended to model other hyperelastic materials. The bulk modulus and shear modulus are denoted by *K* and *G*,

respectively. Moreover,  $\bar{I}_1 = \text{tr}(\bar{\mathbf{C}}_e) = \int^{-\frac{2}{3}} \text{tr}(\mathbf{C}_e)$  is the modified invariant, following the standard definition in continuum mechanics (Belytschko et al., 2013). By applying Eqs. (36) and (41), the second Piola–Kirchhoff stress tensor **S** and the chemical potential  $\mu$  can be obtained as follows:

$$\mathbf{S} = \frac{1}{J_c} \frac{2\partial \Psi_b}{\partial \mathbf{C}_e} = \left[ K J_e (J_e - 1) \mathbf{C}_e^{-1} + G J^{-\frac{2}{3}} \left( \mathbf{1} - \frac{1}{3} I_1 \mathbf{C}_e^{-1} \right) \right], \tag{46}$$

and

$$\mu = \frac{\partial \Psi_b}{\partial C} - \nabla \frac{\partial \Psi_b}{\partial \nabla C} - \frac{\Omega}{3} \operatorname{tr}(\mathbf{M}_e) = RT \left[ \ln \overline{C} - \ln \left( 1 - \overline{C} \right) + \chi \left( 1 - 2\overline{C} \right) \right] - \kappa \nabla^2 \overline{C} + \frac{\Omega K}{2} \left[ 1 - (J_e)^2 \right] + \frac{\Omega G}{2} \left( \overline{I}_1 - 3 \right) - \frac{1}{3} \Omega \operatorname{tr}(\mathbf{M}_e).$$
(47)

In a similar manner, the bulk dissipation potential  $\Phi_b$  is decomposed into the mechanical potential  $\Phi_b^e$  and the chemical potential  $\Phi_b^c$ :

$$\Phi_b = \Phi_b^e + \Phi_b^c. \tag{48}$$

In Eq. (48), the mechanical potential can be stated as the function of stress  $\Phi_b^e = f(\mathbf{S})$  (Lemaitre and Chaboche, 1994). While for the chemical part we have (see also Gurtin and Voorhees, 1996; Villani et al., 2014):

$$\Phi_b^c = \frac{1}{2} \boldsymbol{M}(C) : (\nabla \mu \otimes \nabla \mu), \tag{49}$$

where  $\mathbf{M} = DC_{\max}\overline{C}(1-\overline{C})\mathbf{I}$  is the mobility tensor, and D is the diffusion coefficient. In this work, the mobility is considered as the isotropic case, therefore, we rewrite the mobility term as a scalar  $M = DC_{\max}\overline{C}(1-\overline{C})$ . Thereby, by using Eq. (40), we obtain the bulk diffusion flux  $\mathbf{J}$  as follows:

$$\mathbf{J} = -\frac{\partial \Phi_b}{\partial \nabla \mu} = -M(\overline{C}) \nabla \mu.$$
(50)

## 2.4.2. Helmholtz free energies and dissipation potentials for GBs

For the interface, its free energy density functional takes a form  $\Psi_l = \Psi_l(C_l, \Delta, d)$ . Following the same procedure as the bulk, the time derivative of  $\Psi_l$  can be written out as follows:

$$\dot{\Psi}_{I} = \frac{\partial \Psi_{I}}{\partial C_{I}} \cdot \dot{C}_{I} + \frac{\partial \Psi_{I}}{\partial \Delta} \cdot \dot{\Delta} + \frac{\partial \Psi_{I}}{\partial d} \dot{d}.$$
(51)

By putting Eq. (51) into the interface dissipation, namely Eq. (32), we obtain:

$$\mathscr{D}_{I} = \left(\mathbf{t}_{I} - \frac{\partial \Psi_{I}}{\partial \Delta}\right) \cdot \dot{\Delta} + \left(w\mu_{I} - \frac{\partial \Psi_{I}}{\partial C_{I}}\right) \cdot \dot{C}_{I} - \mathbf{J}_{I} \cdot \nabla \mu_{I} - \frac{\partial \Psi_{I}}{\partial d} \dot{d}$$
  
$$\geq \mathbf{0}. \tag{52}$$

Here, the interface traction  $\mathbf{t}_l$  and the interface chemical potential  $\mu_l$  can be written out as follows:

$$\mathbf{t}_{\mathrm{I}} = \frac{\partial \Psi_{\mathrm{I}}}{\partial \Delta},\tag{53}$$

and

$$\mu_{\rm I} = \frac{1}{w} \frac{\partial \Psi_{\rm I}}{\partial C_{\rm I}}.\tag{54}$$

The interface dissipation  $\mathcal{D}_l$  is thereby reduced to:

$$\mathscr{D}_{l} = -\mathbf{J}_{l} \cdot \nabla \mu_{l} - \frac{\partial \Psi_{l}}{\partial d} \dot{d} \ge 0.$$
(55)

Since d has always been positive, the dissipation positiveness can be guaranteed by selecting a convex type dissipation potential  $\Phi_i$ . The interface flux can thereby be expressed as:

$$\mathbf{J}_{I} = -\frac{\partial \Phi_{I}}{\partial \nabla \mu_{I}}.$$
(56)

The insertion of lithium into the particle can lead to the lattice expansion and volume change, which can cause both the normal and tangential failure at the GBs. Meanwhile, the cracks at the GBs can cut off the flux and weaken the transport of lithium across the GBs. Thereby, the impact of the interface debonding on the GBs as well as the lithium transport across the GBs is introduced by a degradation function g(d) (see also Rezaei et al., 2019). Moreover, once damage occurs, the stiffness of the cohesive element is subsequently reduced. Thus the interface Helmholtz free energy should be modified accordingly:

$$\Psi_I = g(d)\Psi_I^e(\Delta) + g(d)\Psi_I^c(C_I).$$
(57)

Here, the interface free energy for the mechanical contribution is introduced as the standard cohesive-zone energy, namely  $\Psi_I^e = \Psi_{CZM}$ . The scalar parameter *d* shows the damage state variable for the irreversible failure of the GBs. To account for the mixed-mode failure and also the flexibility of modeling different fracture behavior of materials, i.e. brittle, quasi-brittle and ductile materials, the PPR model is utilized. For more details, one is referred to the work presented by Park et al. (2009) and Park and Paulino (2012). The mechanical free energy for the interface can thereby be expressed as follows (Park et al., 2009; Park and Paulino, 2012):

$$\Psi_{\text{CZM}}(\boldsymbol{\Delta}) = \Psi_{\text{CZM}}(\boldsymbol{\Delta}_{n}, \boldsymbol{\Delta}_{t}) = \min(\phi_{n}, \phi_{t}) \\ + \left[\Gamma_{n}\left(1 - \frac{\Delta_{n}}{\Delta_{t}}\right)^{\alpha} \left(\frac{m}{\alpha} + \frac{\Delta_{n}}{\delta_{n}}\right)^{m} + \langle\phi_{n} - \phi_{t}\rangle\right] \\ \cdot \left[\Gamma_{t}\left(1 - \frac{|\boldsymbol{\Delta}_{t}|}{\delta_{t}}\right)^{\beta} \left(\frac{n}{\beta} + \frac{|\boldsymbol{\Delta}_{t}|}{\delta_{t}}\right)^{n} + \langle\phi_{t} - \phi_{n}\rangle\right],$$
(58)

where  $\Delta = [\Delta_n, \Delta_t]$  is the displacement jump vector in the local coordinate (n, s), with  $\Delta_n$  and  $\Delta_t$  being the normal and tangential displacement jump, respectively. Parameters  $\delta_n$  and  $\delta_t$  denote the final crack opening widths in normal and tangential direction, respectively. In addition, the expression  $\langle \cdot \rangle$  denotes the *Macaulay bracket* defined as:

$$\langle x \rangle = \begin{cases} 0 & x < 0\\ x & x \ge 0 \end{cases}.$$
(59)

The normal and tangential displacement jump vector are written as follows:

$$\begin{split} \Delta &= \Delta_n + \Delta_t, \\ \Delta_n &= \left( \vec{n}_l \otimes \vec{n}_l \right) \Delta, \qquad \Delta_n = \Delta \cdot \vec{n}_l, \\ \Delta_t &= \Delta - \Delta_n, \qquad \Delta_t = \Delta \cdot \vec{s}_l, \end{split}$$
(60)

where  $\vec{s}_l$  is the vector of tangential direction. Then the traction vector can be derived as:

$$\mathbf{t}_{I} = \frac{\partial \Psi_{I}^{e}}{\partial \Delta} = T_{n} \vec{\boldsymbol{n}}_{I} + T_{t} \vec{\boldsymbol{s}}_{I}.$$
(61)

Therefore, by applying Eq. (53), the traction vector  $\mathbf{t}_{l} = [T_{n}, T_{t}]$  can thus be obtained from the derivative of the interfacial free energy as follows:

$$T_{n}(\Delta_{n},\Delta_{t}) = \frac{\partial \Psi_{I}}{\partial \Delta_{n}} = g(d) \frac{\partial \Psi_{\text{CZM}}}{\partial \Delta_{n}} = g(d) \frac{\partial \Psi_{I}}{\partial \Delta_{n}} = g(d) \frac{\Gamma_{n}}{\delta_{n}} \\ \left[ m \left( 1 - \frac{\Delta_{n}}{\delta_{n}} \right)^{\alpha} \left( \frac{m}{\alpha} + \frac{\Delta_{n}}{\delta_{n}} \right)^{m-1} - \alpha \left( 1 - \frac{\Delta_{n}}{\delta_{n}} \right)^{\alpha-1} \left( \frac{m}{\alpha} + \frac{\Delta_{n}}{\delta_{n}} \right)^{m} \right] \quad (62) \\ \cdot \left[ \Gamma_{t} \left( 1 - \frac{|\Delta_{t}|}{\delta_{t}} \right)^{\beta} \left( \frac{n}{\beta} + \frac{|\Delta_{t}|}{\delta_{t}} \right)^{n} + \langle \phi_{t} - \phi_{n} \rangle \right],$$

and

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$$T_{t}(\Delta_{n},\Delta_{t}) = \frac{\partial \Psi_{I}}{\partial \Delta_{t}} = g(d) \frac{\partial \Psi_{CZM}}{\partial \Delta_{t}} = g(d) \frac{\partial \Psi_{I}^{e}}{\partial \Delta_{t}} = g(d) \frac{\Gamma_{t}}{\delta_{t}} \\ \left[ n \left( 1 - \frac{|\Delta_{t}|}{\delta_{t}} \right)^{\beta} \left( \frac{n}{\beta} + \frac{|\Delta_{t}|}{\delta_{t}} \right)^{n-1} - \beta \left( 1 - \frac{|\Delta_{t}|}{\delta_{t}} \right)^{\beta-1} \left( \frac{n}{\beta} + \frac{|\Delta_{t}|}{\delta_{t}} \right)^{n} \right]$$
(63)  
 
$$\cdot \left[ \Gamma_{n} \left( 1 - \frac{\Delta_{n}}{\delta_{n}} \right)^{\alpha} \left( \frac{m}{\alpha} + \frac{\Delta_{n}}{\delta_{n}} \right)^{m} + \langle \phi_{n} - \phi_{t} \rangle \right] \frac{\Delta_{t}}{|\delta_{t}|}.$$

In Eqs. (62) and (63),  $\phi_n$  and  $\phi_t$  represent the fracture energy of normal and tangential failure, respectively. For the related energy constants  $\Gamma_n$  and  $\Gamma_t$ , we have:

$$\Gamma_{n} = \begin{cases} \left(-\phi_{n}\right)^{\frac{\langle\phi_{n}-\phi_{t}}{\phi_{n}-\phi_{t}}} \left(\frac{\alpha}{m}\right)^{m} & \phi_{n} \neq \phi_{t} \\ -\phi_{n}\left(\frac{\alpha}{m}\right)^{m} & \phi_{n} = \phi_{t} \end{cases} \\ \Gamma_{t} = \begin{cases} \left(-\phi_{t}\right)^{\frac{\langle\phi_{t}-\phi_{n}}{\phi_{t}-\phi_{n}}} \left(\frac{\beta}{n}\right)^{n} & \phi_{n} \neq \phi_{t} \\ \left(\frac{\beta}{n}\right)^{n} & \phi_{n} = \phi_{t} \end{cases},$$
(64)

where m and n are the non-dimensional exponents, defined as follows:

$$m = \frac{\alpha(\alpha - 1)\lambda_n^2}{\left(1 - \alpha\lambda_n^2\right)}, n = \frac{\beta(\beta - 1)\lambda_t^2}{\left(1 - \beta\lambda_t^2\right)}.$$
(65)

Here the shape parameter  $\alpha$  and  $\beta$  are introduced in Eq. (65) to characterize different material softening responses, e.g. plateau ( $\alpha, \beta < 2$ ) and quasi-brittle ( $\alpha, \beta > 2$ ), as shown in Fig. 2. The initial slope in normal and shear direction is indicated by  $\lambda_n$  and  $\lambda_t$ , respectively, which are the ratio of the critical crack opening width  $\delta_{nc}, \delta_{tc}$ to the final crack opening width  $\delta_n, \delta_t$ , i.e.  $\lambda_n = \delta_{nc}/\delta_n, \lambda_t = \delta_{tc}/\delta_t$ . The final crack opening width  $\delta_n$  and  $\delta_t$  can be expressed as follows:

$$\delta_n = \frac{\phi_n}{\sigma_{\max}} \alpha \lambda_n (1 - \lambda_n)^{\alpha - 1} \left(\frac{\alpha}{m} + 1\right) \left(\frac{\alpha}{m} \lambda_n + 1\right)^{m - 1},\tag{66}$$

and

$$\delta_t = \frac{\phi_t}{\tau_{\max}} \beta \lambda_t (1 - \lambda_t)^{\beta - 1} \left(\frac{\beta}{n} + 1\right) \left(\frac{\beta}{n} \lambda_t + 1\right)^{n - 1},\tag{67}$$

where  $\sigma_{\text{max}}$  and  $\tau_{\text{max}}$  are the normal and tangential cohesive strengths, respectively. For the details of the PPR model, readers are referred to Park et al. (2009) and Park and Paulino (2012).

The complete normal failure occurs when the normal separation  $\Delta_n$  reaches the final crack opening width  $\delta_n$ . Similarly, the complete tangential failure occurs when  $\Delta_t = \delta_n$ . In this work, the fracture mode is a combination of both the normal and tangential failure. The mode-mixity is considered by the effective displacement jump  $\Delta_{\text{eff}}$ :



(a)  $\alpha, \beta = 1.5$  for the plateau type

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$$\Delta_{\rm eff} = \sqrt{\Delta_n^2 + \Delta_t^2}.$$
 (68)

The damage evolution functions for the mode-mixity failure can be defined as follows:

$$d = \begin{cases} 0 & \Delta_{\text{eff}} \leqslant \delta_{c,\text{eff}} \\ \frac{\delta_{\text{eff}}}{\Delta_{\text{eff}}} \frac{\Delta_{\text{eff}} - \delta_{c,\text{eff}}}{\delta_{\text{eff}} - \delta_{c,\text{eff}}} & \Delta_{\text{eff}} > \delta_{c,\text{eff}} \end{cases},$$
(69)

where  $\delta_{\text{eff}} = \sqrt{\delta_n^2 + \delta_t^2}$  is the effective final crack opening width and  $\delta_{c,\text{eff}} = \sqrt{\delta_{nc}^2 + \delta_{tc}^2}$  denotes the effective critical crack opening width. The contour plot of damage evolution is shown in Fig. 3. For the irreversible crack propagation as damage evolves it is assumed that  $\dot{d} \ge 0$ . In this work, the damage parameter d is introduced as the history-dependent state variable, namely  $d = \max_{s \in [0,t]} \hat{d}(x,s)$  over the full temporal history  $s \in [0, \mathcal{F}]$  of damage state  $\hat{d}$ . In this work, the degradation function is introduced as a linear function as g(d) = 1 - d. The discussion of the degradation function's influence

on the interface debonding will be presented in the future work. Following the same procedure as the bulk, namely Eq. (49), the interface dissipation potential can be expressed as:

$$\Phi_I^c = \frac{1}{2} \mathbf{M}_I(C_I) : \left( \nabla \mu_I \otimes \nabla \mu_I \right), \tag{70}$$

by using Eq. (56), we can have the interface flux as follows:

$$\mathbf{J}_{I} = -\mathbf{M}_{I} \nabla \boldsymbol{\mu}_{I},\tag{71}$$



**Fig. 3.** Damage function for the mixed-mode failure with  $\lambda_n = 0.2, \lambda_t = 0.1$ .



(b)  $\alpha, \beta = 5.0$  for the convex type

**Fig. 2.** The traction-separation law (TSL) under different  $\alpha$ ,  $\beta$ , with  $\phi_n = \phi_t = 4\frac{j}{m}$ ,  $\lambda_n = \lambda_t = 0.1$ ,  $\sigma_{max} = \tau_{max} = 100mp$ .

where  $\mathbf{M}_{l}$  is the mobility tensor of the interface. Similar to the bulk, we adopt the isotropic case of the interface mobility. Therefore, the interface mobility can be rewritten out as a scalar  $M_{l}$ . Thereby, the across-GB flux can be expressed as:

$$J_I = \mathbf{J}_I \cdot \vec{\mathbf{n}}_I = -M_I \nabla \mu_I \cdot \vec{\mathbf{n}}_I \tag{72}$$

Next, by extracting the interfacial free energy from the bulk one Eq. (42) with the consideration of interface fracture, we can have:

$$\Psi_l^c = wg(d)\Psi_b(C_l). \tag{73}$$

Then, by using Eq. (54), the damage dependent interface chemical potential can be obtained as follows:

$$\mu_{l} = \frac{1}{w} \frac{\partial \Psi_{l}^{c}}{\partial C_{l}} = g(d) \frac{\partial \Psi_{b}(C_{l})}{\partial C_{l}}, \tag{74}$$

considering that, the interface flux can be expressed as:

$$\begin{aligned}
J_I^+ &\approx J_I + \frac{w}{2} \nabla J_I \cdot \vec{\mathbf{n}}_I, \\
J_I^- &\approx J_I - \frac{w}{2} \nabla J_I \cdot \vec{\mathbf{n}}_I,
\end{aligned}$$
(75)

therefore, by using Eqs. (72) and (75), the across-GB flux can be expressed as:

$$J_{I} = \mathbf{J}_{I} \cdot \vec{\mathbf{n}}_{I} = \frac{1}{2} \left( J_{I}^{+} + J_{I}^{-} \right) = \frac{1}{2} \left( -M_{I}^{+} \nabla \mu_{I}^{+} + M_{I}^{-} \nabla \mu_{I}^{-} \right) \cdot \vec{\mathbf{n}}_{I},$$
(76)

where  $M_l^+$  and  $M_l^-$  are the mobility coefficient of the GB. Accordingly, the chemical potentials  $\mu_l^+$  and  $\mu_l^-$  at the upper and low GBs are calculated from Eq. (74), where  $C_l^+$  and  $C_l^-$  are adopted. It should be mentioned that, the models presented by Zhang et al. (2019), Xu et al. (2018) and Sun et al. (2016) are based on the assumption with the smooth profile of concentration across the GBs, where no concentration jumps and chemical potential jumps are considered.

## 2.5. Numerical implementation

By using the test functions  $\delta C$ ,  $\delta \mu$  and  $\delta U_i$ , we can write out the *weak forms* for the system equations as follows:

$$\int_{\mathscr{R}} \dot{C} \delta C dV = -\int_{\partial \mathscr{R}} \mathbf{J} \cdot \mathbf{\vec{n}} \delta C dS - \int_{\Gamma_{I}} \mathbf{J}_{I} \cdot \mathbf{\vec{n}}_{I} \delta C d\Gamma - \int_{\mathscr{R}} M \nabla \mu \nabla \delta C dV,$$
(77)

and

$$\int_{\mathscr{B}} \mu \delta \mu dV = \int_{\mathscr{B}} \mu_{\text{net}} \delta \mu dV - \int_{\mathscr{B}} \bar{\omega} \delta \mu dV, \tag{78}$$

and

$$\int_{\mathscr{B}} P_{ij} \delta U_{i,j} dV + \int_{\Gamma_1} t_i \delta \Delta_i dS = 0$$
<sup>(79)</sup>

Therefore, the residuals for each equation can be expressed as:

$$R_{C}^{l} = \int_{\mathscr{B}} \dot{C} N^{l} dV + \int_{\partial \mathscr{B}} \mathbf{J} \cdot \vec{\mathbf{n}} N^{l} dS + \int_{\Gamma_{I}} \mathbf{J}_{I} \cdot \vec{\mathbf{n}}_{I} N^{l} d\Gamma + \int_{\mathscr{B}} M \nabla \mu \nabla N^{l} dV,$$
(80)

and

$$R^{l}_{\mu} = \int_{\mathscr{B}} \mu N^{l} dV - \int_{\mathscr{B}} \mu_{\text{net}} N^{l} dV + \int_{\mathscr{B}} \bar{\omega} N^{l} dV, \qquad (81)$$

and

$$R_{U_{i}}^{l} = \int_{\mathscr{B}} P_{ij} N_{J}^{l} dV + \int_{\Gamma_{1}^{+}} t_{i}^{+} N^{l} dS - \int_{\Gamma_{1}^{-}} t_{i}^{-} N^{l} dS,$$
(82)

where the superscript *I* and *J* are the node index of the current element, respectively. It should be mentioned that, the traction  $t_i^{I+}$  and  $t_i^{I-}$  at the interface are calculated at the local coordinates system.

Thereby, the global to local coordinates transformation operator  $\Lambda$  and the rotation matrix **R** are introduced as follows:

$$\mathbf{x} = \mathbf{\Lambda} \cdot \mathbf{X},\tag{83}$$

and

$$\hat{\mathbf{U}} = \mathbf{R} \cdot \mathbf{U},\tag{84}$$

where **x** represents the local coordinates of a cohesive zone element, and **X** is the global one. **U** and  $\hat{\mathbf{U}}$  are the global and local displacements, respectively. Thus the local displacement jumps  $\Delta$  can be calculated as follows:

$$\Delta = \mathbf{L} \cdot \mathbf{U},\tag{85}$$

where **L** is the local displacement–separation relation matrix. Then the global traction can be found as:

$$\mathbf{T} = \mathbf{B} \cdot \mathbf{T}_{\text{loc}},\tag{86}$$

where **T** is the global traction vector at the interface, and **B** = **NLR** is the global displacement-separation relation matrix. The shape functions of the interface is denoted by **N**. Based on the local displacement jump  $\Delta$ , the local traction **T**<sub>loc</sub> can be calculated from Eqs. (62) and (63). As an example, in the two-dimensional quadratic element with four nodes, the interface between the two nearby elements is a two-node line element, as illustrated in Fig. 4. As a result, the transformation matrix  $\Lambda$  can be written out as follows:

$$\mathbf{\Lambda} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix},\tag{87}$$

then the rotation matrix **R** can be expressed as:

$$\mathbf{R} = \begin{bmatrix} \Lambda & 0 & 0 & 0 \\ 0 & \Lambda & 0 & 0 \\ 0 & 0 & \Lambda & 0 \\ 0 & 0 & 0 & \Lambda \end{bmatrix}.$$
 (88)

The local displacement jump  $\Delta$  can thus be obtained from the local displacements as follows:

$$\Delta_1 = \overline{U}_7 - \overline{U}_1, \quad \Delta_2 = \overline{U}_8 - \overline{U}_2, \quad \Delta_3 = \overline{U}_5 - \overline{U}_3, \quad \Delta_4 = \overline{U}_6 - \overline{U}_4,$$
(89)

where  $\overline{U}_i$  is the displacement in the local coordinates. The local transformation matrix **L** can be read as:

$$\mathbf{L} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 \end{bmatrix}.$$
 (90)

# 3. Results and discussions

The models mentioned above have been implemented in the open source FEM package MOOSE (Gaston et al., 2009) and libMesh (Kirk et al., 2006). Particularly, the *interface kernel* from MOOSE (Gaston et al., 2009) have been used for the implementation of both the cohesive zone model and the across-GB transport model. The coupled sets of PDEs of the bulk element are also solved in MOOSE and libMesh based on our previous work (Bai et al., 2019). The coupled equations of the whole system are solved by PETSc (Abhyankar et al., 2018; Balay et al., 2019) with Preconditioned Jacobian-Free Newton Krylov (PJNFK) method from MOOSE.



Fig. 4. The representative two-dimensional linear cohesive zone element in (a) the global coordinates and (b) the local coordinates.

## 3.1. Benchmark test for two-grains case

A particle containing two grains (left grain and right grain) with the dimensions 10 mm × 5 mm, as shown in Fig. 5, has been used to demonstrate the across-GB transport and its impact on the GB cracking. The sample is subjected to the external loading, namely the chemical flux, at the right edge. Therefore, the boundary condition for the right edge can be read as  $\mathbf{J} \cdot \mathbf{\vec{n}} = J$ , where *J* is calculated by the C-rate in (91), where 1 C-rate specify the flux of lithium which can fully discharge/charge the particle in 1 h (3600s). The relationship between the species flux and C-rate can be read as follows:

$$\mathbf{J} = \mathbf{J} \cdot \vec{\mathbf{n}} = \frac{VC_{\max} \text{Crate}}{A \cdot 3600} \tag{91}$$

with *V* and *A* being the volume and surface area of the sample, respectively. In this section, C-rate = 0.6 is applied. While the constraint  $u_x = 0$  is applied to the left edge, and  $u_y = 0$  is applied to the bottom edge, respectively. During the discharge process, the whole sample experiences the gradient change of the concentration from the left edge towards the right side. At the beginning stage, the interaction between two grains tries to reduce the concentration differences at the GB, which can be confirmed by the smooth stress contour plot with a continuity profile across the GBs in Fig. 5(c)<sub>1</sub>. However, once damage initiates, it can cut off the flux and weakens

the lithium exchange across the GBs. Whereby, the concentration jumps becomes larger than the previous case, as shown in the second column in Fig. 5. As more lithium goes into the grains, the concentration jumps at the GBs will become even larger, where the cracks become more obvious than the first and second column, as shown in Fig. 5(b). As a consequence, the crack cuts off the flux, which leads to the high concentration of lithium in the right grain, as shown in Fig. 5(a). Moreover, the stress level is reduced by crack propagation at the GBs. Therefore, it is evident that the GB cracking and its impact on the diffusion is quite important.

To further investigate the change of the field variables at the interface, the node pair at the center of the sample, where x = 5 mm and y = 2.5 mm, is chosen to demonstrate the impact of the across-GB transport. The node pair contains the *left* node on the left grain side and the *right* node on the right grain side. Fig. 6a confirms that, at the beginning stage of discharge, the concentration field experiences a smooth profile across the GB. Moreover, the across-GB transport can also enforce the stresses to be continued at the interface, as shown in Fig. 6c. Meanwhile, the flux on the two sides of the GB is almost the same as shown in Fig. 6d. However, this interaction is proportional to the chemical potential gradient, therefore, the chemical potentials  $\mu_i^+$  and  $\mu_i^-$  of lithium on the two sides of the GB are quite different from each other as shown in Fig. 6b. Once the crack propagation starts, damage cuts off the flux. As a consequence, the concentration field and the



Fig. 5. The distribution of the lithium concentration (a), damage state (b) and maximum principal stress  $\sigma_{sp1}$  (c) for a particle with two grains.



**Fig. 6.** The profiles of (a) concentration  $C_l^+$  and  $C_l^-$ , (b) chemical potential  $\mu_l^+$  and  $\mu_l^-$  in two grains, (c)  $\sigma_{vonMises}^+$ , (d) flux  $J_l^+$  and  $J_l^-$ . In all the plot except (b), the red line indicates the change of the damage variable *d* over time. In all the figures, the line with black color indicates the quantities of the *left* node (belongs to the left grain), and the dashed line with blue color represents the quantities of the *right* node (belongs to the right grain).

Table	1
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Physical parameters used in this work.

Material properties for NMC particle.					
Description	Unit	Value			
Particle radius r	mm	5			
Fracture energy of normal $\phi_n, \phi_t$	jm <sup>-2</sup>	2.0, 2.0			
Shape parameter $\alpha, \beta$	-	5.0, 1.5			
Initial slope indicator $\lambda_n, \lambda_t$	-	0.1, 0.1			
Cohesive strength $\sigma_{\max}, \tau_{\max}$	mp	100, 100			
Diffusivity of NMC particle D	$m^2 s^{-1}$	$7.0 * 10^{-15}$			
Diffusivity of GBs $D_I^{\pm}$	$m^2 s^{-1}$	$7.0 * 10^{-15}$			
Young's modulus E	GPa	140			
Poisson ratio v	-	0.3			
Partial molar volume $\Omega$	$m^3 mol^{-1}$	$4.566 * 10^{-6}$			
Max. concentration $C_{max}$	mm <sup>-3</sup>	32860			
Phase parameter $\chi$	-	2.4			
Interface parameter $\kappa$	Jm <sup>2</sup> mol <sup>-1</sup>	$2.5\times10^{-10}$			
Gas constant R	$I \text{ mol}^{-1} \text{K}^{-1}$	8.314			
Temperature T	K	298.15			
Farady's constant F	$\mathrm{Cmol}^{-1}$	96,487			

chemical potentials experience greater differences as more lithium goes into the grains (see Fig. 6a,b). The stresses on the two sides are distinct. The flux increase smoothly increases until the complete failure occurs. As such, new free surfaces are generated at the GB after the failure begins. Then, once the complete failure occurs, the flux is reduced to zero. Besides, the crack causes the blocking effect which leads to the uniform distribution of concentration and chemical potential on the left grain. See Fig. 6a,b where the black solid line is almost flat after  $t \ge 4000$  s.

## 3.2. Influence of across-GB transport on interconnected particles

To account for the interaction between grains, the V<sub>2</sub>O<sub>5</sub> nanowires are considered in this section, as shown in Fig. 7(A), the related illustration is shown in Fig. 7(F). On the nanowire/electrolyte surface, the reaction  $Li^+ + H^- \ll LiH$  is considered with H being the host material, where the galvanostatic discharge process is applied. Accordingly, the GB model mentioned in Section 2.4.2 is utilized for this study. The parameters for V<sub>2</sub>O<sub>5</sub> are listed in Table 2.

Collected SEM images for a set of particles including a nanowire with a split end is indicated in Fig. 7(A). In Fig. 7(B), the spectra are ordered according to increasing lithiation (bottom to top). Cluster 1, Cluster 2, and Cluster 3 in Fig. 7(C)-(E) are identified as unlithiated  $\alpha$ -V<sub>2</sub>O<sub>5</sub>, lithiated  $\alpha$  –  $Li_{0.1}$ V<sub>2</sub>O<sub>5</sub>, and  $\varepsilon$  –  $Li_{0.3}$ V<sub>2</sub>O<sub>5</sub> phases, respectively. Further details about the LiV<sub>2</sub>O<sub>5</sub> phase diagram are detailed in Santos et al. (2020) and De Jesus et al. (2017). Fig. 7(-G)-(I) show the concentration, damage and stress fields inside the V<sub>2</sub>O<sub>5</sub> single nanowires, respectively, as deduced from compositional maps derived from the hyperspectral scanning transmission X-ray microscopy dataset.

Experimental evidence of intraparticle phase heterogeneity is presented in Fig. 7, where Cluster 1 (red) is primarily localized at



**Fig. 7.** (A) Scanning electron microscopy (SEM) image of nanowires. (B) Spectroscopically distinct profiles across the V L- and O K- X-ray absorption edges corresponding to differently lithiated V<sub>2</sub>O<sub>5</sub> domains. Panels (C), (D), and (E) represent composition maps generated by a singular value decomposition (SVD) analysis performed by using the XANES spectra (shown in (B)) as inputs. (F) Illustration of nanowires. (G), (H), and (I) denote the distribution of the concentration, damage state and  $\sigma_{sp1}$  (mp) of V<sub>2</sub>O<sub>5</sub> nanowires.

## Table 2

Physical	parameters	for	$V_2O_5$	used in	n this	work	(Santos	et al	., 2020	I)
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Material properties for V <sub>2</sub> O <sub>5</sub> nanowires.				
Description	Unit	Value		
Fracture energies $\phi_n, \phi_t$	Jm <sup>-2</sup>	4.0, 4.0		
Shape parameter $\alpha, \beta$	-	6.0, 6.0		
Initial slop indicator $\lambda_n, \lambda_t$	-	0.015, 0.015		
Cohesive strength $\sigma_{\max}, \tau_{\max}$	mP	100, 100		
Diffusivity of $V_2O_5 D$	$m^2 s^{-1}$	$5.4\times10^{-15}$		
Young's modulus E	GPa	43		
Poisson ratio v	-	0.3		
Partial molar volume $\Omega$	$m^{3}m^{-1}$	$4.85\times10^{-6}$		
Max. concentration $C_{max}$	mm <sup>-3</sup>	12400		
Phase parameter χ	-	2.4		
Interface parameter $\kappa$	Jm <sup>2</sup> mol <sup>-1</sup>	$2.5\times10^{-10}$		
C-rate	_	0.05		

the core of the nanowire and is characteristic of the unlithiated  $\alpha$ -V<sub>2</sub>O<sub>5</sub> phase, an unlithiated core suggests a regime where bulk diffusion cannot keep pace with ion insertion at the surface as shown in Fig. 7(G). In contrast, Clusters 2 (blue) and 3 (green) are assigned to the lithiated  $\alpha - Li_{0.1}V_2O_5$  and  $\varepsilon - Li_{0.3}V_2O_5$  phases, respectively and clearly describe the high concentration regime at the outer shell of the nanowire, which can also be confirmed in Fig. 7(G). This heterogeneity arises from the sequential (as opposed to concurrent) nucleation of the Li-rich phase at the nanowire tips which

are subject to a high local potential gradient relative to the rest of the particle.

One can see from Fig. 7(G) and (I) that once the crack occurs, the newly opened surfaces will become in contact with each other. The latter point lead to higher stresses around the cracks than other parts as shown in Fig. 7(I). Moreover, at the front of the crack tip, the undamaged part still experience high stresses. The compressive stresses push lithium away from GBs to other parts. As a consequence, even though the nanowires are under the lithiation process, the Li-poor phase is captured at the center of the fork, which is confirmed by the experimental study as shown in Fig. 7(-C)-(E). Therefore, we can conclude that, in addition to the apparent modification of the split-end in the nanowire on the resulting concentration gradients, we expect that this defect may similarly represent a nucleation point for delamination during lithiation as a result of the lithiation-induced stresses.

## 3.3. Impact of the across-GB transport on the crack pattern

Different structures of spherical NMC particles generated by Quey et al. (2011) are shown in Fig. 8. The number of primary particles is determined by the mean size of the primary grains. By setting the diameter of the primary particle among  $r_{\text{primary}} = 500nm$ , 400nm and 300nm, one can have three different grain numbers, namely grains = 89, 174 and 413. The different color in Fig. 8 indicates the different id index of each primary particle, while the

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Fig. 8. NMC particles with different numbers of primary particles, where the color indicates the id index of primary particles.

white solid line represents the interface or the GB between primary grains. After the geometry data is generated, the FEM mesh is produced by the open-source package Geuzaine and Remacle (2009).

In this section, we examine the impact of the across-GB transport between grains on the crack pattern of NMC particles. As a comparison, particles with and without the GB model have been considered. The secondary particles with different numbers of primary particles are considered, as shown in Fig. 8. For all the particles, three different diffusion models listed in Table 3 (namely, the chemo-mechanical GB model, the chemo-mechanical GB without concentration jumps, and the simple cohesive zone model) are considered. The mechanically coupled diffusion model as described in Section 2.4.2 is applied for all particles. The parameters listed in Table 1 are used in the simulation. All the particles are subjected to the constant lithium flux for 1 C-rate discharge process, and the center of the particle is fixed to get rid of the rigid body motion.

The concentration and damage fields within the considered secondary particles are shown in Figs. 9, 10, respectively. For all particles, the chemo-mechanical GB model (Case-I) results in a high concentration in the outer layer primary grains, together with several concentration hot spots. Additionally, the pronounced concentration jumps towards inner primary particles is recognized. It is attributed to the surface blocking effect of across-GB transport. The insertion of lithium contributes to the volume expansion of the outer layer primary particles as the lithium goes through the particle, resulting in a large strain mismatch between adjacent grains along GBs. Additionally, as more and more lithium goes into the particle, the mismatch strain will increase. This process continues until the mismatch strain-induced stresses are beyond the strength of the GBs and the damage initiation occurs. Furthermore, as described in Eq. (76), the existence of cracks reduces the flux across the GBs and weaken the across-GB transport. Once the crack occurs, the flux between neighbor grains is cut off and the diffusion of lithium cannot progress towards the core of the secondary particles. As a consequence, the lithium will accumulate in the outer layer grains. The lithium accumulation leads to the high concentra-



Fig. 9. Lithium concentration distribution of NMC particles with different numbers of primary particles and different GBs interactions.

tion gradient around cracks, as shown in Fig. 9. Simultaneously, the concentration gradient will lead to an even larger mismatch strain, which accelerates the crack propagation. As a consequence, the surface blocking effect will contribute to the surface delamination as several small primary grains are 'squeezed' out from the secondary particle (see Fig. 10).

#### Table 3

The diffusion models at the grain boundary.

Diffusion dynamics at GBs					
Model type	Model description	Governing equation			
Chemo-mechanical GB model	damage-dependent ion transport and mechanical failure	Eqs. (62), (63) and (76)			
Chemo-mechanical GB model	damage-dependent ion transport and mechanical failure, no concentration jumps are allowed before damage	Eqs. (62), (63) and (76) with $\llbracket C \rrbracket = C^+ - C^- = 0$			
Mechanical GB model	damage-dependent cohesive zone model, without ion transport interaction at GBs	Eqs. (62) and (63) with $C_I^+ = C_I^-, \mu_I^+ = \mu_I^-$			



**Fig. 10.** Damage state of NMC particles with different numbers of primary particles and different GBs interactions.

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**Fig. 11.** Distribution of the maximum principal stress  $\sigma_{sp1}$  (mp) of NMC particles with different primary particles and different GBs.

Different from the particle with across-GB transport, the particles consider the GB model but without the concentration jumps (Case-II) and the particles with only cohesive zone model (Case-III) experience the smoothly varying concentration field along the particles' radius direction. The latter observation is also known as the core-shell type concentration distribution, as shown in Fig. 9. In this scenario, the strain mismatch is comparatively small and the concentration of lithium has a gradient change from the center towards the outward surface. Moreover, as shown in Fig. 10, the concentration jumps can only be captured around the crack of the particle in Case-II, where cracks mainly form in the core of the secondary particle. Distinct from particles with across-GB transport, the crack has a limited influence on the lithium diffusion of particles in Case-II and Case-III. The surface delamination is suppressed in these cases due to the absence of surface blocking effects.

To corroborate these findings, the maximum principal stress  $\sigma_{sp1}$  of each particle is plotted in Fig. 11. One can see that the strain mismatch is concentrated along the phase interface, as are the first principal stresses. The tensile stress state is established in the secondary particle's center at the initial states of discharge, which is relaxed by the formation and the subsequent (low) growth of cracks. Hence the low-stress state is capture at both the core part and shell part, where the crack occurs. However, for the particle without across-GB transport, the high-stress state mainly focuses on the core part. Moreover, the stress state of the particle with Case-III, where the GBs are ignored, is lower than the other two cases. Meanwhile, the crack pattern of the particle in Case-II and Case-III is analogous to each other. In addition, the smaller grains are approached as the number of primary particles (grains) increases, then the interaction distance between grains becomes even shorter. For the particle with across-GB transport, the crack propagation will be accelerated by the neighboring stresses. As a consequence, the surface blocking effect is stronger in the particle with more grains, as shown in Fig. 10. However, for the particle with Case-II and Case-III, even though the interaction distance is

shorter, the absence of the across-GB transport restricts the concentration jumps along the GBs, thus the strain mismatch between primary particles is retarded. As the number of primary particles increases, the stress state is decreasing. Thus particles with more grains in these two cases have fewer cracks than the particle with fewer grains.

To further examine the differences between each model, the damage fraction is introduced as follows:

damage fraction = 
$$\frac{\int_{\Gamma_1} ddA}{\int_{\Gamma_1} dA}$$
, (92)

and the average surface concentration is expressed as:

$$\overline{C}_{\text{surface}} = \frac{\int_{\partial \mathscr{R}} C_{\text{surface}} dA}{\int_{\partial \mathscr{R}} dA},$$
(93)

where the integration has been carried out along the GBs or the interfaces ( $\Gamma_1$ ) and the surface of the particle ( $\partial \mathscr{B}$ ) at the end of each time step, respectively. According to Fig. 12, for the particle with across-GB transport, the larger number of grains result in stronger anisotropy of GB orientations, which leads to greater surface blocking effects. Thus the surface concentration increases faster than other particles with fewer grains, which is shown in Fig. 12a (given as the solid lines). Moreover, as the number of grains increases, the shorter interaction distance of stresses between neighboring grains can result in the drastic increase of the damage fraction as shown in Fig. 12b. However, for the particles in Case-II and Case-III, a larger number of grains results in a slower increase of surface concentration. This is attributed to the fact that, cracks mainly come from the volume expansion between grains. Therefore, even though the anisotropy of GB orientations is stronger, omitting the explicit role of concentration jumps alleviate the effect of GBs' blocking effect in Case-I. Thus the damage fraction value firstly increases to a certain value then keeps a stable state, where the crack is in balance with the chemical loading (the applied flux). Additionally, the ignorance of GBs in Case-III has similar trends. Thus the profiles between



(a) average surface concentration of each case

Fig. 12. The average surface concentration  $\bar{c}_{surface}$  and damage fraction of different cases. Different line styles indicate different models while different colors represent different numbers for grains.

Case-II and Case-III are quite close to each other. Compared to the cases with across-GB transport, the crack inside the NMC particle has limited influence on the concentration distribution once the across-GB interaction is ignored.

In light of the above observations, one concludes that the major contributor to the surface blocking effect that results in chemical hot spots, is the cross-GB transport. Both the surface delamination and cracks within the particle occur for particles with across-GB transport. However, when the across-GB transport or the GB is ignored, the surface delamination is suppressed, cracks mainly occur in the core of the secondary particle. Besides, the continuity of concentration across the GB alleviates the differences between Case-II and Case-III, where similar crack patterns are found between these two models. In addition, the smaller size of primary particles contributes to a greater anisotropy of GB orientations. Consequently, in Case-I, where the more detectable surface delamination is noted, a stronger surface blocking effect is captured. This size effect, however, demonstrates an adverse effect on the particle's crack patterns for the cases without cross-GB transport or GBs, where more primary particles contribute to fewer cracks. Accordingly, the damage percentage of NMC particles could be underestimated once the GB interaction is ignored.

#### 4. Conclusion

In this work, we proposed a thermodynamically consistent framework for the chemo-mechanical coupling in both the bulk diffusion inside polycrystalline materials and also the across-GB interaction between grains. Whereby, the constitutive laws for the chemo-mechanically coupled process inside the bulk and at the GB are derived from the system free energy and thermodynamic considerations. In particular, the cohesive zone model (CZM) for mechanical failure as well as the lithium diffusion across the GBs are derived from the system free energies. This model thus enables us to study the propagation of cracks along the GBs in a chemo-mechanically coupled system. In addition, the implemented formulation has the flexibility to model the effect of various types of GBs on the propagation of cracks, i.e. the across-GB ion transport and also the exchange reaction of lithium through the GBs. We first benchmark our model for the particle with two grains case. Simulation results show that across-GB transport can be alleviated by the existence of cracks, which can contribute to the concentration inhomogeneity at the GBs. Additionally, the GBs induced inhomogeneous lithiation of V<sub>2</sub>O<sub>5</sub> single nanowires has been studied and is used to explain cohesive delamination and large lithiation gradients across a split end observed by highresolution scanning transmission X-ray microscopy. Results show that, as more lithium is inserted into the nanowires, the strain mismatch leads to damage initiation, which cuts off the exchange of lithium and reduces the stresses at the GBs. Furthermore, it leads to local Li poor phase segregation at the fork of nanowires due to the stresses. Thereby, the pronounced local delithiation phenomenon captured by the experiment is reproduced at the forkshape part.

Finally, we examine the influence of different across-GB transports. Simulation results show that the across-GB transport results in large concentration differences across the GBs, which leads to the strain mismatch at the interface. Once cracks occur along the GBs, the flux across the GBs is cut off, thus the lithium will accumulate in grains at the outward layer. Consequently, the surface blocking effect occurs. The latter point is the major contributor to the surface delamination of polycrystalline materials, i.e. NMC. Influenced by this, the chemical hot spots are captured at the outward primary grains. A stronger anisotropy of GB orientation and greater interaction between neighboring grains are approached as the number of primary particles increases, so the surface blocking effect will be enhanced. Polycrystalline particles with more grains thus experience a greater impact of surface delamination. The comparative study also confirms that the omission of the across-GB transport and the GBs results in similar results. Once the across-GB transport or the GB is ignored, the surface delamination is suppressed, cracks mainly occur in the core part. In contrast to the particle with across-GB transport, the increase of grains leads to fewer cracks. Thus the damage percentage of polycrystalline materials could be underestimated.

Overall, we argue that the across-GB transport inside the polycrystalline materials has a significant impact on the propagation of cracks and lithium diffusion. These points should not be ignored in estimating the fracture behavior and chemical performance studies. In the future, this model should be applied to consider the interaction between the newly opened surface and the electrolyte. In addition, the crack propagation across the grains should also be discussed in the future work. Moreover, one need to consider the contribution of defects in polycrystalline materials to cell performance. The anisotropic cracking at GBs and the lithium embrittlement effect on the crack propagation should also be mentioned.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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