Porous Electrode Model with Particle Stress Effects for $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ Electrode

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A porous electrode model, incorporating particle stress effects, is developed for the electrode kinetic processes in the positive $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ or NMC111 electrode. The model is used to analyze experimental data from galvanostatic intermittent titration technique (GITT) during charging at the beginning of life. The equilibrium potential accounts for the influence of mechanical stress in the electrode particles. While the standard Newman-based model proves unable to capture the dynamic performance of NMC111, the extended model with stress allows good fits of the GITT responses for NMC half cells for a voltage range from 3.7–4.1 V vs Li/Li^+ at 10°C, 25°C and 40°C. Four physical parameters are extracted to analyze the underlying diffusive, kinetic, thermodynamic and stress phenomena from polarization to relaxation during a GITT transient. Strong dependencies of the kinetic rate constant k , slope of the open-circuit potential curve $dE_{\text{oc}}/dx_{\text{pos}}$ and stress proportionality factor γ_{stress} with lithium concentration are found. The effective diffusion coefficients $D_{\text{s,eff}}$ are $\sim 10^{-14} - 10^{-13} \text{ cm}^2/\text{s}$ across voltages and temperatures. Diffusion limitation and particle surface stress are more profound at higher voltages and at higher temperatures. This leads to large lithium concentration gradient near particle surface, requiring longer relaxation time during GITT.

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Lithium transition metal oxides are currently the focus of battery manufacturers as attractive positive intercalation electrode materials in lithium-ion batteries (LIB).^{1–3} After LiCoO_2 (LCO) was firstly introduced by Goodenough,⁴ its commercial success led to the development and research studies of other metal oxides like LiNiO_2 (LNO), $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA), LiMnO_2 (LMO), $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ (NMO) and $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$ (NMC).² Among them, NMC materials have been under the spotlight because of its potential for high energy density applications in portable electronic devices as well as in the expanding market of electric vehicles.^{5,6} A determining factor in the electrochemical performance of LIB is the lithium insertion mechanism within the metal oxides of the positive electrode. In order to elucidate the internal processes of ion migration, diffusion as well as intercalation kinetics, physics-based models like the volume-averaged model^{7–10} and the single particle model¹¹ have been largely preferred. A physics-based model offers not only a better understanding of the internal processes; it also gives the possibility to optimize material properties or operating condition. Nevertheless, model parameterization and the choice of the physical parameters remain a big challenge. Due to the lack of experimental data or manufacturer's specification, most works rely on intrinsic transport and kinetic parameters from literature sources, or guessed values.

One reliable way to obtain and quantify the diffusional and charge transfer properties is to combine a physics-based model with experimental study like galvanostatic intermittent titration technique (GITT). To characterize porous electrode kinetics, different model techniques can be employed. For example, the use of GITT analytical theory¹² has been largely utilized.^{10,13–15} However, care must be taken with the assumption of uniform current distribution and the definition of the electrochemically active area.^{7,13} The single particle model, on the other hand, allows the investigation of the diffusion of lithium throughout the particle bulk but neglects the porosity of the particle agglomerate which consists of many primary particles.¹¹ A particular phenomenon reported in using GITT coupled with a physics-based model to study porous electrode is the long time constant during relaxation.^{9,16} GITT model studies of lithium manganese-rich NMC positive electrode from Dees et al.⁹ showed that the material did not relax to full equilibrium. The reason for that is the difference in the equilibrium potentials of the two active electrode components giving rise to a more dynamic (de)lithiation interaction.⁹ For $\text{LiNi}_{0.5044}\text{Co}_{0.1986}\text{Mn}_{0.2970}\text{O}_2$

(NMC523) material, Verma et al.¹³ proposed a model formulation for the active area for primary/secondary particle agglomerate materials to simulate GITT and half-cell performance. As were shown in these studies, the different physical behaviors exhibited by different electrode materials need to be captured by the model to accurately extract mass transport and kinetic parameters.

Although several modifications have been done to the physics-based models coupled with GITT, none of the modeling studies has, to our knowledge, included stresses in electrode materials. However, many authors have reported stress-related behavior acting on electrode particles. Particle-level strains may be induced by both external loads during production and internal electrochemical processes during cycling.¹⁷ During charging or discharging, lithium is removed (deintercalation) or inserted into (intercalation) the host lattices of the active material particles, causing lattice parameter variation, resulting in expansion or contraction of the particles.^{18,19} Such volumetric strains can also impose stresses on the surrounding active, filler or carbon particles.²⁰ During intercalation, LiMn_2O_4 gives a 6.5% volume change due to a change in lattice parameters.²¹ For NMC materials, lithium slab space increases with delithiation^{14,22} and the lattice parameter c is shown to increase by 1.5%;²³ whereas the lattice parameter c increases by 2.5% for LCO.²³ As a result, stresses arise in the electrode materials.^{17,21,24} An effect of stress generation is its influence on the electrochemical potential of the solid species participating in the electrode reaction, and thus on the open-circuit potential of an electrode,^{20,25–27} the lithiation and delithiation kinetics, and lithium transport. A further issue which has not been widely addressed is the dynamic evolution of stress-related (chemo)mechanical properties of electrode particles at different state-of-charge (SOC). Due to the scarcity of data available for complete mechanical characterization throughout a wide SOC range, stress behavior during battery cycling has been mostly investigated assuming constant mechanical properties, disregarding of the dependency on the lithium concentration.

In this study, a physics-based porous electrode stress model is developed to investigate the GITT potential responses of $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ (NMC111) during charging at the beginning of life (BOL). It is an extended pseudo-two-dimensional (P2D) model based on Newman et al.²⁸ to extract transport, kinetic, stress and thermodynamic properties across different electrode voltages and temperature. In particular, a stress proportionality factor which includes the electrochemo-mechanical properties is derived, stemming from tensile stress that occurs on the electrode particle surface due to volume change, impacting the free energy for lithium intercalation.²⁹

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Table I. NMC111 specifications.

Material	LiNi _{1/3} Mn _{1/3} Co _{1/3} O ₂ (NMC111)
Active material loading	94.2%
Formulation	94.2% active material, 3.2% Super P carbon, 2.6% SBR binder
Porosity	18%
Thickness	0.029 mm
Density	1 g cm ⁻³
Surface area (from BET on powder)	0.2 – 0.6 m ² g ⁻¹
D50	7 – 15 μm

The stress affects not only the equilibrium potential, but it also drives the lithium diffusion in the solid bulk. In this work, we focus on analyzing both the processes of polarization to the end of relaxation during a whole GITT transient and on examining the interfacial behavior responsible for the long times needed for NMC111 to relax to its equilibrium potential during GITT pulses. In contrast to the standard model based on the works on Newman et al.²⁸ which is unable to successfully model these slow relaxation phenomena for all operating conditions, the extended model incorporating stress effect fits the GITT transients. The objective is to show how the four fitting parameters, i.e. an intercalation diffusion coefficient, a reaction kinetic rate constant, the slope of the open-circuit potential (OCP) curve and a stress proportionality constant, can be used to describe the electrode kinetic performance of NMC111 over a voltage range from 3.7 to 4.1 V vs. Li/Li⁺ at 10°C, 25°C and 40°C.

Experimental

Materials.—All measurements were performed in a two-electrode pouch cell set-up, half-cell configuration (NMC111/Li metal). The separator was Whatman glass fibers microfilter, grade GF/A. The electrolyte was 1 M LiPF₆ in EC:DEC 1:1% in volume (BASF, Selectolyte LP40). All cells were assembled in an inert-atmosphere glove box (LC-1, LC Technology Solutions Inc.). NMC111 electrodes were purchased from ElectrodesandMore, and the specifications are reported in Table I. The electrodes were used as received. Figure 1 shows the scanning electron microscope (SEM) of pristine NMC111 (x3.0k magnification), collected by means of a Hitachi S-4800 tabletop SEM.

Electrochemical testing.—**Formation.**—The Li/NMC111 cells were cycled between +2.7 V and +4.3 V (vs. Li/Li⁺) in Constant Current (CC) – Constant Voltage (CV) mode for 4 cycles. 28 mA/g_{NMC} were applied for CC charge and discharge, and 14 mA/g_{NMC} was used as cutoff criterion during CV (at the end of charge only, i.e. +4.3 V). Formation was performed using either Solartron Analytical 1287A (Ametek) or Biologic multi-channel VMP-3 (BioLogic). The tem-

Figure 1. SEM of NMC111.

Porous electrode and separator level:

Figure 2. Schematic diagram of the pseudo-two-dimensional (P2D) model for the NMC positive electrode incorporating particle stress effects. The model has one dimension extending in the cross-cell direction and another *pseudo* dimension extending into the solid active material particles.

perature used was 25°C for all samples, controlled by means of a temperature chamber (Fricell 111 Comfort, MMM Lab).

GITT.—GITT was performed after formation. Two low-current pulses were used, namely +0.064 mA (8.15 mA g⁻¹_{NMC} or C/20) and +0.13 mA (16.6 mA g⁻¹_{NMC} or C/10). Between each pulse, relaxation was allowed for 3 and 2 hours respectively, to allow the potential to relax to its steady-state value. The pulses were repeated until the potential cutoff of +4.3 V (vs. Li/Li⁺) was reached. GITT measurements were performed in a temperature chamber at 10°C, 25°C and 40°C by means of a Solartron Analytical 1287A (Ametek).

Model Development

The porous electrode stress model is an extended *pseudo*-two-dimensional (P2D) physicochemical model based on Newman and Tiedemann.²⁸ The model is developed to fit each GITT charging response of the NMC111 porous electrode based on linearization of equilibrium potential around the initial lithium concentration before a low-current pulse of +0.064 mA is applied and the incorporation of particle stress effect. The P2D model, as depicted in Figure 2, has one dimension extending in the cross-cell direction between a lithium metal counter electrode and the positive current collector, and another *pseudo* dimension extending into the solid active material particles. At the 1D counter electrode-to-current collector level, two domains are used, representing the NMC porous composite electrode and the separator, with the metallic planar lithium counter electrode being represented by boundary condition at the outer separator boundary.

Concentrated solution theory is used to describe the ion transport through the electrolyte. The volume-averaged transport equations account for the porous electrode and separator. The governing equations and the corresponding boundary conditions are presented in Table II. The electrolyte mass and charge transport for concentrated binary electrolyte are described by Equation 1 and Equation 2. The current expressions in Equation 3 account for the overall charge balance. Equation 4 and Equation 5 describe the solid phase charge balance in the electronically conducting matrix. The *pseudo* dimension at the particle level describes the mass transport or solid lithium diffusion across the radius of spherical active material particles (Equation 6). The two dimensions are coupled at the surface of the intercalation particles through Butler-Volmer kinetics (Equation 7). The model takes into account the non-uniform current distribution across the electrode thickness and assumes that the active material is in single solid solution phase. The model input parameters are listed in Table III. The electrolyte properties were taken from the work of Lundgren et al.³⁰

The Newman-based model in Table II is extended to study the stress effect during charging based on the analogy between thermal expansion in solid mechanics and diffusion-induced stress (DIS).^{17,21,31–33} For stressed solids, the equilibrium interfacial potential depends on the entropy contribution, taking into account the concentration effect,

Table II. Newman-based model equations for lithium-NMC111 electrode.

Equations	Equation No.	Boundary conditions
Porous Electrode and Separator level:		
Electrolyte mass transport		
$\varepsilon \frac{\partial c_l}{\partial t} = \varepsilon^\beta \frac{\partial}{\partial x} \left(D_l \frac{\partial c_l}{\partial x} \right) - \frac{i_l t_+}{F} + \frac{a i_F}{F}$	[1]	$x = 0: \frac{\partial c_l}{\partial x} = 0 \quad x = L: \frac{\partial c_l}{\partial x} = 0$
Electrolyte charge transport		
$i_l = -\varepsilon^\beta \kappa \nabla \phi_l + \frac{2 \varepsilon^\beta \kappa R T}{F} \left(1 + \frac{\partial \ln f}{\partial \ln c_l} \right) (1 - t_+) \nabla \ln c_l$	[2]	$x = 0: \phi_l = 0 \quad x = L: i_l = 0$
$\nabla \cdot (i_l + i_s) = 0$	[3]	
Electronic charge transport		
$i_s = -\sigma \nabla \phi_s$	[4]	$x = L: i_s = C/20 \text{ (10 min)}; i_s = 0 \text{ (3 h)}$
$\nabla i_s = i_p \cdot a$	[5]	
Particle level:		
Bulk active material mass transport		
$\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{s,\text{eff}} r^2 \frac{\partial c_s}{\partial r} \right)$	[6]	$r = 0: \frac{\partial c_s}{\partial r} = 0 \quad r = R: \frac{\partial c_s}{\partial r} = -\frac{i_n}{F D_{s,\text{eff}}}$
$i_F = i_0 \left(\exp\left(\frac{\alpha_a F}{RT} \eta\right) - \exp\left(\frac{-\alpha_c F}{RT} \eta\right) \right)$	[7]	
$i_0 = F k (c_{s,\text{max}} - c_{s,s})^{\alpha_a} c_{s,s}^{\alpha_c} \left(\frac{c_l}{c_{\text{ref}}} \right)^{\alpha_a}$	[8]	
$\eta = \phi_s - \phi_l - E_{\text{eq}}$	[9]	

and on the stress experienced by the solid lattice,^{26,27} according to

$$E_{\text{eq}}(c_s, \sigma) = E_{\text{conc}} - \frac{\Delta \mu(\sigma)}{F} \quad [10]$$

where c_s is the solid lithium concentration. The first term on the right hand side, E_{conc} , denotes the equilibrium potential in the stress-free state, while the second term denotes the equilibrium potential change under stress, where $\Delta \mu(\sigma)$ is the change in chemical potential due to stress σ in the particle.

E_{conc} is given by the Nernst equation as

$$E_{\text{conc}} = E_{\text{ref}}^0 + \frac{RT}{F} \ln \frac{a_\theta}{a_{\text{Li}\theta}} \quad [11]$$

where E_{ref}^0 is constant, a_θ is the activity of vacancy in the lattice and $a_{\text{Li}\theta}$ is the activity of lithium in the lattice. During the seven GITT perturbations done in the range of 3.7–4.1 V vs Li/Li⁺ at each temperature of 10°C, 25°C and 40°C, a change in lithium activity and thus its concentration is induced, causing a shift in the equilibrium potential from each of the initial equilibrium potential E_0 . E_0 is obtained experimentally from GITT and used as the initial reference potential

Table III. Model input parameters.

Parameter	Symbol	Separator	NMC111
Thickness	l	250 μm (~195 μm when vacuumed) ^a	29 μm ^a
Electrolyte volume fraction	ε	0.9 ^a	0.18 ^a
Correction factor	β	3.44 ⁴⁶	1.5 ^b
Particle radius	r_p	-	0.5 ^b
Maximum theoretical lithium concentration	$c_{s,\text{max}}$	-	49000 mol/m ^{3b}
OCP proportionality factor	$dE_{\text{conc}}/dx_{\text{pos}}$	-	fitted
Stress proportionality factor	γ_{stress}	-	fitted
Electronic conductivity	σ	-	100 S/m ^b
Lithium diffusion coefficient	$D_{s,\text{eff}}$	-	fitted
Kinetic reaction rate constant	k	-	fitted
Charge transfer coefficient	α_a, α_c	-	0.5 ^b
Initial electrolyte concentration	$c_{l,t=0}$	1000 mol/m ^{3a}	1000 mol/m ^{3a}
Ionic conductivity	κ	10°C: $0.1073 c^3 - 1.890 c^{1.5} + 2.330 c$ S/m ³⁰ 25°C: $0.1147 c^3 - 2.238 c^{1.5} + 2.915 c$ S/m ³⁰ 40°C: $0.1149 c^3 - 2.648 c^{1.5} + 3.595 c$ S/m ³⁰	
Transference number	t_+	10°C: $-0.1247 c^3 + 0.3560 c^2 - 0.4297 c + 0.3027^{30}$ 25°C: $-0.1291 c^3 + 0.3517 c^2 - 0.4893 c + 0.4287^{30}$ 40°C: $-0.1263 c^3 + 0.3521 c^2 - 0.5009 c + 0.4521^{30}$	
Electrolyte salt diffusion coefficient	D_l	10°C: $7.186 \cdot 10^{-11} c^2 - 3.017 \cdot 10^{-10} c + 3.006 \cdot 10^{-10}$ m ² /s ³⁰ 25°C: $7.588 \cdot 10^{-11} c^2 - 3.036 \cdot 10^{-10} c + 3.654 \cdot 10^{-10}$ m ² /s ³⁰ 40°C: $8.371 \cdot 10^{-11} c^2 - 3.470 \cdot 10^{-10} c + 4.219 \cdot 10^{-10}$ m ² /s ³⁰	
Electrolyte salt activity coefficient	$1 + \frac{\partial \ln f}{\partial \ln c_l}$	10°C: $\frac{0.2285c^2 + 0.5196c + 0.4409}{0.1247c^3 - 0.3560c^2 + 0.4297c + 0.6973}^{30}$ 25°C: $\frac{0.2731c^2 + 0.6352c + 0.4577}{0.1291c^3 - 0.3517c^2 + 0.4893c + 0.5713}^{30}$ 40°C: $\frac{0.3209c^2 + 0.7617c + 0.4734}{0.1263c^3 - 0.3521c^2 + 0.5009c + 0.5479}^{30}$	

^ameasured value.

^bassumed value.

Figure 3. Experimental initial equilibrium potential E_0 in the stress and gradient-free state before a GITT perturbation at 10°C, 25°C and 40°C.

in a stress- and gradient-free state before each perturbation. Figure 3 shows the experimental E_0 plotted against the lithium fraction inside the active material, x_{pos} , each time before perturbation. x_{pos} is defined as $c_{s,s}/c_{s,max}$, where $c_{s,s}$ is the lithium concentration on the particle surface and $c_{s,max}$ is the maximum solid bulk concentration. The equilibrium potential which changes along the GITT transient in the stress-free state can then be described as

$$E_{conc} = E_0 + \frac{RT}{F} \ln \frac{x_{pos,0} - x_{pos}}{x_{pos}} \quad [12]$$

where $x_{pos,0}$ is the initial lithium fraction before the current pulse is applied corresponding to each E_0 . Assuming a substantially small change of E_{conc} with x_{pos} curve, the change in E_{conc} with x_{pos} can be linearized. Thus, Equation 12 is approximated as

$$E_{conc} \approx E_0 + \frac{dE_{conc}}{dx_{pos}} (x_{pos,0} - x_{pos}) \quad [13]$$

$$E_{conc} \approx E_0 + \frac{dE_{conc}}{dx_{pos}} \left[\frac{c_{s,s}(R, 0) - c_{s,s}(R, t)}{c_{s,max}} \right] \quad [14]$$

where dE_{conc}/dx_{pos} emulates the slope of the OCP curve. Note that dE_{conc}/dx_{pos} is a fitting parameter.

To derive the expression for σ , we consider the stress developed on the surface of a spherical particle of radius R which affects the free energy for lithium intercalation, as shown in Equation 10. The conventional stress-strain relationships in spherical coordinates,^{17,21,31,32} for the radial and tangential components, are

$$\epsilon_r = \frac{1}{E} (\sigma_r - 2\nu\sigma_\theta) + \frac{1}{3}\Omega c_s \quad [15]$$

$$\epsilon_\theta = \frac{1}{E} ((1 - \nu)\sigma_\theta - \nu\sigma_r) + \frac{1}{3}\Omega c_s \quad [16]$$

where ϵ_r , ϵ_θ , σ_r and σ_θ are the strains and stresses in the radial and tangential direction, E is the Young's modulus, ν is the Poisson's ratio and Ω the partial molar volume. A further assumption is that the elastic properties are constant for the small range of lithium concentration change during each GITT perturbation and relaxation. Due to spherical symmetry, the radial and tangential strains, in the infinitesimal

formulation of deformation are given by

$$\epsilon_r = \frac{du}{dr} \epsilon_\theta = \frac{u}{r} \quad [17]$$

where u is the radial displacement. Since species diffusion in solids is a much slower process than the rate of elastic deformation, mechanical equilibrium is treated as a static equilibrium problem.^{21,34} The equation for static mechanical equilibrium in the bulk of a sphere is given by

$$\frac{d\sigma_r}{dr} + 2\frac{\sigma_r - \sigma_\theta}{r} = 0 \quad [18]$$

Combining the four equations above with the condition of the stress to remain finite at $r = 0$ results in the following expressions for the tangential stress³³

$$\sigma_\theta(r, t) = \frac{E\Omega}{9(1-\nu)} [2c_{s,ave}(R, t) + c_{s,ave}(r, t) - 3c_s(r, t)] \quad [19]$$

where $c_{s,ave}(r)$ is the average concentration in the spherical volume of radius r within the particle of radius R , defined as:

$$c_{s,ave}(r, t) = \frac{3}{R^3} \int_0^R r^2 c_s(r, t) dr \quad [20]$$

The radial stress $\sigma_r(R)$ is zero following the conventional boundary condition at free surfaces.^{17,21,31,32} The tangential stress on the particle surface, $r = R$, takes the form

$$\sigma_\theta(R, t) = \frac{E\Omega}{3(1-\nu)} [c_{s,ave}(R, t) - c_s(R, t)] \quad [21]$$

The stress-dependent shift in chemical potential is expressed as

$$\Delta\mu(\sigma) = \sigma_\theta(R, t) \cdot \Omega = \frac{E\Omega^2}{3(1-\nu)} [c_{s,ave}(R, t) - c_s(R, t)] \quad [22]$$

As the Ω and solid-mechanics parameters (E and ν) are assumed to be constant over each GITT pulse and the concentration difference $c_{s,ave}(t) - c_{s,s}(t)$ is normalized by the maximum bulk concentration $c_{s,max}$, the second term in Equation 10 results in

$$\frac{\Delta\mu(\sigma)}{F} = \gamma_{stress} \left[\frac{c_{s,ave}(R, t) - c_{s,s}(R, t)}{c_{s,max}} \right] \quad [23]$$

where the stress proportionality factor $\gamma_{stress} = \frac{E\Omega^2}{3(1-\nu)} \cdot \frac{c_{s,max}}{F}$ includes the electrochemo-mechanical properties and is a fitting parameter.

The modified equilibrium potential for a solid active material under stress, E_{eq} , in Equation 10 during each GITT transient now takes the form

$$E_{eq}(c_s, \sigma) = E_0 + \frac{dE_{conc}}{dx_{pos}} \left[\frac{c_{s,0} - c_{s,s}}{c_{s,max}} \right] - \gamma_{stress} \left[\frac{c_{s,ave} - c_{s,s}}{c_{s,max}} \right] \quad [24]$$

with $c_{s,0} = c_{s,s}(R, 0)$. Hence, E_{eq} does not only take into account the contribution of the local concentration changes on the particle surface but also the average concentration changes of the particle. At the same time, it depends on the thermodynamic as well as the electrochemo-mechanical properties. As lithium is being removed from the particle during the GITT charging process, the tangential stress is tensile at the particle surface (positive by definition). Therefore, the E_{eq} is expected to be reduced under the effect of tensile stress.³⁵

Stress interacts with diffusion in a two-way coupling in which diffusion induces stress (DIS), which in turn affects diffusion (stress-enhanced diffusion).^{17,21,31–33,36} In this study, the fitted effective intercalation diffusion coefficient $D_{s,eff}$ described by the Fick's second law in Equation 6 includes the impact of gradients of stress as a driving force for diffusion inside the particle:

$$D_{s,eff} \approx \frac{DF}{RT} \left(\frac{dE_{conc}}{dx_{pos}} + \frac{2}{3}\gamma_{stress} \right) \quad [25]$$

Equation 25 is taken from the derivation of a Fickian-type flux equation based on the coupling of concentration and stress presented in Appendix. The $D_{s,eff}$ is assumed constant inside the particle as the particle concentration and stress gradients are not expected to change

significantly. As shown in Equations 24 and 25, the stress impacts both the solid lithium transport and on the insertion kinetics on the particle surface.

The number of parameters extracted by fitting the GITT transients are kept as few as possible to restrict the number of degrees of freedoms. In particular, four parameters are being optimized: the intercalation diffusion coefficient $D_{s,\text{eff}}$, the kinetic rate constant for the electrochemical reaction k , the slope of the OCP curve $dE_{\text{conc}}/dx_{\text{pos}}$ and the stress proportionality factor γ_{stress} . All four parameters are determined for one full GITT transient, i.e. from the start of applying a polarization to the end of the relaxation.

The coupled time-dependent non-linear partial differential equations are solved in COMSOL Multiphysics 5.3.1 and parameter estimation is carried out using the Levenberg-Marquardt optimization solver. The simulated potential response was fitted to the experimental galvanostatic pulses in the GITT experiments. Model optimization and parameterization are carried out by employing the least square fitting method, i.e. by minimizing the following function χ :

$$\chi^2(\alpha) = \min \sum \left[\left(\frac{\varphi_{s,\text{exp}} - \varphi_{s,\text{sim}}(\alpha)}{\varphi_{s,\text{exp}}} \right)^2 \right] \quad [26]$$

where α represents the fitting parameters, $\varphi_{s,\text{exp}}$ and $\varphi_{s,\text{sim}}$ are the experimental and simulated electrode potential values.

Results and Discussion

Figure 4 shows examples of typical GITT potential responses. At 0 min, i.e. as soon as a low-current pulse of +0.064 mA (C/20) is applied, a potential jump can be seen which is then followed by a slower potential increase. The instantaneous response of the potential corresponds to the ohmic drop of the cell, and at this time-scale the initial polarization. Thereafter, the ten-minute non-instantaneous response of potential increase indicates the process as lithium is being extracted from the electrode, slowly building up a concentration gradient in the electrolyte as well as within the solid bulk particles. When the applied current is interrupted after 10 min, the cell is allowed to relax back to the equilibrium condition (OCP), thus the potential decays gradually, corresponding to the relaxation of the concentration gradients. The slowly changing voltage is caused by the slow diffusion processes in the cell. During this process, the concentration of lithium within the particles is gradually redistributed until the concentration of lithium becomes uniform and reaches an equilibrium state.

Firstly we compare the fitted experimental GITT potential response with both the standard Newman porous electrode model²⁸ and the extended model. One example of the comparison for a GITT pulse at around 3.73 V and 3.91 V at 25°C is shown in Figures 4a and 4b. Referring to the example for the GITT transient curve fits at 3.73 V in Figure 4a, both the standard and the extended models are able to fit the GITT experimental data well. However, at a higher voltage of 3.91 V in Figure 4b, discrepancies can be clearly seen between the two models. As can be seen, the slow relaxation behavior right after the pulse is stopped cannot be captured properly by the standard Newman model. The reason for this is that the lithium concentration gradient relaxes too quickly. Thus, there is a need to use an extended model for the fitting of the GITT curves. As shown in both Figures 4a and 4b, both the potential curves can be fitted relatively well with the extended model, justifying the need of including an additional parameter to compare the intercalation behavior during polarization and relaxation for the wide range of voltage studied here.

Figure 5 shows every fitted GITT potential experimental response at 10°C, 25°C and 40°C. All the GITT curves have been fitted with the same extended stress model to create a consistent and comparable parameter set. Hence, the capability of describing and comparing the same physical processes can be carried out at every electrode potential with a uniform set of four physical parameters ($D_{s,\text{eff}}$, k , $dE_{\text{conc}}/dx_{\text{pos}}$, γ_{stress}). The extended model fits the experimental data well at all potentials and temperatures. For all three temperatures, the behavior of a slow relaxation has been observed, predominantly at higher poten-

Figure 4. GITT experimental and fitted potential response data with the standard and the extended porous electrode stress model at around (a) 3.73 V vs Li/Li⁺ and (b) 3.91 V vs Li/Li⁺ for a low-current pulse of +0.064 mA (C/20) at 25°C.

tials. The slow relaxation behavior in NMC111 is very similar to the GITT voltage relaxation profiles reported by Dees et al.⁹ for a blended electrode due to the active material's multiphase region. However, NMC111 behaves as an ideal solid solution in the standard operating voltage window³⁷ and is therefore not expected to exhibit such multiphase behavior. For higher temperatures in combination with higher voltages, the occurrence of the slow relaxation to equilibrium potentials during the three-hour open-circuit stand becomes more apparent. The model predicts that the relaxation to the equilibrium potential can take much longer than the allocated three hours in this work, especially when the potentials are higher. The long-term relaxation process

Figure 5. Experimental and fitted GITT potential responses with the extended porous electrode model for each electrode potential from ~ 3.70 to 4.05 V vs Li/Li^+ at a low-current pulse of $+0.064$ mA ($C/20$) at (a) 10°C , (b) 25°C and (c) 40°C .

during open-circuit stand is in alignment with the findings by Gerschler et al.³⁸ where they measured the OCP for up to 100 hours. The observed behavior that the voltage equalizes slower at higher temperatures is also in agreement with their work.³⁸ While it is common to carry out OCP measurements before any battery cell testing, allowing the cell to rest for up to tens or hundreds of hours at each potential cutoff is exhaustive and seldom done. However, these results indicate that one may have to wait long times in order to be sure that the voltage equilibrium is reached, particularly when the potential or temperature is higher.

In our extended model, we consider solely the effect caused by the nature of NMC111 material and exclude any side reactions that might occur. Factors such as the degradation effects at higher temperature, potentials, and the influence of counter electrode are neglected. In the experiments, the GITT potential responses of the NMC111 electrode were measured versus a lithium metal electrode, acting both acts as counter and reference electrode. We are aware that for this setup there may occur relaxation phenomena stemming from the lithium counter electrode.^{7,11} However, contributions from the counter electrode to the relaxation of the measured potential do not seem likely in this study, since such response behavior should have been seen for all potentials, and not only for certain potentials which we observed here. It is further considered unlikely that the slower relaxation detected at higher potentials, between approximately 3.8 V and 4 V stems from increased side reactions as the electrode potentials still remains relatively low.

Along the GITT potential responses, the polarization and relaxation dynamics involve two mechanisms at two levels simultaneously: a) the inter-particle kinetic lithium exchange to reach a common equilibrium potential at the NMC particle surfaces and b) the intra-particle lithium diffusion to flatten out the concentration gradients. The processes of polarization and equilibration are described by the effective solid lithium transport ($D_{s,eff}$), electrochemical kinetic rate (k), material thermodynamic (dE_{conc}/dx_{pos}) and surface stress (γ_{stress}) parameters. These parameters are extracted and investigated across the voltage range at different temperatures. Figures 6a and 6b show the $D_{s,eff}$ and D as a function of potentials at 10°C, 25°C and 40°C. From Equation 25, the approximation of the lithium diffusion coefficient D can be obtained. As can be seen in Figure 6, $D_{s,eff}$ and D are generally higher when lithium fraction $x_{pos} \approx 0.94$ to $x_{pos} \approx 0.85$ or in the potential region of ~ 3.70 V to 3.75 V during initial state of charging. They decrease thereafter when the charging proceeds. As lithium is further depleted from $x_{pos} \approx 0.80$ onwards or when the potential continues increasing from ~ 3.76 V, $D_{s,eff}$ appears to be quite steady at a value of $\sim 10^{-14}$ cm²/s as seen in Figure 6a. As shown in Figure 6b, D continues decreasing when lithium is further depleted from $x_{pos} \approx 0.80$ onwards. Faster diffusion at lower potentials leads to a relatively faster voltage relaxation, which can be seen in Figure 4 and Figure 5. As the potential increases, the diffusion becomes slower, which contributes to the slower voltage relaxation discussed earlier. In our model, the lithium transport is governed by gradients of the chemical potential gradient, i.e. gradients in the concentration as well as the mechanical stress. Hence, $D_{s,eff}$ not only depends on T and SOC but also on the chemo-mechanical properties.³⁹ Slower diffusion indicates influence from higher Young's Modulus E and/or partial molar volume Ω , particularly for GITT at higher voltages. From Figure 6b, D represents the diffusivity driven by the concentration gradient, but dismissing the stress effect. The dependence of D with x_{pos} is larger across the delithiation process compared to $D_{s,eff}$, implying that stress becomes more apparent at higher voltages, enhancing the lithium transport. $D_{s,eff}$ varies minimally with temperature, which agrees to Cui et al.¹⁴ showing less than an order of magnitude change across a vast range of temperatures. We note that although it is more common to report a tendency of faster diffusion with increasing temperature,^{14,40} the opposite behavior of slightly lower $D_{s,eff}$ at higher temperatures is not previously unreported in scientific literature.¹⁵ Overall, $D_{s,eff}$ at these three temperatures expanding across a voltage window of operation from 3.7–4.1 V vary within the order of magnitude of around 10^{-14} – 10^{-13} cm²/s.

Figure 6. (a) Effective intercalation diffusion coefficients $D_{s,eff}$ extracted from the GITT potential response fittings with the extended model and (b) intercalation diffusion coefficients D calculated from Equation 26 as a function of lithium fraction x_{pos} at 10°C, 25°C and 40°C.

A comparison of the $D_{s,eff}$ obtained for NMC111 electrode from several literature sources^{11,14,15,41–43} shows a large spread of orders of magnitude, such as $\sim 10^{-17}$ – 10^{-13} cm²/s (EIS),⁴³ $\sim 10^{-12}$ cm²/s (GITT),¹⁴ $\sim 10^{-12}$ – 10^{-10} cm²/s (open-circuit relaxation),¹¹ $\sim 10^{-11}$ – 10^{-10} cm²/s (CV)⁴² and 10^{-10} – 10^{-9} cm²/s (EIS and GITT).¹⁵ This could be attributed to a lot of reasons, among them are the different type of experimental and/or techniques and quantitative means of investigating the solid-phase diffusion. Besides, computation of diffusivity also depends on the assumed diffusion length l . Most work relies on the assumption of diffusion occurring in the secondary particles,^{11,14,42} while we assume it to be in the primary particles, whereas others adopted the electrode thickness⁴¹ as characteristic length. The assumption of adopting primary particles is based on the fact that the primary particles are well separated from each other and do not appear to form dense agglomerates, as shown in the SEM image in Figure 1. Due to the different scale of diffusion lengths involved, a comparison using the characteristic diffusion time constant τ would be more reliable and meaningful. In this study, τ lies around $2.5 \cdot 10^4$ – $2.5 \cdot 10^5$ s. This is similar to $\sim 2.5 \cdot 10^5$ s in the work of Cui et al.¹⁴ who used analytical model for the GITT data but lower than $2.25 \cdot 10^2$ – $2.25 \cdot 10^4$ s in the work of Wu et al.¹¹ who adopted single particle model to describe open circuit relaxation. Apart from the choice of diffusion length, another concern lies in how the parameterization in each study is done. Having that said, direct comparison of either the $D_{s,eff}$ or time constant extracted using different techniques can be rendered meaningless if one does not

Figure 7. Electrochemical kinetic rate constants k as a function of lithium fraction x_{pos} extracted from the GITT potential response fittings with the extended model at 10°C, 25°C and 40°C.

make clear of the underlying model assumptions and limitations. The main distinction of our model with the other models is the coupling of a porous electrode model to analyze the physical phenomena at the electrode and particle levels. Besides, the whole GITT pulse, i.e. from polarization to relaxation, is being fitted by the developed model so that both the electrochemical reaction and diffusion are accounted for simultaneously.

The fitted electrochemical kinetic rate constant k from the model in Figure 7 shows a continuous increase as x_{pos} decreases from 0.95 to 0.55 (or as potential increases from 3.7 V to 4.1 V), resulting from a lower activation energy barrier for the lithium deintercalation reaction as the charging process proceeds. As temperature increases from 10°C to 25°C and 40°C, the kinetic rate constants gradually increases. The data are fitted to a polynomial equation (Equation 27) using temperature-independent coefficients.

$$\log k = A_3 x_{pos}^3 + A_2 x_{pos}^2 + A_1 x_{pos} + A_0 \quad [27]$$

The fitted isothermal polynomial equations are shown in black line in Figure 7 and the coefficients for the polynomial fit in Table IV. The activation energies obtained through the Arrhenius equation $k = C \exp(-E_a/RT)$ where C is a constant shows an increase of E_a by a factor of around 30% when x_{pos} drops from ~0.95 to ~0.55.

Figures 8a and 8b show how dE_{conc}/dx_{pos} and Y_{stress} develop with x_{pos} . Both parameters are fitted here as a local average quantity to approximate the extent of the equilibrium potential variation with the particle lithium concentration. dE_{conc}/dx_{pos} remains relatively low from around 0.2 to 0.6 for $x_{pos} = 0.95$ to $x_{pos} = 0.73$ or at voltages 3.70 V to ~3.79 V. As charging continues, dE_{conc}/dx_{pos} increases significantly. Almost similar values can be seen for temperatures 10°C, 25°C and 40°C, indicating that we would expect similar SOC dependencies of

Figure 8. (a) Gradient of the OCP curve dE_{conc}/dx_{pos} and (b) stress proportionality factor Y_{stress} as a function of lithium fraction x_{pos} extracted from the GITT potential response fittings with the extended model at 10°C, 25°C and 40°C.

the OCP curves for the three temperatures. Y_{stress} is from around 0 to 0.5 for $x_{pos} = 0.95$ to 0.73 or at voltages 3.70 V to ~3.79 V. As charging proceeds further from 3.80 V, Y_{stress} increases rapidly. Y_{stress} at 25°C and 40°C are quite comparable whereas it appears to be lower for 10°C. As Y_{stress} is coupled to the electrochemo-mechanical properties, larger values which can be seen at higher voltages imply an increase of the stiffness of the material, or increased expansion upon lithium intercalation-deintercalation, thus contributing to the buildup of surface stress on the NMC particle. Stress has been associated with solid particle volume change which is linked to variation in lattice parameters. Therefore, the increase in stress-related properties could be influenced by an increase in (001) plane distance, which is the total thickness of transition metal oxide slab and the lithium slab space in the bulk, during delithiation, as being reported from an XRD analysis.¹⁴ The change of Y_{stress} with potentials is especially important to be noted, as most literature^{17,21,34} assumes constant solid mechanics properties when modeling particle-level stresses. For example, stress evolution depending on the lithiation rate⁴⁴ and a dramatic change of Young's modulus in layered structures with the degree of lithiation has been reported.⁴⁵ From the expression for Y_{stress} , one can presume an increase in the Young's modulus or/and partial molar volume of the guest lithium with potential increase. From Figure 8, one can conclude that the thermodynamic and mechanical stress effects are more SOC-dependent than temperature-dependent.

Table IV. Optimized coefficients for kinetic coefficient polynomial in Equation 27.

$T/^\circ\text{C}$	$A1 / \text{ms}^{-1}$	$A2 / \text{ms}^{-1}$	$A3 / \text{ms}^{-1}$	$A4 / \text{ms}^{-1}$
10	-8.0	15.9	11.4	-9.2
25	-22.8	61.7	-58.0	6.8
40	-45.3	114.9	-100.2	18.3

Figure 9. Temporal variation of electrode potential change response (ΔE_s), potential differences due to diffusion and stress (ΔE_{conc} and ΔE_{stress}), and activation overpotential (η_{act}) at the positive current collector, i.e. $x = L_s$, at (a) ~ 3.73 V (10°C), (b) ~ 3.83 V (10°C), (c) ~ 3.91 V (10°C), (d) ~ 3.73 V (25°C), (e) ~ 3.83 V (25°C), (f) ~ 3.91 V (25°C), (g) ~ 3.73 V (40°C), (h) ~ 3.83 V (40°C) and (i) ~ 3.91 V (40°C).

Figure 9 shows the temporal variation of the fitted electrode potential response ΔE_s , the potential changes due to diffusion and stress, ΔE_{conc} and ΔE_{stress} , and reaction overpotential η , at ~ 3.73 V, ~ 3.83 V and ~ 3.91 V for 10°C , 25°C and 40°C . ΔE_{conc} minus ΔE_{stress} equals the total change in the equilibrium potential $\Delta E_{eq}(c_s, \sigma)$ from which the system is perturbed during the GITT pulse. For different electrode voltages or temperatures, the performance limiting mechanism varies. In the case of low electrode voltage and low temperature, there is no to little stress contribution; the large overpotential is mainly dominated by the equal contribution from the activation overpotential and diffusion. As the temperature or the voltage increases, diffusion limitation and a prominent contribution from the particle stress term can be seen. At higher electrode potentials, the lower diffusivity and the higher SOC-dependent thermodynamic or stress factor (dE_{conc}/dx_{pos} or γ_{stress}) are responsible for the lithium transport limitation, while the activation overpotential decreases due to better reaction kinetics (higher k). The contribution from stress ΔE_{stress} is slightly lower than the pure diffusive process ΔE_{conc} . However, both ΔE_{conc} and ΔE_{stress} contribute to the polarization and slow potential relaxation seen during GITT. As temperature increases, the overpotential becomes more dominated by diffusion and stress. Better kinetics at higher temperature reduces the activation overpotential. Slightly poorer diffusion at higher temperature increases ΔE_{conc} . However, the stress term ΔE_{stress} that increases with temperature drives diffusion, contributing to the overall lower overpotential during polarization. During the relaxation process, due to slow diffusion, the buildup of large concentration gradients in both ΔE_{conc} and ΔE_{stress} requires more time to subside. In a nutshell, as electrode voltage and temperature increases, electrode performance is mainly limited by slow lithium transport. The effect of SOC on the lithium transport limitation is much more apparent than the temperature effect.

The combination of diffusivity, kinetics, thermodynamic and stress factor has an impact on the lithium concentration distribution that af-

fects the speed of the relaxation process during GITT. As a result of slower interfacial kinetics and non-limiting diffusive behavior at lower potentials, lithium distribution in the spherical particle is smoother, leading to faster relaxation during open circuit. As electrode voltage increases, steeper concentration gradient arises due to the increasing limitation due to diffusion and stress. This leads to the aforementioned longer time constant for the relaxation process. To further illustrate the effect of the physical parameters on the different distribution of lithium, the spatial lithium concentration within the NMC particle is compared in Figure 10 at ~ 3.73 V and ~ 3.91 V, each at 25°C and 40°C respectively. The particle radius is normalized and the lithium concentration is normalized to the corresponding initial concentration. During charging (de-intercalation) in the first ten minutes, the lithium distribution gradually builds up, forming a gradient which drives the lithium transport along the particle radius from the center to the surface. The lithium concentration at the surface corresponds to the potential response of the electrode obtained from the GITT. Figures 10a and 10c show that the lithium concentration distribution at ~ 3.73 V is more homogenous with smaller gradient near the surface as a result of the good diffusive behavior. At ~ 3.9 V, the diffusion occurs only in the particle's near-surface region during the 10-min charging as a result of slow diffusivity and increased stress properties (higher γ_{stress}), leading to steeper concentration gradients build up near the surface, as seen in Figures 10b and 10d. Consequently, the removal of the steep concentration gradients during GITT relaxation after which the current is interrupted takes a longer time.

Conclusions

A *pseudo*-two-dimensional porous electrode model incorporating a particle surface stress proportionality factor is developed. The equilibrium potential is based on linearization of the potential around the initial lithium concentration in a stress- and gradient-free state and

Figure 10. Simulated lithium concentration along the radius of the NMC particle in the middle position of the electrode ($X = L_{\text{sep}} + 0.5 L_{\text{pos}}$) at (a) ~ 3.73 V at 25°C , (b) ~ 3.90 V at 25°C , (c) ~ 3.73 V at 40°C and (d) ~ 3.90 V at 40°C during 10-min polarization and relaxation thereafter. The lithium concentration is normalized by the corresponding initial lithium concentration before which the pulse is being applied.

the chemical potential change due to stress experienced by the solid lattice. The stress affects not only the equilibrium potential, but it also drives the lithium diffusion in the solid bulk. As the Newman-based standard model fails to describe sufficiently the dynamic performance of NMC111, the extended model with stress effect proves to be an improved version in successfully fitting the processes of polarization to the end of relaxation during a whole GITT transient. The GITT potential response curves are fitted well for NMC111 over a voltage range of 3.7–4.1 V vs Li/Li⁺ at 10°C , 25°C and 40°C . Across the voltage range, $D_{s,\text{eff}}$ varies within an order of magnitude at around 10^{-14} – 10^{-13} cm²/s. The strong dependency of the extracted k , $dE_{\text{conc}}/dx_{\text{pos}}$ and γ_{stress} with lithium fraction suggests the necessity of using varying kinetic, thermodynamic and electrochemo-mechanical properties to study intercalation materials. The fitting procedure shows minimal variance of $D_{s,\text{eff}}$ and $dE_{\text{conc}}/dx_{\text{pos}}$ with temperature. From the model, low stress contribution is observed at low electrode voltage and low temperature; the overpotential dominated by the equal contribution from the activation overpotential and diffusion. As the temperature or/and the voltage increases, the limitation from the diffusion and particle surface stress are profound. The lithium transport behavior in solid NMC bulk as a result of the combined physical intercalation properties is further analyzed and compared. At higher potentials, a large lithium concentration gradient requires long relaxation time during GITT; at lower potentials, the lithium distribution is more homogenous leading to faster relaxation. The slow relaxation phenomenon is more prominent at higher temperatures. Therefore, this gives the cautious note that longer time could be needed to reach the equilibrium state at higher potentials and higher temperatures, which is particularly useful when doing measurements for the OCP curve. The generality of the derived stress proportionality factor in this model offers the possibility to be applied in other variants of NMC or insertion electrodes. It also serves as a groundwork for solid mechanics' analysis of stress during battery cycling to study electrode durability.

List of Symbols

a	Specific interfacial area ($a = 3\varepsilon_s/r_p$)
c_l	Electrolyte salt concentration
c_{ref}	Electrolyte reference concentration
c_s	Lithium concentration in bulk active material
$c_{s,s}$	Lithium concentration at particle surface
$c_{s,\text{max}}$	Maximum lithium concentration
D_l	Salt diffusion coefficient in electrolyte
$D_{s,\text{eff}}$	Effective lithium diffusion coefficient in bulk active material
E_{eq}	Equilibrium potential
$1 + \partial \ln f / \partial \ln c_l$	Electrolyte salt activity coefficient
F	Faraday's constant
i_F	Faradaic current density
i_l	Electrolyte current density
i_s	Electronic current density
i_0	Kinetic exchange current density
k	Kinetic reaction rate constant
L_{pos}	Thickness of the positive electrode
L_{sep}	Thickness of the separator
r	Radial coordinate
R	Universal gas constant
r_p	Particle radius
t_+	Transference number of Li ⁺
T	Temperature
x	Cell coordinate

Greek

α_a, α_c	Reaction transfer coefficients (a:anode, c:cathode)
σ	Electronic conductivity
ε	Electrolyte volume fraction
β	Bruggeman correction factor

κ	Ionic conductivity
η	Electrochemical reaction overpotential
φ_l	Electrolyte potential
φ_s	Potential of electronically conducting phase
τ	Diffusion time constant

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Appendix

Intercalation-induced stress influences the intercalation process itself. This is incorporated into the diffusion equation based on the description of linear thermodynamics of irreversible processes. The chemical potential gradient $\nabla \mu$ acts as a driving force for the lithium movement

$$J = -Mc_s \nabla \mu(c_s, \sigma) \quad [A1]$$

where J describes the flux of lithium ions, M the lithium mobility in the solid particle and μ is the chemical potential lithium in the active particle.

The chemical potential in the solid solution μ depends on both the lithium concentration and the stress experienced by solid lattice

$$\mu(c_s, \sigma) = \mu(c_s, 0) - \Omega \sigma \quad [A2]$$

where $\mu(c_s, 0)$ denotes the chemical potential in the stress-free state. By substituting Equation A2 into Equation A1, the flux can be written as³⁶

$$J = -Mc_s \left(\frac{\partial \mu}{\partial c_s} \nabla c_s - \Omega \nabla \sigma \right) \quad [A3]$$

Describing the term $\partial \mu / \partial c_s$ in terms of the equilibrium potential on the OCP profile gives

$$J \approx \frac{D}{RT} \left(\frac{dE_{conc}}{dx_{pos}} F \nabla c_s + \Omega c_{s,max} \nabla \sigma \right) \quad [A4]$$

where $D = MRT$ is the lithium diffusion coefficient in bulk active material.

The stress tensor contains two components, namely the radial stress σ_r and the tangential stress σ_θ . $\sigma_\theta(r, t)$ is given by Equation 21, whereas $\sigma_r(r, t)$ is defined as

$$\sigma_r(r, t) = \frac{2E\Omega}{3(1-\nu)} \left[\frac{1}{3} c_{s,ave}(R, t) - \frac{1}{3} c_{s,ave}(r, t) \right] \quad [A5]$$

Equations 21 and A5 allow the calculation of σ (hydrostatic stress) as

$$\sigma(r, t) = \frac{(\sigma_r(r, t) + 2\sigma_\theta(r, t))}{3} = \frac{2E\Omega}{9(1-\nu)} [c_{s,ave}(R, t) - c_s(r, t)] \quad [A6]$$

Combining Equations A4, A5 and the previously defined γ_{stress} , the flux takes the form

$$J \approx D_{s,eff} \nabla c \approx \frac{DF}{RT} \left(\frac{dE_{conc}}{dx_{pos}} + \frac{2}{3} \gamma_{stress} \right) \nabla c \quad [A7]$$

as the governing equation for the flux for the diffusion process where the effective solid diffusion coefficient $D_{s,eff}$ accounts for stress-induced transport. As can be seen in Equation A7, the coupling between the concentration and stress yields Fickian-type transport equation in which the flux is proportional to the concentration gradient.

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