Abstract

Differential voltage analysis (DVA) is a conventional approach for estimating capacity degradation in batteries. During charging, a graphite electrode goes through several phase transitions observed as plateaus in the voltage response. The transitions between these plateaus emerge as observable peaks in the differential voltage. The DVA method utilizes these peaks for estimating batteries capacity. Unfortunately, at higher C-rates (above C/2) the peaks flatten, and their locations become unobservable. In this work, we show that, unlike the differential voltage, the peaks in the expansion response of lithium-ion batteries remain observable up to 1C and this makes differential expansion an excellent method for capacity estimation at these charging rates. To understand why that is the case, we have developed an electrochemical and expansion model suitable for model-based estimation. In particular, we demonstrate that single particle models are not able to capture the peak smoothing effect, therefore we augment these models by considering a particle size distribution for the graphite electrode. We then identify the model parameters using experimental data from a graphite/NMC pouch cell. Our model produces an excellent fit for the observed electric and mechanical swelling response of the cells and also captures the smoothing effect of voltage at different charging rates.

1. Introduction

Lithium ion (Li-ion) batteries have been widely adopted in the consumer electronics market and projections for the number of battery electric vehicles (BEV) indicate a drastic increase in the near future. Consumer preference motivates development of technologies that support fast charging of these devices. Although fast charging is very desirable and perhaps necessary for adoption of electric vehicles, the accelerated degradation of the lithium-ion battery is a major downside. Therefore, to protect against cell failures and for safety and reliability of BEVs with fast charging, it is essential to track the degradation state of the cells.

In state-of-the-art battery management systems, the State of Health (SOH) of the battery is measured by estimating remaining capacity and the ohmic resistance of the cell. There are a number of degradation mechanisms [1] that are responsible for the capacity loss and resistance growth. Thus, it is also advantageous to have more information about the internal state of a degraded cell, especially in cases of fast charging that
can induce accelerated degradation. For example, it has been shown that without knowledge of the internal state of the cell we could operate the cell blindly with respect to lithium plating, even in cases of moderate capacity fade [2]. Many studies have been done estimating the degradation mechanisms [3, 4, 5, 6, 2, 7] using voltage, using the differential voltage and phase transitions [8], and most recently using cell swelling in addition to voltage [9]. A requirement of all these methods is that data needs to come from the open circuit (OC) state or pseudo-OC state, which is gathering data while (dis)charging at a very low rate. This is a major limitation in practice because a slow charge from a high depth of discharge is not possible in many applications (e.g. plug-in hybrid electric vehicles), and inconvenient for consumers in most cases. In [10], the estimability of electrode parameters are also studied with respect to limited operating windows. In [9] we have already shown that we can greatly reduce the requirement of high depth of discharge by incorporating cell swelling data into the estimation. Note, however, that this method still relies on open circuit measurements.

Ideally we want to be able to do the same kind of estimation as above during normal and especially fast charging. To this end, one of the candidates for a diagnostic algorithm is an extension of the peak alignment method [8]. In that method, using a pseudo-OCV data, the distance between two observable peaks in the differential voltage (refer to Fig. 1) is used to estimate the negative (graphite) electrode’s operating window and capacity. These peaks are the result of the phase transitions in the graphite at specific lithiation states, and it is in fact the study of these states that enables the estimation. As can be seen in Fig. 1, as the C-rate increases there is an appreciable shift in the location and reduction of height for these peaks. Furthermore, at 1C the peaks are effectively flattened and are unobservable. The same analysis in Fig. 1 is done for the cell expansion. The peaks in the second differential of the expansion correspond to the same peaks in the differential voltage [11], since they also result from the same phase transitions in the graphite. Therefore, in principle, we can apply that same method of peak alignment using the peaks in the second derivative of expansion. Moreover, there are some advantages in using expansion, namely, as it can be seen from Fig. 1, the second peak remains observable up to 1C, which is important for application of this method at fast charging rates. We should also note that in spite of these benefits, there are still challenges to instrumenting cell expansion sensors in battery packs. However, recent developments in new thin film sensors [12] show a potential to overcome some of these challenges for future battery pack designs.

To understand the above electrical and mechanical response, and ultimately extend the peak alignment method to dynamic charging rates, it is necessary to develop a mathematical model. Phenomenological voltage and mechanical models for batteries have been developed previously [13, 14], usually by applying equivalent circuit models (ECM). However, it can be shown that ECMs are unable to capture the smoothing effect in the voltage response. Hence, higher fidelity models are needed in this case. One approach is a physics-based model. Such models provide a deeper understanding into the mechanical-chemical processes inside the cell. There are number of electro-mechanical-chemical models developed for batteries [15, 16, 17]. However, most of these model are too complex to be useful for creating model-based estimators, mainly because of
their high computation cost, therefore, simplified electrochemical models, such as the single particle model (SPM) [18] and the single particle model with electrolyte (SPMe) are used instead [19, 20]. Unfortunately, the SPMe is not able to capture the smoothing dynamics of differential voltage at high charging rates.

In Section 2 of this paper, an extension to SPMe is developed by considering a particle size distribution for the negative electrode. Note that the inclusion of a particle size distribution for the positive electrode has been proposed before in [21] to improve the voltage fit at higher rates. However, the goal here is to not only match the voltage response, but to study the differential voltage. Second, a mechanical model is also proposed and it is based on lattice/particle expansion. A lumped energy balance is also considered to model the temperature rise and resultant thermal expansion of the cell. Section 3 describes the experimental method. The model is verified using experimental data at different charging rates, presented in Section 4 and results of the differential voltage and expansion is discussed and compared, in Section 5. Finally, in Section 6 the contributions of the paper are summarized.

2. Model Development

2.1. Electrochemical Model

The electrochemical model in this section is primarily based on the well known Doyle Fuller Newman (DFN) model. As mentioned in the introduction, the distribution of particle size for the graphite electrode is considered here. A model for electrodes with multiple materials has been proposed in [22]. The treatment of multiple particle sizes is similar to models with multiple materials, with only difference being the fact that instead of multiple materials there are multiple particle sizes of the same material. The model schematics
is shown in Fig. 2. For generality the particle size distribution is considered for both positive and negative electrodes in the model description below, although in practice we only considered a particle distribution in the negative electrode.

2.1.1. Full order model

The multiparticle DFN (MP-DFN) model is presented here. The main difference in MP-DFN model is that at each point in the $x$ direction instead of the single particle configuration, there are multiple particles with a size distribution. The particle size distribution is the same along the length of the electrode. In the following equations the symbol ($\ast$) is a place holder for either positive ($p$) or negative ($n$) electrodes. The number of particle sizes is denoted by $N_{\ast}^R$. The particle ($i$) represents the particles with size $R_{p,i}^\ast$. The lithium concentration, ($c_{\ast,i}$), for each particle ($i$) is given by the following solid diffusion equations

$$\frac{\partial c_{\ast,i}^\ast}{\partial t}(x,r,t) = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ D_{s,i}^\ast r^2 \frac{\partial c_{\ast,i}^\ast}{\partial r}(x,r,t) \right],$$

(1)

$$\frac{\partial c_{\ast,i}^\ast}{\partial r}(x,0,t) = 0,$$

(2)

$$D_{s,i}^\ast \frac{\partial c_{\ast,i}^\ast}{\partial r}(x,R_{p,i}^\ast,t) = -j_i^\ast(x,t),$$

(3)
where \( j_i \) is the pore wall flux between electrolyte and the solid, and \( D_s \) is the solid state diffusion coefficient. The Butler-Volmer equation is given by

\[
j_i^*(x,t) = \frac{i_{0,i}^*(x,t)}{F} \left( e^{\frac{\alpha_\ell^F \eta_i^*(x,t)}{RT}} - e^{-\frac{\alpha_\ell^F \eta_i^*(x,t)}{RT}} \right),
\]

where \( i_{0,i}^*(x,t) = k_0^e(c_e(x,t))^{\alpha_s}(c_{s,max,i}^* - c_{se,i}^*(x,t))^{\alpha_s} (c_{se,i}^*(x,t))^{\alpha_c} \),

where \( c_{se,i}^*(x,t) = c_{s,i}^*(x,R_{p,i}^e,t) \) is the concentration at the surface of the particle, the \( k_0 \) is the reaction rate constant, \( (\alpha_s, \alpha_c) \) are the charge transfer coefficients, and \( \eta_i^*(x,t) \) is the surface overpotential given by

\[
\eta_i^*(x,t) = \Phi_1(x,t) - \Phi_2(x,t) - U_s(c_{se,i}^*(x,t)) - V_{f,i}^*(x,t),
\]

where \( \Phi_1 \) is the potential of the solid, \( \Phi_2 \) is the potential of electrolyte, \( U \) is the half-cell open circuit potential. The \( V_{f,i}^*(x,t) = ASR_f^e F j_i^*(x,t) \) is the voltage drop due to the film resistance, where \( ASR_f \) is the area specific resistance. The modified current balance is as follows

\[
\begin{align*}
\nabla . i_2(x,t) &= \sum_{i=1}^{N^p} a_i^p F j_i^p(x,t) \quad 0 \leq x < l_n, \\
\nabla . i_2(x,t) &= 0 \quad l_n \leq x \leq l_n + l_s, \\
\nabla . i_2(x,t) &= \sum_{i=1}^{N^p} a_i^p F j_i^p(x,t) \quad l_n + l_s < x \leq l_c,
\end{align*}
\]

where \( i_2 \) is the current density in the electrolyte, the \( a_i \) is the active interfacial surface area of particle \((i)\) per electrode unit volume, and the \( l_c = l_n + l_s + l_p \) is denoting the total length of the cell. The boundary conditions are the continuity of \( i_2, \) and \( i_2(0,t) = i_2(l_c,t) = 0. \)

The following equations remain unchanged from the DFN model. The electrolyte material balance is

\[
\epsilon_2^* \frac{\partial c_e}{\partial t}(x,t) = \nabla . \left( D_e^e \nabla c_e(x,t) \right) + \frac{1 - \rho^0_+}{F} \nabla . i_2(x,t) - \frac{i_2 \cdot \nabla \rho^0_+}{F}(x,t),
\]

where \( \epsilon_2 \) is the porosity, \( \rho^0_+ \) is the transference number of Li ions, and the \( D_e^e = D_e(\epsilon_2^*)^{brug} \) is the effective electrolyte diffusion coefficient. The boundary conditions are continuity of \( c_e, \) and \( \nabla c_e(0,t) = \nabla c_e(l_c,t) = 0. \)

The liquid-phase Ohm’s law is

\[
i_2(x,t) = -\kappa^e \nabla \Phi_2(x,t) + \frac{2\kappa^e RT}{F} \left( 1 - \rho^0_+ \right) \left( 1 + \frac{d \ln f_\pm}{d \ln c_e(x,t)} \right) \nabla (\ln c_e)(x,t),
\]

where \( f_\pm \) is the mean molar activity coefficient in the electrolyte, and the \( \kappa^e = \kappa(\epsilon_2^*)^{brug} \) is the effective bulk ionic conductivity of the electrolyte. The boundary conditions are continuity of \( \Phi_2, \) and \( \Phi_2(0,t) = 0. \)

The solid-phase Ohm’s law is

\[
i_1(x,t) = -\sigma^e \nabla \Phi_1(x,t),
\]

where \( i_1 \) is the current density in the solid, and the \( \sigma^e = \sigma(1-\epsilon^*)^{brug} \) is the effective electronic conductivity.

Also, \( i_1(x,t) + i_2(x,t) = I(t), \) where \( I(t) \) is the current density input to the model. Finally, the output of the model, voltage, is written as follows

\[
V(t) = \Phi_1(l_c,t) - \Phi_1(0,t).
\]
Finally, the energy balance for the lithium ion battery assuming local thermal equilibrium is given by the following equations

$$\frac{\partial (\rho C_p T)}{\partial t} = \nabla \cdot (\lambda \nabla T) + q,$$

where $\rho$ is the volume average density, $C_p$ is the volume averaged specific heat, $T$ is the temperature, and $\lambda$ is the volume averaged thermal conductivity. The heat generation term, $q$, is given by

$$q = \sum_{i=1}^{N_s} a_i^* F_j^* (x, t) \left( \eta_i^* (x, t) + T(t) \frac{\partial U_i^*}{\partial \Phi_i^*} (c_{se,i}(x, t)) \right) - i_1^* \nabla \Phi_1 (x, t) - i_2^* \nabla \Phi_2 (x, t).$$

It is worth mentioning that this form neglects the enthalpy of mixing, since it is generally small and ignored in practice. Furthermore, the boundary conditions are defined based on the types of heat flux considered at the cell boundary such as, convection, conduction, and radiation.

2.1.2. Reduced order model

Here, the asymptotic method of [20] is utilized for the derivation of the reduced order model. The advantage of this method is that it results in a more accurate approximation of the full-order model compared to similar models in the literature and requires no assumptions about the spatial distributions of variables. The resulting equations of the multi-particle model with electrolyte (MPMe) are presented in the following.

The behavior of all particles in each electrode can be represented by a single representative particle, with concentration ($c_{s,i}$)

$$\frac{\partial c_{s,i}^*}{\partial t} = \frac{1}{r^2} \frac{1}{\partial r \left[ D_i^* r^2 \frac{\partial c_{s,i}^*}{\partial r} (r, t) \right]},$$

$$\frac{\partial c_{s,i}^*}{\partial r} (0, t) = 0,$$

$$D_i^* \frac{\partial c_{s,i}^*}{\partial r} (R_{p,i}, t) = -j_i^* (t).$$

Furthermore, for simplification it is assumed that the solid diffusion is independent of the concentration. The current exchange density, $i_0$, is approximated by integration over the electrode thickness, which results in the following for the Butler-Volmer equations

$$j_i^* (t) = \frac{i_{0,i}^* (t)}{F} \left( e^{\frac{a_c^e \eta_i^*}{T}} - e^{-\frac{a_c^e \eta_i^*}{T}} \right),$$

$$i_{0,i}^* (t) = \frac{1}{l_i} \int_0^{l_i} k_0^i (c_e (x, t))^\alpha (c_{s,max,i} - c_{s,se,i} (t))^\alpha (c_{se,i} (t))^\alpha c_e dx,$$

$$i_{p,i}^* (t) = \frac{1}{l_p} \int_{l_c-l_p}^{l_c} k_0^p (c_e (x, t))^\alpha (c_{s,max,i} - c_{s,se,i} (t))^\alpha (c_{se,i} (t))^\alpha c_e dx.$$
Therefor using Eq. (7) results in

\[ I = \sum_{i=1}^{N_n} l_n a_{n,i} F j_i^n, \quad I = - \sum_{i=1}^{N_p} l_p a_{p,i} F j_i^p. \]  

(21)

Because of the conservation of lithium in the electrolyte the average lithium concentration over the cell length is equal to the initial concentration. Therefore, for the electrolyte concentration, an average transfer-number and diffusion coefficient based on electrolyte initial concentration is considered. The resulting equation when combining with Eq. (21) is

\[ \epsilon^* \frac{\partial c_e}{\partial t}(x,t) = \nabla \cdot (D_e(\epsilon^*)^{brugg} \nabla c_e(x,t)) + \frac{1 - \bar{\rho}^0_+}{F} \times \begin{cases} \frac{I(t)}{l_n} & 0 \leq x < l_n, \\ 0 & l_n \leq x \leq l_n + l_s, \\ \frac{-I(t)}{l_p} & l_n + l_s < x \leq l_c, \end{cases} \]  

(22)

where \( \bar{\rho}^0_+ = t^0_+ (\epsilon^0_e) \) and \( D_e = D_e(c_e^0) \) with the same boundary conditions as the ones for Eq. (8). Similarly for solving the liquid-phase Ohm’s law, Eq. (9), the conductivity, \( \kappa \), and the thermodynamic factor, \( t_f = (1 - t^0_+) \left( 1 + \frac{d}{d \ln c_e} f \right) \), are calculated based on the average(initial) electrolyte concentration. Integrating and applying the boundary condition results in

\[ \Delta \Phi_2(t) = - \left( \frac{l_n}{3(\epsilon^0_e)^{brugg}} + \frac{l_s}{(\epsilon^0_e)^{brugg}} + \frac{l_p}{3(\epsilon^0_p)^{brugg}} \right) \frac{I(t)}{\kappa} + \frac{2RT}{F c_{e,init}} tf(c_{e,p} - c_{e,n}), \]  

(23)

where \( \bar{c}_{e,*} \) denotes the average electrolyte concentration over the electrode, the \( \kappa = \kappa(c_e^0) \), and \( tf = tf(c_e^0) \). The solid electrical conductivity is large in the electrodes, which means the ohmic potential drop in the solid is relatively small, and the solid electric potential is independent of \( x \). Hence, the solid-phase potential drop is negligible, and all the particles in an electrode have the same solid-phase potential and are essentially in a parallel configuration. This results in the following \((N_n^R - 1)\) and \((N_p^R - 1)\) equality equations for negative and positive electrodes, respectively,

\[ \Phi_{1,1}^* = \Phi_{1,2}^* = \ldots = \Phi_{1,N_e^*}^*. \]  

(24)

Because of the above equations, the output voltage can be written for any index \( i = 1, \ldots, N_p^R \) and \( j = 1, \ldots, N_n^R \), therefore

\[ V(t) = \eta^p_i(t) + U_p(c_{e,i}^p(t)) + V^p_{f,i}(t) - \eta^n_j(t) - U_n(c_{e,j}^n(t)) - V^n_{f,j}(t) + \Delta \Phi_2(t). \]  

(25)

As for the energy balance equation, a lumped temperature model is considered, which reduces the complexity of the model. Furthermore, since the thickness of the cell is much smaller than the length scale for the heat conduction, the cell dissipates heat only through convection. With these assumptions the energy balance in reduced form is given by

\[ \rho C_p \frac{dT}{dt}(t) = -\frac{hA_e(T(t) - T_a)}{V_c} + \frac{1}{V_c} \int_{V_c} q dV, \]  

(26)
where $h$ is the heat transfer coefficient for convection, $A_c$ is the battery surface area, $V_c$ is the cell volume, and $T_a$ is the ambient temperature. Eq. (6) is used to substitute the over potential term, $\eta$, in Eq. (13), and further simplification of the above equation is done using the procedure in [23]. Finally, the energy balance equation reduces to

$$
\rho C_{pl} \frac{dT}{dt}(t) = -h(T(t) - T_a) - \sum_{s=p,c} \sum_{i=1}^{N_R} a_i^s F_j^s(t) \{ U_s(c_{se,i}(t)) + V_f^s(t) - T(t) \frac{\partial U_s}{\partial T}(c_{se,i}(t)) \} - I(t)V(t).
$$

(27)

2.2. Mechanical Model

In this section a model for the expansion of the lithium ion battery during cycling is presented. The model is developed by incorporating several simplifying assumption pertaining to this paper.

2.2.1. Intercalation induced expansion

Since the expansion of graphite is relatively small ($\approx 8\%$), the effect of stress induced diffusion in the solid on voltage for materials like graphite is negligible [15], and hence it is not considered here. Furthermore, the infinitesimal strain theory is used for modeling the deformation. Thus the Cauchy strain tensor, $\epsilon$, is given by

$$
\epsilon = \frac{1}{2} (\nabla \mathbf{u} + (\nabla \mathbf{u})^T),
$$

(28)

where $\mathbf{u}$ is displacement vector. The quasi-static condition is also assumed for the evolution of strain in the particle. With body forces neglected, the equilibrium condition reads as

$$
\nabla \cdot \mathbf{\sigma} = 0,
$$

(29)

where $\mathbf{\sigma}$ is the Cauchy stress tensor. Furthermore, it is assumed that the bulk electrode particle is a linear elastic solid. The graphite material used in lithium-ion batteries is the mesophase carbon microbeads (MCMB), which is generally disordered, and thus it is assumed to be isotropic. The constitutive equations written using Young’s modulus, $E$, and Poisson’s ratio, $\nu$, are given by

$$
\epsilon_{ij} = \frac{1}{E} \{ (1 + \nu)\sigma_{ij} - \nu \sigma_{kk} \delta_{ij} \},
$$

(30)

where the equations are expressed with respect to a Cartesian coordinate system (e.g. $i, j, k = r, \theta, \phi$), and Einstein summation convention of summing on repeated indices is used.

During cycling the intercalation of lithium leads to changes in the lattice parameters. These changes can be represented as a volume change of some unit lattice volume, which in a macroscopic scale, is a function of local lithium concentration. This change is represented by a volumetric strain, which is denoted by $\Delta V$. Because of the assumptions of linear elasticity and small strain, this volumetric strain can be added to Eq. (30) linearly. This is equivalent to the treatment of the stress and strain induced by thermal expansion, first presented in [24], and in agreement with other studies [15, 16, 17, 25]. Furthermore, the volumetric
strain is equal in all direction, and hence it is trivial to show that the strain in the normal stresses direction is one third of the volumetric strain. Thus, the stress-strain relationship with intercalation expansion is given by

$$\epsilon_{ij} = \frac{1}{E}[(1 + \nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij}] + \frac{\Delta V(c_s(r,t))}{3}\delta_{ij},$$  \hspace{1cm} (31)$$

where $\delta_{ij}$ is the Kronecker delta. It is assumed that the every active material particle is sphere, so a spherical coordinate system is utilized. Furthermore, due to the symmetry $\sigma_{\theta\theta} = \sigma_{\phi\phi}$, the normal strains in Eq. (31) can be written as

$$\epsilon_{rr} = \frac{1}{E}[\sigma_{rr} - 2\nu\sigma_{\theta\theta}] + \frac{\Delta V(c_s(r,t))}{3}, \hspace{1cm} (32)$$

$$\epsilon_{\theta\theta} = \frac{1}{E}[(1 - \nu)\sigma_{\theta\theta} - \nu\sigma_{rr}] + \frac{\Delta V(c_s(r,t))}{3} \hspace{1cm} (33)$$

The spherical symmetry of the particle also results in the radial and tangential stresses to be only a function of radial position. Therefore, the stress equilibrium equation (see Eq. (29)) in radial direction simplifies to

$$\frac{\partial \sigma_{rr}}{\partial r} + 2\left(\frac{\sigma_{rr} - \sigma_{\theta\theta}}{r}\right) = 0, \hspace{1cm} (34)$$

and the strain tensor equations (see Eq. (28)) in spherical coordinates are

$$\epsilon_{rr} = \frac{\partial u_r}{\partial r} \hspace{1cm} (35)$$

$$\epsilon_{\theta\theta} = \frac{u_r}{r} \hspace{1cm} (36)$$

where $u_r$ denotes radial displacement. Based on Eqs. (32) to (36), a second order differential equation for the radial displacement is obtained:

$$\frac{\partial^2 u_r}{\partial r^2} + 2\frac{\partial u_r}{r}\frac{\partial r}{\partial r} - \frac{2u_r}{r^2} = \frac{1 + \nu}{1 - \nu} \frac{\partial}{\partial r} \left(\frac{\Delta V(c_s(r,t))}{3}\right). \hspace{1cm} (37)$$

The boundary conditions are the displacement at the center being zero, and the stresses at the surface of particle being zero,

$$u_r(0,t) = 0, \hspace{1cm} (38)$$

$$\sigma_{rr}(R_p,t) = 0. \hspace{1cm} (39)$$

Integration of this equation and using the two boundary conditions gives the solution for $u_r$,

$$u_r(r,t) = \left[\frac{1 + \nu}{1 - \nu} \frac{1}{3r^2} + \frac{2(1 - 2\nu)}{1 - \nu} \frac{r}{3R_p^2}\right] \int_0^r r^2 \Delta V(c_s(\rho,t)) d\rho. \hspace{1cm} (40)$$

Finally, the displacement at the surface of the particle is calculated using Eq. (40) at $r = R_p$, which is the following,

$$u_R(t) = \frac{1}{R_p^2} \int_0^{R_p} \rho^2 \Delta V(c_s(\rho,t)) d\rho. \hspace{1cm} (41)$$
2.2.2. Electrode level expansion

The electrode consists of active material, binder, and conductive material. This means that in practice the expansion of the particles in the electrode, would also result in deformation in other components. In addition the electrode is fixed at the one side to the current collector and free on the separator side. In order to simplify the modeling of electrode expansion, the volume changes in other components is assumed to be negligible. Hence, the volume change of the electrode is given by

\[ \Delta V_e^* = \sum_{i=1}^{N^R} p_i^* \left( 4\pi R_{p,i}^* \right)^2 u_{R,i,\ast}, \]  

(42)

where \( p_i \) is the total number of particles with a radius \( R_{p,i} \) in the electrode. Furthermore, because of the large electrode length to thickness ratio and high stiffness, it is assumed that the electrode only expands in the through-plane direction [26]. Therefore, the volume change can also be written as

\[ \Delta V_e^* = A \Delta t_\ast. \]  

(43)

Following the definition of \( a_\ast^i \), which is the active interfacial surface area of particles with size \( R_{p,i}^* \) per unit volume of the electrode, we have:

\[ a_\ast^i = p_i^* \left( 4\pi R_{p,i}^* \right)^2 / Al_\ast^i. \]  

(44)

Using Eqs. (42) to (44) together results in the following equation for the change in electrode thickness,

\[ \Delta t_\ast = \sum_{i=1}^{N^R} a_\ast^i u_{R,i,\ast} l_\ast. \]  

(45)

2.2.3. Thermal and battery level expansion

Since it was assumed that the temperature is uniform in the cell, a lumped expansion model is also considered for the battery. Therefore, the thermal expansion, \( \Delta t_{th} \), is given by

\[ \Delta t_{th} = \alpha_{th} (T - T_0), \]  

(46)

where \( \alpha_{th} \) is the thermal expansion coefficient of the battery. The total expansion of the electrodes in the cell is simply the sum of the expansion of individual electrodes. Furthermore, in the case of this paper, the battery consists of multiple layers of cells stacked on top of each other in a pouch cell. Hence, the total expansion of electrodes is given by

\[ \Delta t_e = n_c (\Delta t_p + \Delta t_n), \]  

(47)

where \( n_c \) is the number of parallel cells stacked on top of each other in the battery. However, for the expansion at the battery level it is also necessary to consider the influence of the inactive components such as separator, current collectors, and the casing. The expansion and the strain rate during the battery cycling
is small enough to consider a linearized regime for the deformation of these components. Furthermore, the assumption of quasi-equilibrium is considered. Therefore, the modeling of the inactive components is achieved with a linear spring in series with the electrodes. Additionally, a linear spring is also considered to account for the effects of the fixture on the expansion. The configuration of the spring model is shown in Fig. 3(b).

As the amount of force is the same in the springs, following equation can be written for the expansion at the battery level

$$\Delta t_b = \kappa_b \Delta t_e,$$

where $\kappa_b = \frac{k_{ic}}{k_{ic} + k_f}$ with $k_{ic}$ and $k_f$ denoting the inactive components and fixture spring constants, respectively. Finally,

$$\delta = \Delta t_b + \Delta t_{th},$$

where $\delta$ denotes the total expansion of the battery.

3. Experimental Method

The pouch cell was built using the manufacturing equipment at the University of Michigan Battery Lab (UMBL). The cell was of graphite/NMC chemistry, and the specifications of the battery is shown in Table 1. Initial formation cycles were performed after the manufacturing to ensure the safety and performance stability of the cell. Then the cell was assembled inside the fixture shown in Fig. 3(a). The fixture was designed such
that the top and bottom plates are fixed in place while the middle plate is free moving. For pouch cells, added pressure is needed to ensure the optimal performance of the battery. Hence, the fixture was designed to apply an uniform pressure on the pouch cell. This was achieved by using compression springs and polymer poron (Rogers, USA) sheets. The applied pressure was around 5 psi, and knowing the springs constants the springs were compressed to reach this pressure. The expansion was measured using a displacement sensor (Keyence, Japan) mounted on the top plate. The dynamic testing were carried using a battery cycler (Biologic, France). The temperature was measured using a K-type thermocouple (Omega, USA) place on the surface of the battery.

The fixture was installed inside a climate chamber with the temperature set to 25°C, then the cell was cycled 10 times at C/3 between 3.0 V and 4.2 V to ensure the repeatability of the expansion data. The cell was charged with a constant current (CC) from the fully discharged state at different rates (C/20, C/10, C/5, C/2.5, 1C, and 2C) to 4.2 V, followed by a constant voltage (CV) period until the current dropped below C/40, followed by a rest of 3 h. Then, the cell was discharged to 3 V at the same constant current. Each cycle was repeated three times and the measurements from the final cycle were reported.

The thermal tests were done to characterize the thermal expansion and cooling behavior of the fixture. The cell was charged at C/3 to 50% SOC, followed by a rest for 3 h. Then a pulse excitation profile was applied. The profile was a charge pulse at 1C for 5 s, followed by a discharge pulse at the same rate for 5 s. The profile was repeated until the temperature reached the steady state (about 3 h), then the current profile was stopped and temperature was recorded during the cooling stage. The test was repeated with the current rate of 2C. The expansion was also monitored during these tests to be used in thermal expansion coefficient estimation.

In order to measure the potential of graphite and NMC electrodes, coin cells for individual electrodes were built. The electrode sheets were collected from the production line after going through the calendering process, and the coating on one side of the electrode was carefully removed. Then circular electrodes were extracted by using a puncher. Lithium metal foil was used as the counter electrode with a glass fiber sheet as the separator. Finally, the electrolyte consisted of a 1 mol/l LiPF6 was added and coin cells (CR2032-type) were assembled.

Initial formation cycles were performed for the coin cells. The Li/NMC coin cell was cycled at constant current (C/50) between 2.8 and 4.35 V for three times. Similarly, the Li/graphite coin cell was cycled at constant current (C/50) between 0.005 and 1.0 V for three times. The measurements from the last cycle were utilized.

4. Parameter Identification

4.1. Half-cell voltage functions

In order to develop a model for the half cell potentials, several basis function are used to capture the behavior of each electrode the best. The main goal for the graphite function is to have the phase transitions
Pouch cell

Nominal capacity 5.0 Ah
Operating voltage 3.0-4.2 V
Thickness 4.0 mm
Length 132 mm
Width 90 mm

Positive electrode

Material NMC:CB:PVDF (94:3:3)
Number of double sided electrode sheets 14

Negative electrode

Material Graphite:PVDF (95:5)
Number of double sided electrode sheets 15

Separator

Material Polyethylene (PE)

Electrolyte

Material 1 M LiPF$_6$
Organic solvent in electrolyte 2% EC:EMC (3:7)

| Table 1: The pouch cell specifications. |
|----------------------------------------|

observed in the derivative of voltage. The basis functions are fitted to lithiation data for the Li/graphite coin cell and delithiation data for the Li/NMC coin cell (cell charging). The half cell functions are presented in Table 2. In Fig. 4(a) and (b) the data and the fit for graphite and NMC potential is shown, respectively. The potential derivative of the data and the model is also shown in Fig. 4(c) and (d). As can be seen the data and model are in excellent agreement, especially at the phase transitions of the graphite.

![Graphite half-cell potential and fit](a)  
![NMC half-cell potential and fit](b)  
![Differential voltage data and fit](c)  
![NMC differential voltage data and fit](d)  

Figure 4: a) The graphite half-cell potential and fit. b) The NMC half-cell potential and fit. (c) The differential voltage data and fit for graphite and (d) for NMC.

4.2. Full cell stoichiometric window

The identification of the operating window parameters is needed for correct initialization of the concentration. The data at lowest rate (C/20) is utilized to approximate the open circuit state of the cell. The
Figure 5: The resulting a) voltage and c) expansion fit using C/20 data to approximate the open circuit condition and identifying the operating windows of the cell. Furthermore, b) the differential voltage is showing a good fit with respect to the peak locations.

Voltage functions identified previously are used to estimate the stoichiometric operating window of each electrode, which is defined as \((x_0, x_{100})\) for graphite, and \((y_0, y_{100})\) for NMC. The estimation is done by means of a non-linear least squares with the steps detailed in [9]. The identified parameters are reported in Table 2 and the voltage fit is depicted in Fig. 5(a,b) for voltage and voltage derivative. Using the identified operating windows, the relationship between initial state of charge (SoC) and concentration is given by [27]

\[
c_{s, \text{init}} = c_{s, \text{max}} \times (\theta_{100} - \theta_0) + \theta_0,
\]

where \(\theta = x, y\) depending on the electrode.

4.3. Half-cell expansion functions

For the expansion of the graphite the methodology of [9] with data of the lattice parameters reported in [28] is used to find a functional fit for the volumetric strain. For the NMC according to the data in [29], the volumetric strain is approximately linear with a maximum value of 1 - 1.5 %. Here, using this measurement as a guideline, the volumetric strain of NMC is treated as a tuning parameter to fit the cell expansion data. The approach is similar to the method in [9] for fitting the full cell expansion. However, here the stoichiometric window is already known using the voltage and instead the NMC volumetric strain is fitted to the data. It should be noted that in this method the expansion is fitted to pseud-OCV (C/20) data, as a result, the temperature rise is negligible and the contributions of thermal expansion is not considered. Furthermore, according to Eq. (48), the measured expansion at the fixture is also depend on the \(\kappa_b\) ratio. For the fixture utilized in this work, the modulus of the springs in the fixture are much lower than the modulus of the battery, so the \(\kappa_b\) ratio is assumed to be 1. Following the above methodology, the fitted maximum expansion function for NMC is found to be 1.1 %. The resultant expansion of the full cell using this value
and graphite model is shown in Fig. 5(c). The volumetric strain functions of graphite and NMC are also presented in Table 2.

4.4. Thermal properties

The thermal expansion coefficient is estimated using the pulse excitation data. The density of the cell is estimated by measuring weight and the dimensions of the cell. The heat transfer coefficient is also estimated using the same data. Furthermore, for the entropy data from [30] and [31] is used to fit an entropy function for graphite and NMC, respectively. The estimated parameters and functions are presented in Table 2.

4.5. Dynamic charge response fitting procedure

The parameters considered here for fitting the experimental data during different charge rates are the solid diffusion rate, reaction rate constant, and particle size. The fitting process consist of two iterative steps. The other model parameters are either identified using the steps described previously, or measured directly, and are reported in Table 2. In the first step, it is assumed that all the particle are the same size, which essentially reduces the model to the standard SPMe. Then, the solid diffusion rates and the reaction rates are fitted to the voltage and expansion charging data (C/5, C/2, 1C, 2C) at the same time. Meanwhile, the heat transfer coefficient is further tuned to fit the temperature rise data.

In the second step, a particle size distribution is considered for the graphite electrode. For the NMC electrode a single particle size configuration is considered. There are several factors that need to be considered here, which are the particle size distribution and the number of discrete particle sizes. The average particle size was found in the first step by fitting the only voltage and expansion at different rates. In this step, the goal is to fit both the voltage/expansion and their derivatives. It is assumed that the particle size follows an approximately normal distribution about the average particle size. The standard deviation of this distribution was found by finding the best-fit case in terms of the smoothing effect of the voltage derivative at high rates. Regarding the selected number of discrete particle sizes, it was observed that having five particles was a good balance between model accuracy and simplicity. Increasing the number of particle sizes produces a smoother response for the derivatives, but the model complexity and computation time greatly increased with only negligible improvements for the voltage fit. The identified particle size distribution for the graphite electrode is shown in Fig. 6 as a fraction of the total number of particles $\zeta$, defined as the following

$$\zeta_i^* = \frac{p_i^*}{\sum_{k=1}^{N_i^*} p_k^*}.$$  \hspace{1cm} (51)

Using this fraction the active intefacial surface area, $a_i^*$, is given by

$$a_i^* = 3\zeta_i^* \epsilon_i^* \frac{R_k}{R_{p,i}}.$$  \hspace{1cm} (52)

The particle sizes and their corresponding number fraction is also presented in Table 2.
5. Results and Discussion

5.1. Model output at different rates

In order to compare the output of the model at different rates four different charge rates, namely C/5, C/2, 1C, and 2C are selected. The starting point for all the cases are the fully discharged (SoC = 0) state. Using these inputs the model is simulated forward in time until the terminal voltage reaches the maximum voltage (4.2 V). The potential, expansion, and temperature rise curves are shown in Figs. 7 to 9, respectively. The simulated and measured voltage curves (Fig. 7) are in good agreement for the entire charge. The computed expansion profiles from Fig. 8 show a good correlation to the experimental data in the maximum displacement and the region with a lower expansion rate in the middle is captured in the low charging rates.

5.2. Differential curves at different rates

In Fig. 10 the first differential of the voltage and second differential of expansion is depicted for the C/5 and 1C rates. At C/5 the differential voltage and expansion is represented accurately by our model. At 1C the model only shows a slight deviation. This is due to the fact that our model is simplified with only limited number of particle sizes. Therefore, the wavy shape of the differential voltage is observed instead of a smooth curve. Nevertheless, the model is able to capture the smoothing effect of the voltage peak at the 1C rate qualitatively well while maintaining the peak for the expansion differential at the lower rates.

5.3. Particle size distribution and peak smoothing

In order to elucidate the connection between the particle size distribution and peak smoothing, in Fig. 11, the surface lithiation state of the particles during charge at low (C/5) and high (1C) rates are depicted. As can be seen, there are three regions in that lithiation states diverge, which correspond to the three plateaus
Electrochemical

| Parameter | Symbol | Unit | Negative electrode | Separator | Positive electrode |
|-----------|--------|------|---------------------|-----------|-------------------|
| Thickness | $t_0$  | $\mu m$ | 62$^m$ | 12$^m$ | 67$^m$ |
| Particle radius, total number fraction | $R_{p,1}$, $\zeta_1$ | $[\mu m, -]$ | [1.5, 0.10]$^f$ | [3.5, 1]$^f$ |
| Particle radius, total number fraction | $R_{p,2}$, $\zeta_2$ | $[\mu m, -]$ | [2.0, 0.22]$^f$ | - |
| Particle radius, total number fraction | $R_{p,3}$, $\zeta_3$ | $[\mu m, -]$ | [2.5, 0.30]$^f$ | - |
| Particle radius, total number fraction | $R_{p,4}$, $\zeta_4$ | $[\mu m, -]$ | [3.0, 0.25]$^f$ | - |
| Particle radius, total number fraction | $R_{p,5}$, $\zeta_5$ | $[\mu m, -]$ | [3.7, 0.13]$^f$ | - |
| Active material ratio | $c_1$ | - | 0.610$^f$ | 0.445$^f$ |
| Reaction rate constant | $k_0$ | $m^2 s^{-1} (\frac{mol}{m^3})^{-1}$ | 1.1e−11$^f$ | 5.0e−11$^f$ |
| Charge transfer coefficient | $\alpha_c = \alpha_a$ | - | 0.5$^a$ | 0.5$^a$ |
| Solid diffusion rate | $D_s$ | $\frac{m^2}{s}$ | 5.0e−15$^f$ | 8.0e−15$^f$ |
| Film resistance | $ASR_f$ | $\Omega m^2$ | 1.0e−3$^3[3]$ | 0$^a$ |
| Volume fraction in electrolyte | $c_2$ | - | 0.3$^a$ | 0.4$^m$ | 0.3$^a$ |
| Maximum lithium concentration | $c_{z,max}$ | $\frac{mol}{m^3}$ | 28746$^a$ | 35380$^a$ |

| Electrolyte |
|-------------|
| Value |
| Initial electrolyte concentration | $c_o^0$ | $\frac{mol}{m^3}$ | 1000$^a$ |
| Thermodynamic factor | $t_f$ | - | 1.34$^{[34]}$ |
| Transference number | $P_l$ | - | 0.38$^{[34]}$ |
| Electrolyte conductivity | $\tilde{k}$ | $\frac{W}{m K}$ | 1.3$^{[21]}$ |
| Electrolyte Diffusion Coefficient | $D_o$ | $\frac{m^2}{s}$ | 5.2e−10$^{[21]}$ |
| Bruggman exponent | $brugg$ | - | 1.5$^a$ |

| Thermal and cell properties |
|-----------------------------|
| Value |
| Total electrode area | $A$ | $m^2$ | 0.205$^m$ |
| Cell density | $\rho$ | $kg/m^3$ | 3100$^m$ |
| Cell lumped specific heat capacity | $C_p$ | $J/m^3 K$ | 1100$^f$ |
| Air convective coefficient | $h$ | $m^2 K$ | 5$^f$ |
| Cell thermal expansion coefficient | $\alpha_{th}$ | $\frac{m^3}{K m}$ | 1.48$^f$ |

| Stoich. window for the neg. electrode | $[x_0, x_{100}]$ | - | [0.002, 0.8332]$^f$ |
| Stoich. window for the pos. electrode | $[y_0, y_{100}]$ | - | [0.890, 0.033]$^f$ |

| Fitted functions | Data source |
|-----------------|-------------|
| $U_n(x)[V] = 0.063 + 0.8e^{x(−75(x + 0.001))} − 0.0120tanh(x^2) − 0.0118tanh(x^3) − 0.0035tanh(x^4) − 0.0095tanh(x^5) − 0.0145tanh(x^6) − 0.0800tanh(x^7)$ | This paper |
| $U_p(y)[V] = 4.3452 − 1.6518y + 1.6225y^2 − 2.0843y^3 + 3.5146y^4 − 2.2166y^5 − 0.5623e−4xexp(109.451y − 100.006)$ | This paper |
| $\Delta V_n(x)| = (x < 0.12)(0.2x) + (0.12 \leq x < 0.18)(0.16x + 5e−3) + (0.18 \leq x < 0.24)(0.17x + 3e−3) + (0.24 \leq x < 0.50)(0.05x + 0.03) + (0.50 \leq x)(0.15x − 0.02)$ | This paper, [28] |
| $\Delta V_p(y)| = −1.1e−2(1 − y)$; | This paper, [29] |
| $\frac{\partial V_n(x)}{\partial V_n} \frac{\partial V_n}{\partial x} = 0.28 − 1.56x − 8.92x^2 + 57.21x^3 − 110.7x^4 + 90.71x^5 − 27.14x^6$ | [30] |
| $\frac{\partial V_p(V)}{\partial V_p} \frac{\partial V_p}{\partial V} = −800 + 779V − 284V^2 + 46V^3 − 2.8V^4$ | [31] |

Table 2: List of model parameters and functions (25°C), $m$: measured, $f$: fitted to the experimental data, $a$: assumed. $^1$written as a function of the open-circuit potential $U_p$.

in the graphite voltage. At the low C-rate, because the charge time is long enough for the slow diffusion process in the solid, the particles converge as they transition between the plateaus. However, at the high C-rate, because of limits in the diffusion process, the particles surface concentration remain separated, where
The smaller particles charge faster at the second plateau. The increase divergence between the particle surface concentrations results in a smooth transition between the voltage plateaus, which is observed as peak smoothing in the voltage derivative data.

As mentioned in the previous sections, the peak in the differential expansion stay observable at the high C-rate, which is also captured using the model. The prevailing reason for this behavior is that the expansion is approximately a function of the average concentration of lithium in the particle (see Eq. (41)), whereas, the voltage is driven by the surface concentration (see Eq. (6)). Slow solid diffusion rate increases the concentration at the surface, whereas the average concentration is unchanged at the same SoC at higher C-rates as shown in Fig. 11(c). Moreover, the reduced order MPMe indicates that the total expansion is
the summation of the individual particle expansions, in other words, the particle are in series in terms of expansion. As a result, the expansion is less sensitive to the non-uniformity of the lithiation and the peak of the differential expansion stays observable at the high C-rate. This means that the differential expansion provides useful information about the average lithiation state of the graphite at high C-rates that can be utilized in diagnostic methods.

6. Conclusion

In this paper, we have demonstrated that unlike differential voltage, the peaks in the differential expansion curve are observable up to 1C rate and this makes the differential expansion an excellent method for capacity estimation during fast charging scenarios (above C/2). To understand why that is the case, a reduce order
Particle Increase C-rate

The voltage is determined by the surface concentration. The expansion corresponds to the average concentration in the particle.

Figure 11: (a) The surface lithiation state of the graphite particles at C/5, and (b) 1C. Note that the states diverge more at the higher C-rate compared to the low C-rate. Also, notice that the three regions where states are diverging correspond to the plateaus in the graphite potential. (c) Schematics of the concentration profile inside of a particle with respect to the C-rate.

A 5 Ah graphite/NMC pouch cell was fabricated at the University of Michigan Battery Lab. A fixture was designed to measure the mechanical response of the cell. The expansion was measured using a displacement sensor mounted on the top plate, and a battery cycler was used for measuring the voltage. The fixture was installed inside a climate chamber with the temperature set to 25C. The cell operating window was estimated using C/20 charge voltage and expansion data. In general, all simulated profiles fit the measured data well after determining the additional thermal expansion by pulse excitation measurements. The experimental and simulated expansion curves for constant current charge rates at C/5, C/2, 1C and 2C were in good agreement. Furthermore, both experimental and simulated data showed a small peak smoothing of the cell’s differential expansion as the charge rates increases.

Finally, the multi-particle model with different particle sizes results in a distribution of concentration...
among the particles. This non-uniform charging of particles can happen at higher rates and this is causing the smoothing effect. The peaks in the differential expansion are sustained at higher rates, while the differential voltage peaks disappear because voltage is a function of the surface concentration while expansion is a function of the average concentration in the particle.

Acknowledgment

The modeling work in this material was funded by the National Science Foundation under Grant No. 1762247. The experimental work in this material was thanks to the support of the Automotive Research Center (ARC) in accordance with Cooperative Agreement W56HZV-14-2-0001 U.S. Army CCDC GVSC. The authors would also like to thank Yi Ding, and Matt Castanier of GVSC. Distribution A. Approved for public release; distribution unlimited.

References

[1] M. Dubarry, C. Truchot, and B. Y. Liaw, *J. Power Sources*, vol. 219, pp. 204–216, (2012).

[2] S. Lee, P. Mohtat, J. B. Siegel, and A. G. Stefanopoulou, *Am. Control Conf.*, pp. 2288–2293, (2018).

[3] M. Dubarry and B. Y. Liaw, *J. Power Sources*, vol. 194, no. 1, pp. 541–549, (2009).

[4] I. Bloom, A. N. Jansen, D. P. Abraham, J. Knuth, S. A. Jones, V. S. Battaglia, and G. L. Henriksen, *J. Power Sources*, vol. 139, no. 1, pp. 295–303, (2005).

[5] K. Honkura, H. Honbo, Y. Koishikawa, and T. Horiba, *ECS Trans.*, vol. 13, no. 19, pp. 61–73, (2008).

[6] C. R. Birkl, M. R. Roberts, E. McTurk, P. G. Bruce, and D. A. Howey, *J. Power Sources*, vol. 341, pp. 373–386, (2017).

[7] P. Mohtat, F. Nezampsandarbabi, S. Mohan, J. B. Siegel, and A. G. Stefanopoulou, *Am. Control Conf.*, pp. 98–103, (2017).

[8] S. Lee, J. B. Siegel, A. G. Stefanopoulou, J. Lee, and T. Lee, *ASME Dyn. Syst. Control Conf., Proc.*, vol. 2, (2018).

[9] P. Mohtat, S. Lee, J. B. Siegel, and A. G. Stefanopoulou, *J. Power Sources*, vol. 427, pp. 101–111, (2019).

[10] S. Lee, P. Mohtat, J. B. Siegel, A. G. Stefanopoulou, J. Lee, and T. Lee, *IEEE Trans. Ind. Informat.*, vol. 16, no. 5, pp. 3376–3386, (2020).

[11] Z. J. Schiffer, J. Cannarella, and C. B. Arnold, *J. Electrochem. Soc.*, vol. 163, pp. A427–A433, (2015).
[12] A. Knobloch, C. Kapusta, J. Karp, Y. Plotnikov, J. B. Siegel, and A. G. Stefanopoulou, *J. Electron. Packag.*, vol. 140, (2018).

[13] S. Mohan, Y. Kim, J. B. Siegel, N. A. Samad, and A. G. Stefanopoulou, *J. Electrochem. Soc.*, vol. 161, no. 14, pp. A2222–A2231, (2014).

[14] K.-Y. Oh, B. I. Epureanu, J. B. Siegel, and A. G. Stefanopoulou, *J. Power Sources*, vol. 310, pp. 118–129, (2016).

[15] J. Christensen, *J. Electrochem. Soc.*, vol. 157, no. 3, pp. A366–A380, (2010).

[16] F. Yang, *Materials Science and Engineering: A*, vol. 409, no. 1-2, pp. 153–159, (2005).

[17] B. Rieger, S. V. Erhard, K. Rumpf, and A. Jossen, *J. Electrochem. Soc.*, vol. 163, no. 8, pp. A1566–A1575, (2016).

[18] B. S. Haran, B. N. Popov, and R. E. White, *J. Power Sources*, vol. 75, no. 1, pp. 56–63, (1998).

[19] S. J. Moura, F. B. Argomedo, R. Klein, A. Mirtabatabaei, and M. Krstic, *IEEE Trans. Control Syst. Technol.*, vol. 25, no. 2, pp. 453–468, (2017).

[20] S. G. Marquis, V. Sulzer, R. Timms, C. P. Please, and S. J. Chapman, *J. Electrochem. Soc.*, vol. 166, no. 15, pp. A3693–A3706, (2019).

[21] M. Farkhondeh, M. Safari, M. Pritzker, M. Fowler, T. Han, J. Wang, and C. Delacourt, *J. Electrochem. Soc.*, vol. 161, no. 3, pp. A201–A212, (2014).

[22] P. Albertus, J. Christensen, and J. Newman, *J. Electrochem. Soc.*, vol. 156, no. 7, pp. A606–A618, (2009).

[23] W. Gu and C. Wang, *J. Electrochem. Soc.*, vol. 147, no. 8, pp. 2910–2922, (2000).

[24] S. Prussin, *J. Appl. Phys.*, vol. 32, no. 10, pp. 1876–1881, (1961).

[25] X. Zhang, W. Shyy, and A. M. Sastry, *J. Electrochem. Soc.*, vol. 154, no. 10, pp. A910–A916, (2007).

[26] B. Rieger, S. Schlueter, S. V. Erhard, and A. Jossen, *J. Electrochem. Soc.*, vol. 163, no. 8, pp. A1595–A1606, (2016).

[27] D. Di Domenico, A. Stefanopoulou, and G. Fiengo, *J. Dyn. Syst. Meas. Contr.*, vol. 132, no. 6, p. 061302, (2010).

[28] Y. Qi, H. Guo, L. G. Hector, and A. Timmons, *J. Electrochem. Soc.*, vol. 157, no. 5, pp. A558–A566, (2010).
[29] O. Dolotko, A. Senyshyn, M. Mühlbauer, K. Nikolowski, and H. Ehrenberg, *J. Power Sources*, vol. 255, pp. 197–203, (2014).

[30] K. E. Thomas and J. Newman, *J. Power Sources*, vol. 119, pp. 844–849, (2003).

[31] W. Lu, I. Belharouak, D. Vissers, and K. Amine, *J. Electrochem. Soc.*, vol. 153, no. 11, pp. A2147–A2151, (2006).

[32] V. Sulzer, S. G. Marquis, R. Timms, M. Robinson, and S. J. Chapman, “Python Battery Mathematical Modelling (PyBaMM)”. ECSarXiv, (2020) doi:10.1149/osf.io/67ckj.

[33] M. Safari and C. Delacourt, *J. Electrochem. Soc.*, vol. 158, no. 5, pp. A562–A571, (2011).

[34] L. O. Valøen and J. N. Reimers, *J. Electrochem. Soc.*, vol. 152, no. 5, pp. A882–A891, (2005).