Analyzing Heterogeneity in Battery Cathodes Using Computational Modeling

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Abstract

The performance and longevity of lithium-ion batteries are strongly influenced by the local current density within the positive electrode. To investigate the current density profile and identify potential sites of failure along the length of the cathode, this work presents a one-dimensional homogeneous electrochemical model of the lithium-ion Nickel Manganese Cobalt (NMC) cathode. Sensitivity analysis on the presented model suggests that the electronic and ionic conductivity are the two most dominant parameters affecting heterogeneity of local current density along the cathode.

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1 Introduction

An ever-growing energy demand motivates the search for advanced battery technology. Within the last three decades, lithium-based battery development has achieved enormous improvements in energy density and performance over other battery chemistries [1]. Lithium-ion batteries can be used in numerous applications and offer a multitude of advantages, including increased charge capacity and a low self-discharge rate. As a result, the lithium-ion battery has since replaced competing battery chemistries as the leading energy provider for most portable electronics [2].

The internal structure of a lithium-ion battery includes four main components: cathode, anode, electrolyte, and separator [3]. **Figure 1** provides an illustration of this basic internal structure. The cathode (positive electrode) is comprised of a layered oxide and determines the capacity and cell voltage of the battery [3]. The anode (negative electrode) is often composed of graphite, silicon, and silicon oxides and either stores or releases lithium ions while enabling a flow of electrons through the external circuit [3]. The electrolyte is an electronically insulating and ionically conducting medium of salts, solvents, and additives [3]. The separator, a thin porous membrane often composed of synthetic resin, functions as a barrier between the cathode and anode and facilitates the exchange of lithium ions from one side to the other [4].

Using these four structural components, lithium-ion batteries convert chemical energy into electrical energy. This conversion requires intercalation and deintercalation, two reversible electrochemical mechanisms in which a mobile lithium ion is inserted into (or extracted from) a layered structure without deformation of the crystalline matrix [5]. Intercalation and deintercalation occur when lithium ions transfer between the positive and negative electrodes during charging and discharging, thus storing or releasing energy.

The potential difference that exists between the cathode and anode is a key factor in determining the overall capacity and energy density of the battery [6]. Because there exists a larger range of potentials among available cathode materials than anode materials, the choice of cathode composition is highly important in optimizing battery performance [6]. This work focuses on the cathode portion of the lithium-ion battery and presents an electrochemical model of a lithium-ion Nickel Manganese Cobalt (NMC) cathode. Although the current modeled system includes NMC particles within the cathode, the presented model can be used to describe any lithium-ion cathode consisting of any generic metal oxide.
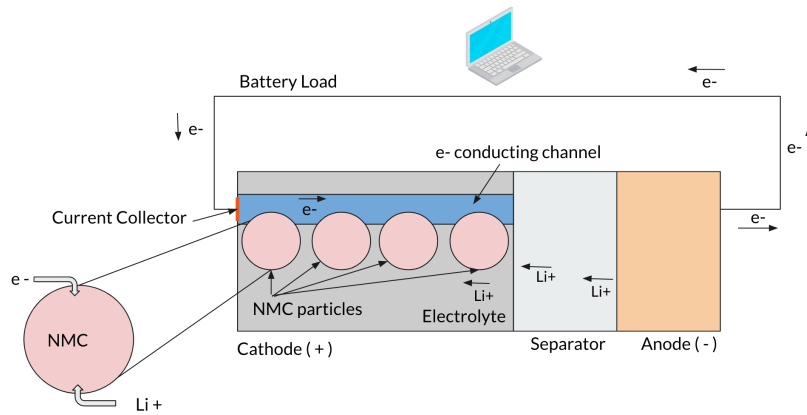

Figure 1 Internal structure of a lithium-ion battery. This includes four main components: cathode, anode, electrolyte, and separator.

The mathematical model presented in this work combines concepts of electroneutrality, Butler-Volmer kinetics, and Ohm's Law to determine the current density profile along the length of the cathode. The model additionally solves for charge heterogeneity, a measure of non-uniformity among the length scales in which redox reactions occur [7]. Significant charge heterogeneity during battery charging or discharging is often indicative of local over-activity within the cathode, and thus lower battery performance [7]. Charge heterogeneity can result from a variety of factors, including battery electrode composition, battery particle properties, or operational conditions [7]. A sensitivity analysis on the cathode model was conducted to determine the extent to which relevant parameters affect heterogeneity along the cathode. The results of the presented sensitivity analysis will hopefully focus future efforts on optimizing a few sensitive parameters in attempt to better homogenize current density along all length scales and increase individual particle input to improve overall battery capacity.

2 Methods

2.1 Electrochemical Model Equations

Advanced battery models have recently been developed to observe heterogeneity in electrode materials using a three-dimensional heterogeneous system [8–10]. Though these models are advantageous with respect to the information they provide on the spatial and temporal dependence of heterogeneity in electrode utilization during battery cycling, the models are quite complex. This complexity typically limits model development to finite element simulation packages, such as COMSOL, that streamline the setup and numerical solving of systems of equations [8–10]. For simplicity and ease of use, a one-dimensional steady state homogeneous model spanning across the thickness of the cathode was developed in python. It was assumed that the kinetics of the electrode can be described by the Butler-Volmer equation, shown in **Eq 1** [11, 12].

$$i = a \times i_0 \times (exp(\frac{\alpha_a F(\phi_s - \phi_l)}{RT}) - exp(-\frac{\alpha_c F(\phi_s - \phi_l)}{RT})) \tag{1}$$

This equation includes the simplification that the concentration of ions at the electrode surface is approximately equal to their bulk concentrations in the electrolyte. Since the model being developed will describe the activity of the cathode at the instant a current begins to flow, the concentrations of species at the surface of the electrode are equal to that of the bulk electrolyte, and therefore the aforementioned simplification is valid. Ohm's Law can then be used to define the potential drop in the electronically and ionically conducting phases, shown in **Eq 2** and **Eq 3**, respectively.

$$i_s = -\sigma \frac{d\phi_s}{dx} \tag{2}$$

$$i_l = -\kappa \frac{d\phi_l}{dx} \tag{3}$$

These equations use the electronic and ionic conductivities, σ and κ, to relate the current density of electrons and ions with their respective potential gradient along the thickness of the cathode. Furthermore, it can be safely assumed that electroneutrality is maintained throughout the system, such that **Eq 4** is valid as there is no accumulation of charge [11, 12].

$$\frac{di_s}{dx} + \frac{di_l}{dx} = 0 \tag{4}$$

To simplify the implementation of this set of equations in python, the derivative of **Eq 1** was solved analytically, and is shown in **Eq 5**.

$$\frac{di}{dx} = -a \times i_0 \times \alpha \times F \times (-\frac{i_s}{\sigma} + \frac{i_l}{\kappa}) \times (exp(\frac{\alpha F(\phi_s - \phi_l)}{RT}) - exp(-\frac{\alpha F(\phi_s - \phi_l)}{RT})) \tag{5}$$

It is typical to assume symmetry between reduction and oxidation kinetics, such that α_a and α_c are equal, and were therefore replaced with α in **Eq 5** [8–12]. With the set of relevant equations assembled, boundary conditions were established so the system could be fully specified. Since the property of *potential* is relative, an arbitrary reference point of $0V$ was set for the electronic potential at the separator. Additionally, the electroneutrality of the system requires that the total current density across the electrode is constant and must be equal to the sum of the ionic and electronic current densities. Since the separator is electronically insulating and the current collector blocks ionic flux, the electronic current density must be equal to the total current density at the current collector and zero at the separator. Finally, it is assumed that the electronic current density at the surface of the current collector can be taken as constant.

To compare the heterogeneity of initial cathode activity for various input parameters, the model results were generalized into two forms. The first generalization aimed to capture the severity of heterogeneity across the entire thickness of the cathode using an arbitrary parameter defined in **Eq 6**.

$$heterogeneity_{overall} = \log_{10} \frac{max(\frac{di}{dx}) - min(\frac{di}{dx})}{mean(\frac{di}{dx})} \tag{6}$$

In addition to the severity in heterogeneity in the overall cathode, it is also important to understand *where* the heterogeneity is along the length of the cathode. Therefore, the model results were generalized using a second arbitrary parameter used to identify the location and relative intensity of heterogeneity in the cathode, shown in **Eq 7**.

$$heterogeneity_{boundary} = \log_{10}(max(\frac{di}{dx}|_{x=0}, \frac{di}{dx}|_{x=L}) - min(\frac{di}{dx}|_{x=0}, \frac{di}{dx}|_{x=L}))(-1)^{\frac{di}{dx}|_{x=l} > \frac{di}{dx}|_{x=0}} \tag{7}$$

As per Porous Electrode Theory, local maxima in electrode activity will be at the electrode's interfaces with the current collector and separator, and is the basis for **Eq 7** [11, 13].

2.2 Methods and Challenges of Python Modeling

A number of programming challenges were overcome before this electrochemical system was accurately modeled in Python. The first difficulty was choosing the correct solver necessary to solve the system of selected equations. Although even an unpracticed chemical engineering undergraduate could recognize that the system described above is a boundary value problem, the authors of this paper initially regarded this system of equations as an initial value problem. A significant portion of time was spent attempting (and failing) to solve the system using the solve_ivp() method imported from the SciPy module. Only after a concerning amount of time did the authors recognize their blunder and re-program the Python script to solve the model using solve_bvp(), a function in SciPy that solves a first order system of ordinary differential equations with two-point boundary conditions.

The SALib module was used to conduct a sensitivity analysis on the presented model. The Method of Morris (also called the Elementary Effects Method) was implemented to conduct a global sensitivity analysis to determine sensitive parameters. An array of sample sets, each with only a single parameter varied, was generated and iterated through

the model to calculate new values of heterogeneity along the length of the cathode. Although the final code for this sensitivity portion is somewhat straightforward, reading the indecipherable documentation offered by SALib proved disastrous. As a consequence, implementing the sensitivity analysis took much longer than anticipated.

3   Results and Discussion

A sensitivity analysis was performed to determine how heterogeneity in electrode activity is impacted by the relevant input parameters: $\sigma, \kappa, a, i_0, T, i_{tot}, L$. The Morris Method was used to obtain **Figure 2** showing the significance of the input parameters on the heterogeneity of the system, based on **Eq 6**.
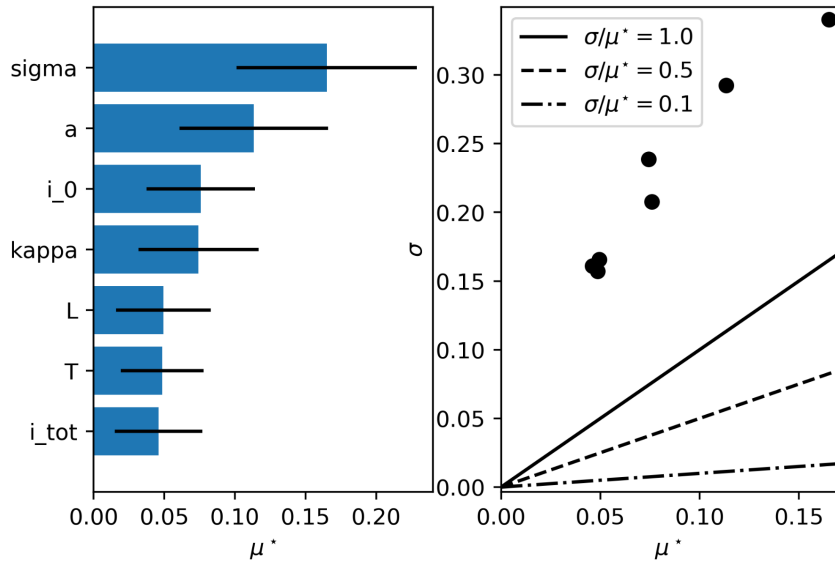

Figure 2 Sensitivity analysis of the relevant input parameters: $\sigma, a, i_0, T, i_{tot}, L$.

Though it is expected that all the parameters have an impact on the heterogeneous utilization of the cathode, it is valuable to understand which parameters in particular are the most impactful to achieve a more uniform cathode utilization. The most important parameters included the ionic and electronic conductivities, the specific surface area, and the exchange current density, while temperature, current density, and cathode thickness still remained significant. Many of these parameters are difficult to adjust, so the significance of their impact on electrode heterogeneity should be considered alongside the challenges involved in modifying each parameter. For instance, it may not be economical to control the temperature of the battery, and since it's impact on heterogeneity is relatively low it can be neglected. Alternatively, some parameters cannot be freely adjusted and are instead determined by the desired use of the battery. The total current density, i_{tot}, across the electrode is determined by the power that is required from the battery, meaning i_{tot} should be treated as a design restriction. Likewise, the thickness, L, of the cathode will control the energy density of the battery and will also be restricted based on the desired use of the battery. Of the four most significant variables, the exchange current density and specific area of the electrode are not as easily adjusted as the ionic and electronic conductivities. This is because the exchange current density, i_0, is governed by the electrochemical kinetics of the electrode material, and an adjustment of i_0 would require a different electrode material. As for the specific area, a, this is a convoluted

parameter that is impacted by active material particle size, electrode porosity, and electrode fabrication methods [11–15]. Therefore, the electronic and ionic conductivities, σ and κ, are the optimal parameters for their relative ease of control and significant impact on electrode heterogeneity.

To understand the effects of σ and κ on the overall and boundary heterogeneity, contour plots were created for the two factors described in **Eq 6** and **Eq 7**, as seen in **Figure 3** and **Figure** 4, respectively.
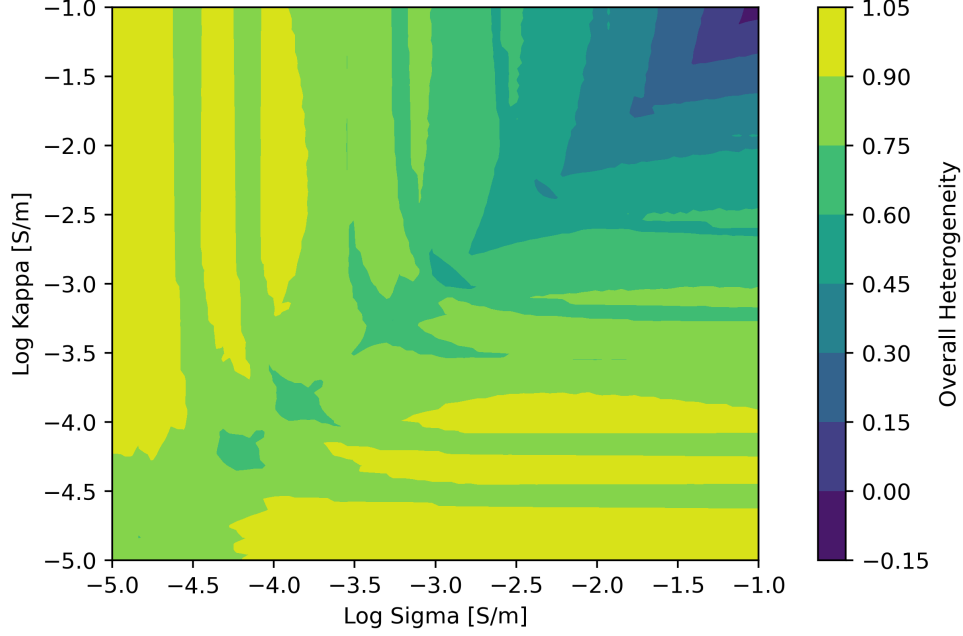

Figure 3 Contour plot of the overall heterogeneity factor defined by **Eq 6** as a function of σ and κ.
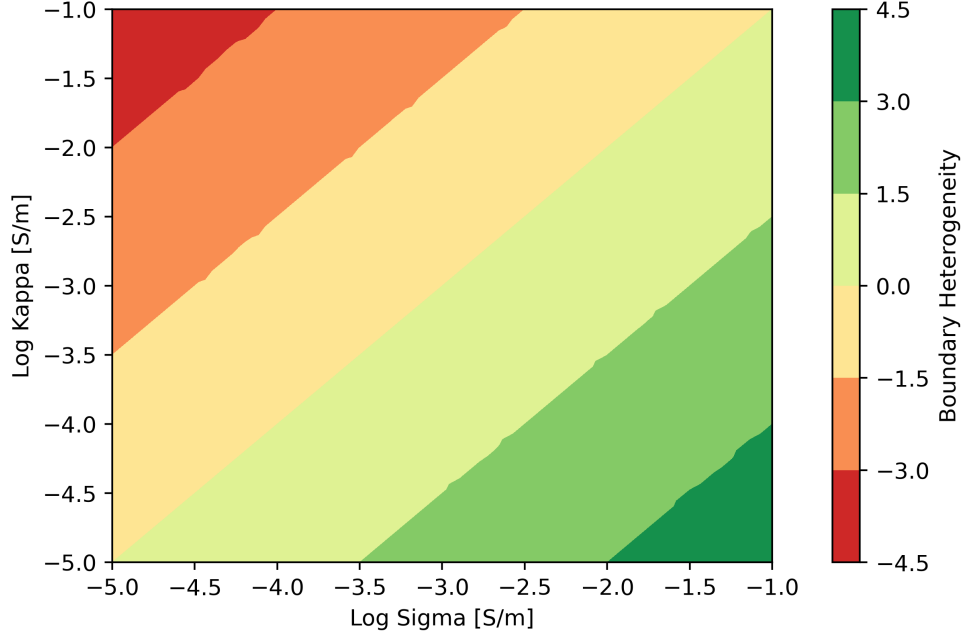

Figure 4 Contour plot of the boundary heterogeneity factor defined by **Eq 7** as a function of σ and κ.

When examining the impact of σ and κ on the overall heterogeneity in **Figure 3**, it becomes clear that a system with relatively low electronic and ionic conductivities will have severe heterogeneity, while increasing these conductivities will enable a more uniform electrode utilization. However, it can also be seen that the lowest overall heterogeneity is achieved when electronic and ionic conductivities are balanced. This is of high significance

for current battery research, as increasing conductivity improves cell performance by reducing the internal voltage drop, as per **Eq 2** and **Eq 3**. Although Ohm's Law dictates that an increase in conductivity will increase cell voltage, improving the conductivity of a single phase may imbalance the relative ease of electronic and ionic transport and induce heterogeneity into the system. Though cell voltage may be somewhat higher in this case, the uneven utilization of active material will simulate more strenuous use and exacerbate aging of the cell. The importance of having balanced electronic and ionic conductivities is highlighted in **Figure 4**, where the values computed from **Eq 7** show the imbalance of material utilization at each end of the electrode. In agreement with that discussed above, the figure shows that increasing the conductivity of one phase while leaving the other constant leads to orders of magnitude change in the *boundary heterogeneity* when testing reasonable combinations of σ and κ [8–15]. In the case of high electronic conductivity and low ionic conductivity, initial cathode activity will be extremely localized to regions near the separator. Not only will the active material degrade more rapidly in this region, but also if the active material undergoes a volume expansion during cycling the ionically conductive pore channels could become restricted, decreasing ionic conductivity further [11–15]. Alternatively with high ionic conductivity and low electronic conductivity, initial activity will be localized near the current collector. Similarly, this will lead to degradation of the active material in the region of high activity, and risks disrupting the electronically conductive network near the current collector.

4   Conclusions

A one-dimensional homogeneous model was used to simulate the cycling of an NMC cathode within Li-ion batteries to observe the severity and location of non-uniform utilization. A sensitivity analysis was performed on the relevant parameters, the results of which suggest that the electronic and ionic conductivities are vital to controlling the heterogeneity within the electrode. Combinations of electronic and ionic conductivities were simulated and compared using two generalized parameters designed to capture the severity and location of heterogeneity in the initial activity of the cathode. Results show high conductivities achieve more uniform electrode utilization, but perhaps more critically, show that the electronic and ionic conductivities *must* be balanced to avoid high local activity at the electrode's interfaces with the current collector and separator.

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