

Effect of Intercalation Diffusivity When Simulating Mixed Electrode Materials in Li-Ion Batteries

E. Wikner^{*1}

¹Chalmers University of Technology

*Hörsalvägen 11, evelina.wikner@chalmers.se

Abstract: When building physics-based battery models, the large amount of needed parameters is a difficult issue. Some parameters can easily be measured while others cannot. Studying the published literature, researchers have reached different results when measuring the same parameter. This is a tedious problem when building physics-based models. One of these parameters is the intercalation diffusion coefficient. In this contribution, the impact of the diffusion coefficient when simulating mixed electrode materials have been investigated using COMSOL Multiphysics. The result shows that when the transport in one of the electrode materials is the limiting factor, the diffusion coefficient strongly affects the simulated potential curve and capacity of the battery. The relaxation and dynamic response of the cell is also strongly affected. The conclusions is that when simulating dynamic behavior of batteries with mixed electrode materials the diffusion coefficients has a higher impact on the result compared to batteries using one electrode material.

Keywords: Diffusion coefficient, mixed electrode material, Li-ion Battery

1. Introduction

Lithium ion battery models and simulations are important tools in deepening the understanding of processes occurring in the battery during usage. Electrochemical or physics-based models gives an insight to the processes that empirical model cannot capture. The drawback with physics-based models is the number of variables and material parameters required. Most physics-based models today build on the electrochemical battery model developed by Doyle, Newman, and Fuller in the 90's [1, 2]. These physics-based models requires around 80-90 material parameters [3]. Several of these parameters are difficult to measure and therefore have to be estimated. The complexity is further increased by the parameters dependency on concentration or temperature or in worst case both. Depending on the process in study the

problem can be simplified by neglecting one or more parameters dependency on the concentration or temperature. One parameters concentration dependency that often is neglected is the solid phase intercalation diffusion coefficient. In this article the impact of the solid phase intercalation diffusion coefficient is investigated when simulating mixed electrode materials. The dynamic behavior of the battery cell during and after applied load is strongly affected by the diffusion coefficients.

1.1 Intercalation diffusion coefficient

The intercalation diffusion coefficient can be difficult to measure and several researchers' reported different results. The intercalation diffusivity has also proven to hold a dependency to the lithium concentration that can differ two orders of magnitude over the material operation area [4, 5]. This further builds on the complexity of the model. The lithium concentration in the material also determines the potential of the electrode. When simulating mixed electrode materials the intercalation coefficient therefore affects the resulting potential of the cell during operation.

2. Battery model

The battery cell is modeled in 1D as indicated by the red line in fig. 1. An extra pseudo dimension is added to solve the concentration in the active particles. The anode is graphite and the

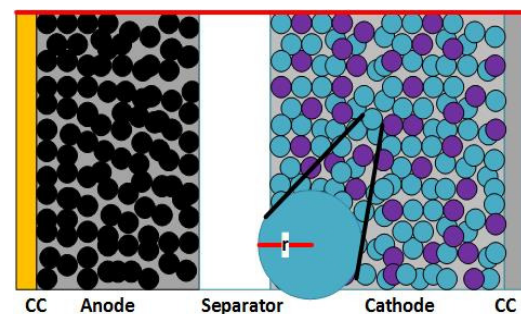


Figure 1. Battery model, the red lines indicates the components included in the 1D model.

cathode is a 50/50 mixture of Lithium Manganese Oxide (LMO) and lithium Nickel Manganese Cobalt oxide (NMC). The graphite is connected to a Copper current collector (CC) and the mixed electrode to an Aluminum CC. The electrolyte is 1:2 EC:DMC with 1M LiPF₆. The material parameters were taken from the COMSOL material library. Model parameters can be seen in table 1 in the appendix.

3. Mathematical Model

The model is built in the Lithium-Ion battery interphase in COMSOL. The governing equation is the conservation of mass

$$\frac{dc_l}{dt} = -\nabla \cdot \mathbf{N} + \sum_{reaction} v_{Li,reactions} \quad (1)$$

where c_l is the lithium concentration in the electrolyte, \mathbf{N} the molar flux of lithium and $v_{Li,reactions}$ the number of moles li-ions produced or consumed by reactions. The subscripts l and s denotes the electrolyte and solid phase respectively. The solid phases are the porous electrodes and CC.

The flux is described by

$$\mathbf{N} = -D_{l,eff} \nabla c_l + \frac{\mathbf{i}_l t_+}{F} \quad (2)$$

where t_+ is the transport number, F faradays constant, $D_{l,eff}$ the effective diffusion coefficient in the electrolyte, the current

$$\mathbf{i}_l = -\sigma_{l,eff} \nabla \phi_l + \left(\frac{2\sigma_{l,eff} RT}{F} \right) \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_l} \right) (1 - t_+) \nabla \ln c_l \quad (3)$$

R is the gas constant, T the temperature, f_{\pm} the salt activity coefficient, $\sigma_{l,eff}$ the effective conductivity in the electrolyte and ϕ_l the electrolyte potential.

The currents in the electrodes and electrolyte is connected by the conservation of current

$$\nabla \cdot \mathbf{i}_l = i_{v,total} + Q_l \quad (4)$$

$$\nabla \cdot \mathbf{i}_s = -i_{v,total} + Q_s \quad (5)$$

where $i_{v,total}$ is the volumetric current from electrochemical reactions in the porous electrodes and Q is an arbitrary current source. The current in the solid phase volumes is

$$\mathbf{i}_s = -\sigma_s \nabla \phi_s \quad (6)$$

The effective conductivity is used for the porous electrode.

The concentration in the active material is solved in a 1D pseudo dimension. The electrochemical reactions are considered to occur on the surface of the active spherical particles. The current produced by the reactions is coupled back to the cell model together with the lithium concentration in the material, according to

$$i_{v,total} = \sum i_{reaction} \cdot S_a \quad (7)$$

$$i_{reaction} = i_0 \left(e^{\frac{\alpha_a F \eta}{RT}} - e^{-\frac{\alpha_c F \eta}{RT}} \right) \quad (8)$$

where

$$i_0 = F k_c^{\alpha_a} k_a^{\alpha_c} (c_{s,max} - c_s^{\alpha_a}) c_s^{\alpha_c} \left(\frac{c_l}{c_{l,ref}} \right)^{\alpha_a} \quad (9)$$

S_a is the specific surface area, k the reaction constant, α the anodic and cathodic transfer coefficient respectively and η the over potential.

$$\eta = \phi_s - \phi_l - \phi_{eq} \quad (10)$$

The concentration in the particles is solved by the mass balance in spherical coordinates

$$\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_s}{\partial r} \right) \quad (11)$$

With the boundary conditions:

$$\frac{\partial c_s}{\partial t} \Big|_{r=0} = 0 \quad (12)$$

$$-D_s \frac{\partial c_s}{\partial t} \Big|_{r=r_p} = -N_{particle} \quad (13)$$

4. Results

Two different investigations were made. The first only studied the voltage response during constant discharge. The second studied the

dynamic response to a 10s charge pulse at approximately 50% state of charge (SOC).

4.1 Discharge behavior

The study were made for four different cases, three base type and one including the concentration dependence. Case 1 is considered the reference case.

1. $D_{LMO}=D_{NMC}=D_{Graphite}$,
2. $D_{LMO}=D_{Graphite}\gg D_{NMC}$
3. $D_{LMO}\ll D_{NMC}=D_{Graphite}$.
4. $D_{LMO}(c_s)$ and $D_{NMC}(c_s)$ according to [4, 5]

The discharge behavior of the cell was studied by constant discharge of the cell with 1C current from 4.14 V to a cutoff voltage of 2.8 V. Here the cell capacity is defined for case 1. The diffusion

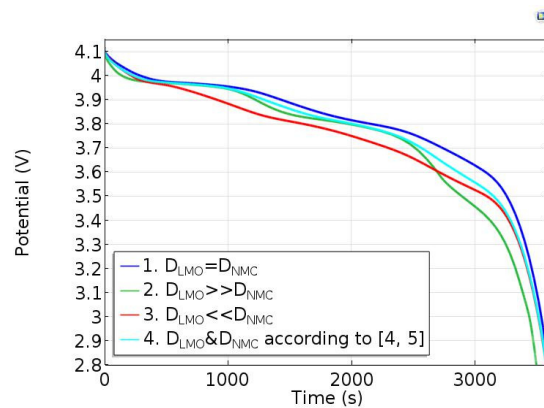


Figure 2. 1C discharge curves for the three different base cases and when using measured diffusion coefficients from [4, 5] as a function of the lithium concentration in respectively material.

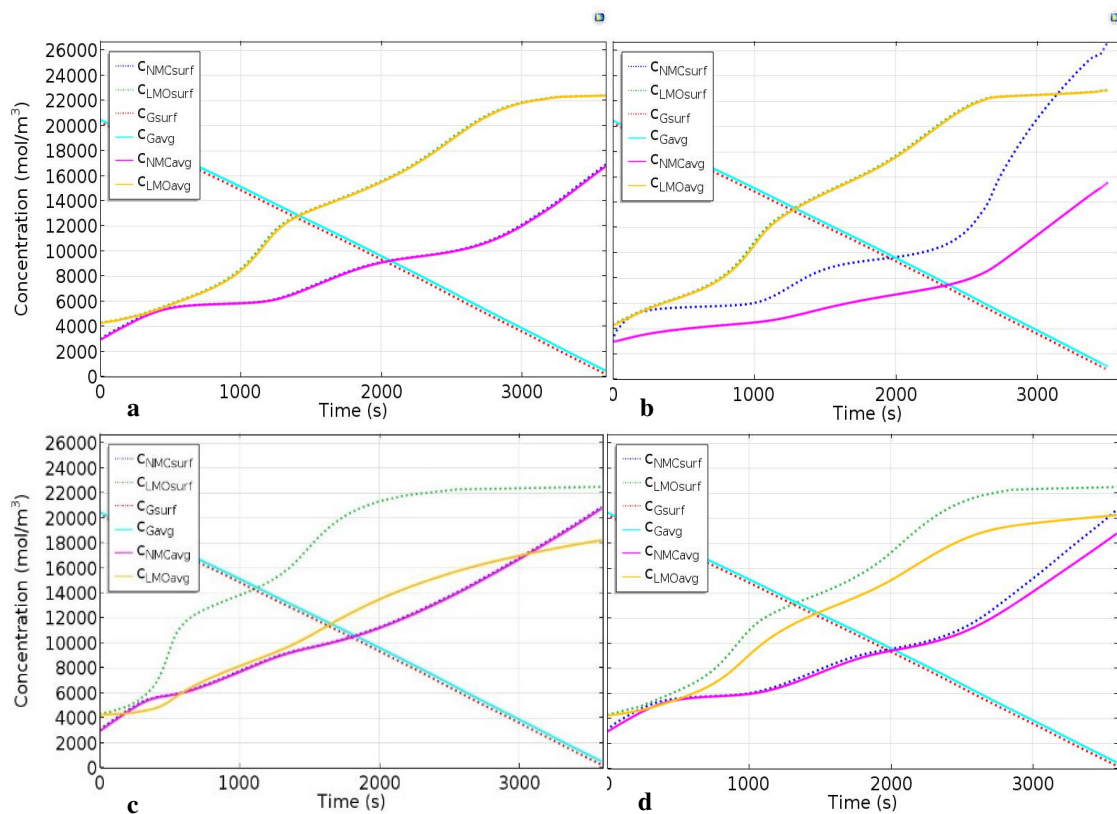


Figure 3. Surface and average lithium concentration in the electrode materials during 1C discharge at the interphase to the CC. **a)** case 1. represents the reference case where the diffusion coefficients are set equal, $D_{LMO}=D_{NMC}=D_{Graphite}=1e-13$ m²/s, **b)** case 2. represents when NMC has slower diffusion coefficient than the other two materials, $D_{LMO}=D_{Graphite}\gg D_{NMC}=1e-15$ m²/s and **c)** case 3. representing the opposite of case 2, $D_{LMO}=1e-15$ m²/s $\ll D_{NMC}=D_{Graphite}$. **d)** Case 4. represents a more realistic simulation using concentration dependent diffusion coefficients for LMO and NMC according to [4, 5].

coefficient for the anode was kept at $1e-13 \text{ m}^2/\text{s}$ in all cases. The slower diffusion coefficient was set to $1e-15 \text{ m}^2/\text{s}$ while the other was kept at $1e-13 \text{ m}^2/\text{s}$.

The resulting discharge curves for the different cases can be seen in fig 2. The 1C current was determined for case 1 and the same current were used in all cases.

The cell potential during discharge is determined by the difference between the anode and cathode materials potential as a function of lithium concentration and the resistance from the passive materials. The cathode materials are required to have the same potential which is determined by the respectively surface concentration. This results in different discharge curves for the different cases.

As can be seen in fig. 2, when one material has a much slower diffusion coefficient compared to the other materials it influences the discharge curve and the capacity of the cell. The concentration buildup on the surface of the active material with the slow diffusion coefficient gives an increasing voltage drop over the cell. The other active material will then intercalate lithium to a higher degree compared to case 1.

NMC has higher capacity than LMO and when the intercalation kinetics for NMC is slow (as in case 2) this has a greater effect on the cell capacity. It can be seen in fig. 3b that the maximum concentration for LMO is reached earlier in the discharge process while the concentration in NMC slowly increases to just over 50% of the material capacity.

In case 3 (see fig. 3c) when LMO instead is having the slower intercalation kinetics the results shows a higher concentration in NMC.

A very high lithium concentration in the active materials causes stress in the particles due to the structural changes when intercalating high concentration of lithium. From an aging perspective it would therefore be preferable to have a more even concentration distribution between the materials.

In case 2, LMO reaches its maximum concentration while the NMC material is not fully used. It would cause greater stress in the LMO particles and they are more likely to fissure and crack than the NMC particles. LMO is known to have less stability during cycling compared to NMC [6, 7]. This would most likely cause an uneven aging process in the cell.

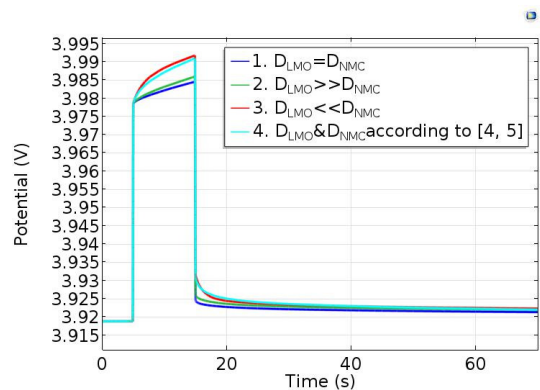


Figure 4. 1C 10s pulse response for the different cases at approximately 50% SOC.

As an extension of the study was case 4. simulated, using concentration dependent diffusion coefficients for LMO and NMC. The values were taken from [4] and [5]. The diffusion coefficients range from $1e-14 \text{ m}^2/\text{s}$ for low to $1e-16 \text{ m}^2/\text{s}$ at high lithium concentrations. The concentration for the different materials can be seen in fig. 3d. It shows that LMO has slower intercalation kinetics than NMC though not as extreme as in case 3. The higher concentration the material gets, the slower kinetics. The result shows a more even distribution of the concentration between the materials.

4.2 Pulse behavior

The dynamic response of the cell and the relaxation is also interesting to investigate. The relaxation time for the cell is strongly depending on the diffusion coefficients. Slow diffusion coefficients means that it will take long time for the cell to relax.

In fig. 4 the behavior for a 10s 1C charge pulse at 50% SOC is shown, using the same cases as for the constant discharge.

The highest voltage response, and highest resistance, can be seen for case 3. As expected, the lowest voltage response can be seen for case 1. Interesting to note is the difference between case 2 and 3. Case 2 gives a similar voltage response as case 1, though slightly higher.

One explanation would be that in case 2 it is more favorable to deintercalate lithium from LMO. It has a flatter potential curve in the concentration region and faster kinetics than NMC. The small potential difference in the LMO

only give rise to a small decrease in the surface concentration on the NMC particles to match the potential.

In case 3 NMC has a sharper potential curve and a small change in concentration give rise to a larger potential difference. Since LMO has a flatter potential curve a larger decrease in the surface concentration is required to match the potential.

In the case when simulating with concentration dependent diffusion coefficients the voltage response is almost as large as in case 3. Here at this concentration level LMO has a slow diffusion coefficient though slightly faster than in case 3. While the diffusion coefficient in NMC is slightly slower than in case 3.

The relaxation time is also highly affected by the diffusion coefficients. In the case with concentration dependent diffusion coefficients both LMO and NMC have slower kinetics than the reference value and this gives the longer relaxation time.

For the other cases the relaxation time is longer when LMO has the slow diffusion coefficient.

8. Conclusions

The diffusion coefficients when simulating mixed electrode materials have an important impact on the results in the dynamic behavior compared to only using one electrode material.

Studying mixed electrode materials with this method shows that the diffusion coefficients are important and needs to be estimated with care or measured.

The concentration dependence of the diffusion parameters should not be neglected when simulating mixed electrode materials using the full SOC region of the cell. The concentration dependence can though be neglected if the study only concerns a reasonably small SOC interval.

From an aging perspective the concentration distribution in the different materials is an interesting aspect. Higher concentration causes larger stress in the particles which can lead to cracks and structural changes in the particle during aging.

This type of simulations can therefore be used to study if two materials would be suitable to be used in a mixed electrode and to find the optimal mix of the two materials.

9. References

1. M. Doyle, T. Fuller, and J. Newman, "Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell," *J. Electrochemical Society*, vol. 140, pp. 1526–1533, (1993).
2. T. Fuller, M. Doyle, and J. Newman, "Simulation and Optimization of the Dual Lithium Ion Insertion Cell," *J. Electrochemical Society*, vol. 141, pp. 1–10, (1994).
2. Author, *Book title*, page numbers. Publisher, place (year)
3. J. C. Forman, S. J. Moura, J. L. Stein, and H. K. Fathy, "Genetic identification and fisher identifiability analysis of the Doyle–Fuller–Newman model from experimental cycling of a LiFePO₄ cell", *Journal of Power Sources*, vol. 210, pp 263-275, (2012)
4. P. C. Goonetilleke, J. P. Zheng and D. Roy, "Effects of Surface-Film Formation on the Electrochemical Characteristics of LiMn₂O₄ Cathodes of Lithium Ion Batteries", *Journal of the Electrochemical Society*, vol. 156, pp. A709-A719 (2009)
5. Wu, Shao-Ling, Wei Zhang, Xiangyun Song, Alpesh K. Shukla, Gao Liu, Vincent S. Battaglia, and Venkat Srinivasan, High Rate Capability of Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ Electrode for Li-Ion Batteries, *Journal of the Electrochemical Society*, vol. 159, pp. A438-A444 (2012)
6. C. M. Julien, A. Mauger, K. Zaghib and H. Groult, Comparative Issues of Cathode Materials for Li-Ion Batteries, *Inorganics*, vol. 2, pp. 132-154 (2014)
7. G.G. Amatucci, C.N. Schmutz, A. Blyr, C. Sigala, A.S. Gozdz, D. Larcher, J.M. Tarascon, Materials' effects on the elevated and room temperature performance of C/LiMn₂O₄ Li-ion batteries, *Journal of Power Sources*, vol. 69, pp. 11-25 (1997)

10. Acknowledgements

The author thanks Torbjörn Thiringer at Chalmers University of Technology, Henrik Markusson and Theresa Granérus at Volvo Cars Corporation and Erik Björklund at Uppsala University for helpful discussions and comments. Financial support kindly provided from the Swedish Energy Agency and Volvo Cars Corporation.

11. Appendix

Parameter values used in the simulations.

Table 1: Parameter values used in the simulations.

Parameter	Value
$c_{\max, \text{NMC}}$	22860 mol/m ³
$c_{\max, \text{LMO}}$	29000 mol/m ³
$c_{\max, \text{Graphite}}$	31507 mol/m ³
$c_{l, \text{ref}}$	1 mol/m ³
r_{Cathode}	5 μm
r_{Anode}	8.5 μm
L_{Anode}	47 μm
L_{Cathode}	75 μm
$L_{\text{Separator}}$	16 μm
$L_{\text{CC, anode}}$	10 μm
$L_{\text{CC, cathode}}$	20 μm
Volume fraction anode	0.45
Volume fraction separator	0.37
Volume fraction cathode	0.45