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Finite Analysis Simulation of a Lithium Metal Battery with Metal Organic Framework (MOF)

Layer using COMSOL Multiphysics

A thesis submitted in partial satisfaction

of the requirements for the degree Master of Science

in Chemical Engineering

by

Campbell Andrew Neil Donnelly

2021

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ABSTRACT OF THE THESIS

Finite Analysis Simulation of a Lithium Metal Battery with Metal Organic Framework (MOF) Layer using COMSOL Multiphysics

by

Campbell Andrew Neil Donnelly

Master of Science in Chemical Engineering University of California, Los Angeles, 2021 Professor Yunfeng Lu, Chair

Lithium Metal Batteries (LMBs) pose themselves as a key contender to increasing the energy density and specific energy of Lithium Ion Batteries (LIBs). This would both decrease cost and increase scope of application and versatility for LIBs across a range of weight and volume sensitive applications. However, lithium dendrite growth poses a key obstacle to LMB commercialization, decreasing cycle life and safety. A novel method published by Wu et al. (2020), involving the formulation of a MOF-based SSI layer, has shown promising results both in dendrite growth suppression and electrochemical performance of LMBs. A Finite Analysis Method simulation was created and investigated in COMSOL Multiphysics to model the MOF layer LMB vs. control. Significant electrolyte concentration and potential polarization reductions were achieved with the MOF layer addition. In addition, higher specific capacities were demonstrated even on a single cycling, especially at higher C rates.

The thesis of Campbell Andrew Neil Donnelly is approved.

Yuzhang Li

Vasilios Manousiouthakis

Yunfeng Lu, Committee Chair

University of California, Los Angeles

2021

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1 Introduction and Background

1.1 Importance of Lithium Ion Batteries (LIBs)

Lithium ion batteries (LIBs) are the main power source in consumer electronics and electric vehicles, comprising 75% of the global rechargeable battery market.¹ The consumer electronics market has not only transformed societies in the past two decades, but it is also projected to continue growing at a compound annual growth rate (CAGR) of 4.9%, reaching 1.538 trillion USD by 2027.² Similarly, as regulatory changes in High Income Countries (HICs) encourage the adoption of Electric Vehicles (EVs), the EV market is expected to grow at a CAGR of 22.6%, reaching a value of 802 billion USD by 2027.³ Commercial and passenger EVs are due to become the primary application of LIBs, as highlighted in Figure 1 below from Bloomberg's NEF 2019 Li-ion battery demand forecast, 2015-2030. Other societal trends increasing reliance on LIB technology include the rise in electric personal mobility vehicles, including hybrid bikes, scooters, wheelchairs and other mobility aids.⁴



Annual lithium-ion battery demand

Figure 1. Bloomberg NEF 2019 Li-ion battery demand forecast for 2015-2030.⁵

In addition, LIBs are being heavily researched to offer grid level energy storage solutions which would improve the power system flexibility of a predominantly renewable energy based grid supply⁶. This latter point is extremely important in facilitating the renewable energy revolution at a majority-supply level scale.

The Global Lithium ion battery (LIB) market itself, across all markets, is expected to reach 897 billion USD by 2025, growing at a CAGR of 14.68%⁷. This enormous market size and growth rate reflects the value of LIBs in solving the energy needs of today and of tomorrow.

LIBs have triumphed due to their relatively high energy density compared to other rechargeable batteries, and due to their higher operating voltages. However, for context, they are still two orders of magnitude less energy dense than common liquid fuels such as Gasoline. There is huge interest in increasing the energy density of LIBs for a wide range of applications.

1.2 Energy Density of Lithium Ion Batteries (LIBs)

Broadly, six characteristics are important for LIBs: energy density, cost, cycle life, rate capability, temperature tolerance, and safety ^{8, 9}. Between all of these however, energy density is perhaps the most important, especially for handheld electronics and electric vehicles (EVs).¹⁰ The growth in the EV market since 2013 has been slower than anticipated, and while this reflects a number of factors, a significant one is range anxiety – a high consumer sensitivity to maximum driving ranges, as dictated by the limited energy densities of LIBs¹¹. Since initial commercialization by Sony in 1991, the energy density of LIBs have steadily increased as in Figure 2. Today, commercial LIBs are largely limited to volumetric energy densities <650 W h L⁻¹ and gravimetric energy densities <250 W h kg⁻¹. However, achieving volumetric energy

densities of >1000 W h L⁻¹ and gravimetric energy densities of ~500 W h kg⁻¹ would exponentially expand the practicality of LIBs.¹²



Figure 2. Development of the specific energy and energy density of LIBs (cell level) from 1991 to 2017, following their commercialization by Sony in 1991. Values are based on the standard cylindrical 18650 lithium ion cell and are taken from cell producers' data.¹³

To a large extent, separators, binders, outer cases, and electrolyte solution have little room for improvement. Therefore a significant increase in LIB energy density will largely be determined by the specific capacities and operating voltages of the anode and of the cathode¹⁴. This is why a majority of LIB research focuses on investigating electrode materials which offer larger voltages, and higher specific capacities. In the near term, silicon anodes and layered Ni and Li and Mn-rich cathodes may prove commercially viable for increasing battery energy densities. In the long term (5+ years) much more substantial increases may come from achieving commercial viability for technologies such as Lithium Metal Anodes, Lithium Sulfur batteries, and Lithium Air batteries.

1.3 Promise of Lithium Metal Batteries (LMBs)

Lithium metal is considered to hold the optimal performance characteristics for the anode thanks to its high theoretical capacity of 3860 mAh g⁻¹ (2061 mAh cm⁻³) ¹⁵ and its low redox potential of -3.04V vs. standard hydrogen electrode (SHE) ¹⁶. However, after its first demonstration in the Li-TS₂ battery in 1976 ¹⁷, severe lithium dendrite formation during experiments in the 1980s practically ruled out the feasibility of a lithium metal anode (LMA).¹⁸ The dendrites cause poor interfacial stability and serious safety issues, since they can puncture the separator and cause a short circuit, and fires.¹⁹

In recent years, significant efforts have been made to suppress the dendrite growth and renew the feasibility of LMAs to be used in LMBs. This is a difficult task given that dendritic growths are initiated by even nanoscale roughness on the anode surface.

1.4 Dendritic Growth Mechanism – Lithium Metal Batteries (LMBs)

Lithium dendrites grow due to a number of factors near the LMA surface.²⁰ First, the solidelectrolyte interphase (SEI) layer is heterogenous, consisting of multiple compounds with unique electrochemical and mechanical properties. Second, there is convection of Li+ ions in the electrolyte. These two factors combined result in the formation of Li nuclei. Third, the Li⁺ cations have a lower diffusivity in the electrolyte (low transference number, t_{Li^+}), which, coupled with consumption of Li⁺ by the anode, results in a concentration gradient near the surface of the LMA. This gradient causes the small protruding dendrites to receive a larger Li⁺ flux, encouraging a cyclical dendritic growth mechanism to snowball as shown schematically in Figure 3.²⁰



Figure 3. Li⁺ flux (arrow) and Li⁺ concentration (grayscale) in the vicinity of the LMA surface and Li deposition morphology.²⁰

Fourth and finally, dendrite growth is furthered by the root-growth mechanism of Li deposition onto new sites that have a thinner SEI layer. As dendrite growth hinders anode performance, and poses safety concerns, it is crucial that dendrite growth it suppressed by controlling the transport, reaction, and deposition of lithium ions at the surface of the Lithium Metal Anode.

1.5 Suppression of Lithium Dendrites – Attempted Solutions

A wide range of methods have been researched to suppress Lithium dendrite growth with some success. Of course, however, each method has had its own drawbacks which have made the solutions not commercially viable. These methods are summarized in Figure 4.²⁰⁻²⁵



Figure 4. Failure and remedies of Li-metal anodes. a | Failure mechanism of Li-metal anodes. b | Approaches to minimize Li-dendrite growth and improve the interfacial stability: approach 1, surface coating with glass or composite; approach 2, surface coating with thin carbon or graphene layers; approach 3, uniform Li-ion flux; approach 4, adding Cs⁺ to the electrolyte; approach 5, incorporating 3D patterns or using Li-metal powder. SEI, solid electrolyte interphase. ²⁰⁻²⁵

1.6 Suppression of Lithium Dendrites – MOF Layer

While the aforementioned approaches face uphill challenges ranging from brittle materials, to low coulombic efficiency, Xu et al. (2020) have demonstrated promising results for a Metal Organic Framework (MOF) Layer solution to lithium dendrite suppression. ²⁰ The layer serves to significantly increase the ion transport at the surface of the LMA by a factor of 2-3x. The MOF

layer was composed of UiO-66, which is a MOF that has a low cost, facile synthesis and high (electro-)chemical stability. The MOF layer creates nanoporous channels that immobilize the anions and form ionic channels for fast Li^+ transport. This is shown by the blue arrows in Figure 5.²⁰



Figure 5. MOF-based SSI formed on LMA with immobilized anions and ionic channels for fast Li+ transport. ²⁰

The MOF layer also reduces the effect of the self-enhanced concentration polarization mechanism which was shown in Figure 3. Instead, the MOF attracts the anions and stifles anionic migration, which removes the driving force for a build up of concentration polarization in the artificial MOF/SEI layer. Furthermore, a relatively high lithium ion conductivity, σ_{Li^+} , for an SEI layer, coupled with a fast lithium ion transport number, t_{Li^+} , results in high performance over extended cycling. The reduction in concentration polarization is shown schematically in Figure 6.²⁰



Figure 6. Li+ flux (arrow) and Li+ concentration (grayscale) in the vicinity of LMA surface and Li deposition morphology with MOF-based SSI. ²⁰

Lastly, it is compelling to note that the dendrite suppression has been observed via SEM images under a range of practical conditions. The images, coupled with electrochemical testing, identified that the morphology of Lithium deposition is vastly changed by the presence of the MOF layer. This morphology change is linked to the decreased nucleation energy barriers for Lithium in the presence of the MOF-based SSI (identified by galvanostatic voltage profiles.) ²⁰ The SEM images are shown in Figure 7. A control and MOF layer cell were subjected to $4 \frac{\text{mAh}}{cm^2}$ at a $2 \frac{\text{mA}}{cm^2}$ to deposit Lithium ions on bare 50-µm Li foil. ²⁰



Figure 7. (C–E) Top-view (C and D) and side-view (E) SEM images of deposited Li $(4 \frac{mAh}{cm^2} at 2 \frac{mA}{cm^2})$ on bare 50-mm Li foil. (F–H) Top-view (F and G) and side-view (H) SEM images of deposited Li $(4 \frac{mAh}{cm^2} at 2 \frac{mA}{cm^2})$ on MOF-SSI protected 50-mm Li. The cells were cycled at $2 \frac{mAh}{cm^2} at 2 \frac{mA}{cm^2}$ for formation. ²⁰

When comparing the control (the top row of images), with the MOF layer LMA (the bottom row of images) it is easy to see that in the case of the MOF layer LMA, the Lithium has deposited in a much more dense, dendrite free morphology. This was confirmed by thickness and areal capacity measurements.

1.7 Electrochemical Results – MOF Layer

In addition to exhibiting remarkable dendrite suppression, the MOF layer study by Xu et al. (2020) demonstrated superior electrochemical performance. Full cells were assembled using thick LiCoO₂ (LCO) cathodes and MOF-Coated LMA in order to assess performance of the MOF coated LMA. The MOF-Coated LMA exhibits significantly greater cycling stability vs. the control (no MOF layer) cell when charged at 0.1C, and discharged at 0.5C over a series of 250 cycles using commercial carbonate based electrolyte. It is shown in Figure 8 that the control only reaches 50 cycles before fading below 80% designed capacity, while the MOF layer cell reaches 220 cycles. ²⁰



Figure 8. Cycling profiles of LMB with a 50- μ m Li Metal Anode and 1.7 $\frac{mAh}{cm^2}$ LCO porous cathode.

Finally, the MOF-based SSI layer Li/LCO battery layer was estimated to have very desirable gravimetric energy density, and specific energy, values as shown in Figure 9. As

discussed in section 1.2, these metrics are extremely important for Lithium Ion Batteries usability in a variety of applications.²⁰



Figure 9. Projected specific energy and energy density of LMBs based on thin LMA with MOFbased SSI (N/P of ~2.5 and 1 for 50 and 20- μm Li, respectively) and various rechargeable battery systems.²⁰

1.8 Further Research – COMSOL Multiphysics Simulations

Finite Analysis Simulations can be used to investigate parameters and relationships that are difficult to test in the lab setting. Using a computer simulation program such as COMSOL Multiphysics, a large number of parameters can be swept, and the real life behavior of lithium ion battery cells can be closely replicated.²⁶ The simulated electrochemical data can be used to explain experimental observations, to expand range of input testing, to observe new relationships, and to guide future research. By closely replicating the experimental setup used by

Xu et al. (2020), and a number of their experimental parameter estimation results, it is possible to replicate and build a computer simulation model of the experiment in COMSOL Multiphysics.²⁰ Using this model in COMSOL Multiphysics, significant further insights can be gained into how the MOF Layer improves the overall cell performance. Further, parametric sweeps can be employed to observe how the MOF layer effects performance over a wide range of input variable values.

2 Materials and Methods

2.1 Introduction

In order to simulate the real world Lithium Metal Battery cell, COMSOL Multiphysics and the Batteries and Fuel Cells Module were employed. A 1-Dimensional (1D) Battery model was created with a large array of input parameters and governing equations. The geometry of the battery model follows that of a 1-Dimensional cross section of the battery, with the lithium metal anode on the far right hand side, and the Lithium Cobalt Oxide cathode on the far left hand side. A software generated "mesh" across the cell geometry determines the thousands of discrete sampling points that the software will record data for during the study. A time-dependent study was followed using this finite element analysis method to assess key output parameters at different time steps at each of these thousands of discrete sample points along the battery model geometry. The electrochemical performance of the cell was then assessed across a large range of output variables, including Specific Capacity vs. Voltage, Electrolyte-Potential vs. x-coordinate and time, and Electrolyte-Concentration vs. x-coordinate and time.

2.2 LMB COMSOL Model Setup - Geometry

The experiment was modeled as a 1-Dimensional (1D) cross section of the battery. Since the model is isothermal, it is common to simplify the real 3D cell to this 1D cross section. This simplification has no significant effect on the specific energy or specific capacity. The simplification also allows for greater complexity in parametric sweeps to be employed while using less computational power, for equally valuable results. The geometry is shown in Figure 10:



Figure 10. Geometry of 1-Dimensional (1D) Lithium Metal Battery Model. Note: lengths changed for illustrative purposes, and not experimental values.

There are 4 domains and 5 nodes in the geometry. The pure Lithium Metal Anode is modeled as a surface node with zero thickness on the right hand side. On the surface of the Lithium Metal Anode, the Metal Organic Framework (MOF) layer is modeled as a porous film domain with unique transport properties, and no chemical reactions. To the left of the MOF layer is the separator domain of thickness $25 \,\mu m$. To the left of the separator, the Lithium Cobalt Oxide (LCO) cathode is modeled as a porous cathode domain with a thickness of 60 μm . Finally, the left most node is the positive current collector. Throughout all 4 domains, LiPF₆ in 1:1 EC:DEC is used as the electrolyte. In order to facilitate direct comparisons, the dimensions used replicate those used experimentally by Wu et al..²⁰ The right LMA node is modeled with zero external electric potential, while the left node is the positive current collector, and this is modeled with constant current density during charge and discharge of the cell. A no flux boundary condition exists for the Lithium at the positive current collector on the left hand side, while Lithium can exit and enter at the LMA surface on the right hand side.

In addition to the 1-Dimensional geometry there is a pseudo-1-Dimensional geometry, r, within the porous electrode domain. This pseudo 1-D dimension describes the solid lithium transport in the porous electrode active material, determined by Fick's Law.²⁷

2.3 LMB COMSOL Model Setup – Parameters and Sweep Variables

In order to accurately simulate the batteries electrochemical performance, an extensive set of variables and governing equations are used to define the system.^{27, 28} Five of these variables are dependent: ϕ_l [V] (electrolyte potential), c_l [mol/m³] (electrolyte salt concentration), ϕ_s [V] (electrode potential), c_s [mol/m³] (electrode solid lithium concentration) and $\Delta \phi_{s,\text{film}}$ [V] (SEI layer potential losses).²⁸

There are seven groups of parameters that will be used to define the cell's values and electrochemical properties: testing, geometry, electrolyte, active particle, reaction constants, known constants and transport number parameters.

The first of these parameter sets is the Testing Parameters, and this is shown in Table 1. In this set of values, the maximum and minimum state of charge, SOC_{max} , SOC_{min} , and maximum and minimum voltages, E_{max_pos} , E_{min_pos} are defined. In addition, the C [h⁻¹], C rates, and i_{1C} [A/m²], 1C discharge current, are defined.

| Name | Calculation | Description |
|-----------------------|--|-------------------------|
| С | 0.1C, 0.2C, 0.5C [h ⁻¹] | C rate |
| i _{1C} | $loading_{pos} 	imes w_{active_{pos}}$ | 1C discharge current |
| SOC _{min} | 0.45 | Minimum State of Charge |
| SOC _{max} | 0.98 | Maximum State of Charge |
| E _{min _pos} | 3.6[V] | Minimum Voltage |
| E _{max _pos} | 4.5[V] | Maximum Voltage |

Table 1. Testing Parameters.

The second set of parameters are the Geometry Parameters, shown in Table 2. In this set of values the press density of porous cathode, $L_{press_density}$, length of lithium metal anode (surface), L_{neg} , length of MOF layer, L_{mof} , Length of separator, L_{sep} , Length of porous cathode, L_{pos} , Length of full cell, L_{total} , are defined.

In addition, the electrode phase volume fraction, porous cathode, ε_{pos} , conductive filler phase volume fraction, porous cathode, ε_{filler_pos} , active material loading, $LCO_{active_loading}$, total solid fraction (active particles and filler), $\varepsilon_{s_pos_total}$, electrolyte phase volume fraction, porous cathode, ε_{l_pos} , cross Sectional area, A_c , electrolyte volume fraction in separator, ε_{l_sep} , MOF volume fraction in separator, ε_{l_mOF} , are also defined.

| Table 2. | Geometry | Parameters. |
|----------|----------|-------------|
|----------|----------|-------------|

| Name | Calculation | Description |
|-------------------------------|--|---|
| $L_{press_density}$ | 4.15 [g/cm ³] | Experimental press density of porous cathode |
| L _{neg} | 0 [m] | Length of lithium metal anode (surface) |
| L _{mof} | 0 or 8e-6 [m] | Length of MOF layer |
| L _{sep} | 25e-6 [m] | Length of separator |
| L _{pos} | 60e-6 [m] | Length of porous cathode |
| L _{total} | $L_{\rm neg} + L_{mof} + L_{sep} + L_{pos}$ | Length of full cell |
| Epos | $1 - \varepsilon_{l_pos} - \varepsilon_{filler_pos}$ | Electrode phase volume fraction, porous cathode |
| E _{filler_} pos | $\varepsilon_{s_pos_total} \times (1$ | Conductive filler phase volume fraction, porous |
| | $-LCO_{active_loading})$ | cathode |
| $LCO_{active_loading}$ | 0.96 | Active material loading |
| $\mathcal{E}_{s_pos_total}$ | 0.70569 | Total solid fraction (active + filler) |
| ç. | $1 - \varepsilon_{s_pos_total}$ | Electrolyte phase volume fraction, porous |
| El_pos | | cathode |
| A _c | 0.785 [cm ²] | Cross Sectional area |
| E _{l_sep} | 0.4 | Electrolyte volume fraction in separator |
| ε _{l_MOF} | 0.4 | MOF volume fraction in separator |

The third set of parameters are the Electrolyte Parameters, shown in Table 3. In this set of values, the electrolyte conductivity in separator at 1M and 298K, $\sigma_{sep_{-1}M_{-}298K}$, electrolyte

conductivity in porous cathode at 1M and 298K, $\sigma_{pos_1M_298K}$, initial electrolyte salt concentration, c_{L_0} , Xu et al. 2020 experimental values used to back calculate MOF conductivity, $\sigma_{mof_1M_298K}$, Xu et al. 2020 Paper Value of Diffusivity measured by Pulsed Field Gradient, D_{l_mof} are defined.²⁰

In addition, the Separator Bruggeman coefficient, β_{sep} , Porous Cathode Bruggeman coefficient, β_{pos} , MOF Layer Bruggeman coefficient, β_{MOF} , are also defined.

| Name | Calculation | Description |
|----------------------------|---|--|
| σ _{sep_1M_298K} | 7.8 [mS/cm] | Electrolyte Conductivity in separator at |
| | | 1M and 298K |
| $\sigma_{pos_{1}M_{2}98K}$ | 7.8 [mS/cm] | Electrolyte Conductivity in porous |
| | | cathode at 1M and 298K |
| C _{L_0} | 1000 [mol/m ³] | Initial electrolyte salt concentration |
| σ _{mof_1M_298K} | F^2 | Xu et al. 2020 experimental values used |
| | $D_{l_mof} \times C_{L_0} \times \overline{R \times T}$ | to back calculate MOF conductivity |
| | 3.23 x 10 ⁻⁷ [cm ² /s] | Xu et al. 2020 Paper Value of |
| D _{l_mof} | | Diffusivity measured by Pulsed Field |
| | | Gradient |
| β_{sep} | 1.5 | Separator Bruggeman coefficient |
| β_{pos} | 2.35 | Porous Cathode Bruggeman coefficient |
| β_{MOF} | 1.5 | MOF Layer Bruggeman coefficient |

 Table 3. Electrolyte Parameters.

The fourth set of parameters are the Active Particle Parameters, shown in Table 4. In this set of values, the Active weight material fraction in porous cathode, w_{active_pos} , Theoretical specific capacity of porous cathode, *theoretical_capacity*_{pos}, Electrical conductivity of porous cathode, $\sigma_{eletrical}$, Liu et al. 2018 LiCoO2 active particle size, rp_{pos} , Density of active material particles lithium metal anode, ρ_{active} , and Tang et al. 2019 Solid-phase diffusivity of porous cathode at 298K, $D_{s\ pos\ 298K}$, are defined. ^{29, 30}

In addition, the Initial specific capacity of porous cathode, *initial_capacity*_{pos}, Liu et al. 2018 LiCoO₂ real capacity of porous cathode, $real_capacity_{pos}$, Initial concentration of solid lithium in porous cathode, csO_{pos} , and Max concentration of solid lithium in porous cathode, csO_{pos} , and Max concentration of solid lithium in porous cathode, cs_{max_pos} , are defined. ²⁹

Table 4. Active Particle Parameters

| Name | Calculation | Description |
|-------------------------------------|--|--|
| Wactive_pos | 0.934 | Active weight material fraction in porous cathode |
| theoretical_capacity _{pos} | 274 [mAh/g] | Theoretical specific capacity of porous cathode |
| $\sigma_{eletrical}$ | 100 [S/m] | Electrical conductivity of porous cathode |
| rp_{pos} | 10e-6 [m] | Liu et al. 2018 LiCoO2 Active particle size |
| $ ho_{active}$ | 2270 [kg/m ³] | Density of active material particles lithium metal anode |
| D _{s_pos_298K} | 1E-11 [m ² /s] | Tang et al. 2019 Solid-phase diffusivity of porous cathode at 298K |
| initial_capacity _{pos} | SOC _{min} × theoretical_capacity _{pos} | Initial specific capacity of porous cathode |
| real_capacity _{pos} | 165 [mAh/g] | Liu et al. 2018 LiCoO2 real capacity of porous cathode |
| cs0 _{pos} | $initial_capacity_{pos} \times \rho_{pos}$ $\times \frac{w_{active_pos}}{F \times \varepsilon_{s_pos}}$ | Initial concentration of solid lithium in porous cathode |
| CS _{max _pos} | $\frac{theoretical_capacity_{pos} \times \rho_{pos}}{\times \frac{W_{active_pos}}{F \times \varepsilon_{s_pos}}}$ | Max concentration of solid lithium in porous cathode |

The fifth set of parameters are the Reaction Constant Parameters, shown in Table 5. In this set of values, Reaction rate coefficient lithium metal anode, k_{neg} , Reaction rate coefficient porous cathode, k_{pos} , Anodic transfer coefficient, α_a , and Cathodic transfer coefficient, α_c , are defined.

 Table 5. Reaction Constant Parameters.

| Name | Calculation | Description |
|------------------|---------------|---|
| k _{neg} | 6.64e-3 [m/s] | Reaction rate coefficient lithium metal anode |
| k _{pos} | 1e-10 [m/s] | Reaction rate coefficient porous cathode |
| α _a | 0.5 | Anodic transfer coefficient |
| α _c | 0.5 | Cathodic transfer coefficient |

The sixth set of parameters are the Known Constant Parameters, shown in Table 6. In this set of values, the Molar Gas constant, R, Faraday's constant, F, Initial electrolyte concentration, c_{ref} , and Isothermal Temperature, T, are defined.

| Name | Calculation | Description | |
|------------------|----------------------------|-----------------------------------|--|
| R | 8.31445 [J/(mol*K)] | Molar Gas constant | |
| F | 9.649e4 [C/mol] | Faraday's constant | |
| C _{ref} | 1000 [mol/m ³] | Initial electrolyte concentration | |
| Т | 298.15 [K] | Isothermal Temperature | |

The final set of parameters are the Transport Number Parameters, shown in Table 7. In this set of values, the Wu et al. 2020 Ionic Diffusivity with MOF estimated by NMR, $t_{plus_mof_nmr}$, Wu et al. 2020 Ionic Diffusivity estimated by NMR, $t_{plus_mof_evans}$, and Tu et al. 2017 Ionic Diffusivity without MOF by Evans Method, $t_{plus_no_mof_control}$, are defined. ^{20, 31}

 Table 7. Transport Number Parameters.

| Name | Calculation | Description |
|----------------------------------|-------------|---|
| t _{plus_mof_nmr} | 0.59 | Wu et al. 2020 Ionic Diffusivity with MOF |
| | | estimated by NMR |
| t _{plus_mof_} evans | 0.52 | Wu et al. 2020 Ionic Diffusivity estimated by |
| | | NMR |
| t _{plus_no_mof_control} | 0.2 | Tu et al. 2017 Ionic Diffusivity without MOF |
| | | by Evans Method |

2.4 LMB COMSOL Model Setup – Governing Equations and Initial

Values

The parameters discussed are used in a series of governing equations, boundary conditions, and initial values in order to accurately model the cell.

2.4.1. Solid Electrode Particles' Equations

The current density is defined via Equation 2.4.1-1 in the solid electrode particles.^{27,28} Here, i_s [C · m⁻² · s⁻¹] is the current density, and $\sigma_{s,eff}$ [S/m] is the effective electrical conductivity.

$$i_s = -\sigma_{s,\text{eff}} \nabla \phi_s \tag{2.4.1-1}$$

The total current density is defined via Equation 2.4.1-2, as $i_{\nu,\text{total}} [\text{C} \cdot \text{m}^{-3} \cdot \text{s}^{-1}]$. In this model, the arbitrary current source term, $Q_s [\text{C} \cdot \text{m}^{-3} \cdot \text{s}^{-1}]$ is considered to be zero.

$$-i_{\nu,\text{total}} + Q_s = \nabla \cdot i_s \tag{2.4.1-2}$$

The solid lithium mass balance is given via Equation 2.4.1-3. Inside the solid electrode particles, lithium diffuses to and from the particle surface. This rate of diffusion is related to the solid phase diffusivity, D_s [m²/s]. COMSOL solves this equation in the pseudo-1D r-dimension. The solid phase concentrations at each discretized nodal point of the particle serve as the independent variables.

$$\frac{\partial c_s}{\partial t} = \nabla \cdot (D_s \nabla c_s) \tag{2.4.1-3}$$

A boundary condition exists at the center of the particles, since the change in concentration with respect to the pseudo-1D r dimension here is zero. This no flux boundary is shown in Equation 3.4.1-4

$$\left. \frac{\partial c_s}{\partial r} \right|_{r=0} = 0 \tag{2.4.1-4}$$

Several initial conditions are used throughout the porous electrode, as described in equations 2.4.1-5,6,7 and 8. Here, the solid particles' initial concentration of lithium is $c_{s,0}$ [mol/m³], the initial electrolyte concentration is $c_{l,0} = 1000$ mol/m³, and the equilibrium potential (a function of SOC) is E_{eq} [V]. These liquid-phase initial conditions also apply to the separator domain.

$$c_l = c_{l,0} \tag{2.4.1-5}$$

$$c_s = c_{s,0} \tag{2.4.1-6}$$

$$\phi_l = \phi_{l,0} = 0 \tag{2.4.1-7}$$

$$\phi_s = \phi_{s,0} = E_{eq}(SOC) \tag{2.4.1-8}$$

2.4.2. Solid Electrode Particle Surfaces' Equations

The conversion of solid lithium to lithium ions occurs at the particle surface, and constitutes the main electrode reaction.^{27,28} The process is defined using Butler-Volmer kinetics as in equation 2.4.2-1 to give the local current, $i_{loc,m}$ [A/m²]. Here, $i_{loc,m}$ [A/m²] is a function of the overpotential, η [V], the anodic transfer coefficient, α_a , the cathodic transfer coefficient α_c and the zero overpotential transfer current, i_0 [A/m²].

$$i_{\text{loc},m} = i_0 \left(\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{\alpha_c F \eta}{RT}\right) \right)$$
(2.4.2-1)

The zero overpotential transfer current, i_0 [A/m²] is defined in equation 2.4.2-2 to be related to the aforementioned electrode transfer coefficients, the Faraday constant, *F*, the anodic rate constant, k_a [m/s], the cathodic rate constant, k_c [m/s], the reference concentration c_{ref} [mol/m³] and the maximum solid lithium concentration, $c_{s,max}$ [mol/m³].

$$i_0 = F(k_a)^{\alpha_c} (k_c)^{\alpha_a} (c_{s,\max} - c_s)^{\alpha_a} (c_s)^{\alpha_c} \left(\frac{c_l}{c_{\text{ref}}}\right)$$
(2.4.2-2)

The charge transfer reaction current, $i_{\nu,m}$ [A/m³] is defined in Equation 2.4.2-3 to be given by the specific surface area of the electrode particle $A_{\nu,m}$ [m²/m³], multiplied by the local current $i_{loc,m}$ [A/m²].

$$i_{\nu,m} = A_{\nu,m} i_{\text{loc},m}$$
 (2.4.2-3)

The total current density, $i_{v,total}$ [A/m³], is defined in Equation 2.4.2-4 to be the sum of charge transfer reactions, $\sum_{m} i_{v,m}$, and the double layer capacitance current, $i_{dl,m}$ [A/m³]. In this model, the double layer capacitance current was assumed to be zero, and only one charge transfer reaction is considered.

$$i_{\nu,\text{total}} = \sum_{m} i_{\nu,m} + i_{\text{dl},m}$$
 (2.4.2-4)

In the porous cathode, the electrode particles were modeled as small solid spherical particles of radius r_{active} [m]. The electrochemistry was modeled as lithium insertion reactions at the surface of these particles. The concentration of free reaction sites c_{Θ_s} [mol/m³] can be related to the total concentration of reaction sites, $c_{s,max}$ by Equation 2.4.2-5. However, since $c_{s,max}$ is assumed to be constant, the equation does not need to be solved to obtain $\frac{\partial c_s}{\partial t}$ or ∇c_s .

$$c_{\Theta_s} = c_{s,\max} - c_s \tag{2.4.2-5}$$

The maximum concentration of solid lithium, $c_{s,max}$, is calculated via Equation 2.4.2-6. This relates the maximum active material capacity, \tilde{Q}_{max} [C/kg], the calendared electrode density, ρ_{cal} [kg/m³], the weight fraction of active material w_{active} , and the active material volume fraction, ε_s .

$$\frac{[\tilde{Q}_{\max}] [\rho_{cal}][w]_{\text{pos}}}{[\varepsilon_s] F}$$
(2.4.2-6)

The Electrode state-of-charge, SOC, is defined by Equation 2.4.2-7 to be the ratio of inserted lithium concentration vs. maximum lithium concentration capacity. This is related to the equilibrium potential, E_{eq} [V], which gives rise to the SOC-OCV curve.

$$SOC = \frac{c_s}{c_{s,\max}}$$
(2.4.2-7)

The activation overpotential, η [V], is defined in equation 2.4.2-8 by relating the potential contributions. Here the SEI layer film resistance, $\Delta \phi_{s,\text{film}}$ [V], is assumed to be zero.

$$\eta = \phi_s - \Delta \phi_{s,\text{film}} - \phi_l - E_{\text{eq}}$$
(2.4.2-8)

A boundary condition exists at the surface of the solid electrode particles for the flux of lithium (according to the lithium insertion reaction). This is defined in Equation 2.4.2-9, where $N_{\text{shape}} = 3$ due to the particles being modeled as spherical, $n_m = 1$, and $v_{\text{Li}\Theta,m} = 1$.

$$-D_s \frac{\partial c_s}{\partial r}\Big|_{r=r_p} = -\sum_m \frac{\nu_{\text{Li}\Theta,m} i_{\nu,m}}{n_m F} \frac{r_p}{N_{\text{shape}} \varepsilon_s}$$
(2.4.2-9)

2.4.3. Lithium Metal Anode Surface Equations

While the lithium metal anode surface and porous cathode share similar charge-transfer equations.^{27,28} However, since the lithium metal anode is modeled as a surface, they have different overpotential, η , and zero overpotential transfer current, i_0 [A/m²], equations. These are given by Equation 2.4.3-1 and 2.4.3-2 respectively. Here, the external potential is zero, $\phi_{s,\text{ext}} = 0$, and the equilibrium potential is zero, $E_{\text{eq}} = 0$.

$$\eta = \phi_{s,\text{ext}} - \phi_l - E_{\text{eq}} \tag{2.4.3-1}$$

$$i_0 = F(k_a)^{\alpha_c} (k_c)^{\alpha_a} \left(\frac{c_l}{c_{\text{ref}}}\right)$$
(2.4.3-2)

A boundary condition also exists at the lithium metal anode surface for the flux of lithium. Here, the local current Equation 2.4.2-1 gives the local current, $i_{loc,m}$ [A/m²]. The double layer capacitance current, $i_{dl,m}$ [A/m³], is assumed to be zero. The lithium flux boundary condition is given by Equation 2.4.3-3, where $n_m = 1$ and $v_{Li\Theta,m} = 1$ for the lithium insertion reaction.

$$n \cdot N_l = -\sum_m \frac{\nu_{\text{Li}^+,m} i_{\text{loc},m}}{n_m F} - \frac{\nu_{\text{Li}^+,m} i_{\text{dl},m}}{n_m F}$$
(2.4.3-3)

2.4.4. Full Cell and Electrolyte Equations

The conservation of current in the electrolyte domains is given by Equation 2.4.4-1.^{27,28} This relates the current at any given point in the electrolyte, i_l [A/m²], to the (isothermal) temperature, T [K], the gas constant, R [J · mol⁻¹ · K⁻¹], the Faraday constant, F [C/mol], and the salt activity coefficient, f.

$$i_l = -\sigma_{l,\text{eff}} \nabla \phi_l + \frac{2\sigma_{l,\text{eff}}RT}{F} \left(1 + \frac{\partial \ln f}{\partial \ln c_l}\right) (1 - t_{\text{Li}^+}) \nabla \ln c_l$$
(2.4.4-1)

The electrolyte current is related to the total current density, $i_{v,total}$ [A/m³], via Equation 2.4.4-2. Here, the arbitrary current source term, Q_l [A/m³] is assumed to be zero.

$$i_{\nu,\text{total}} + Q_l = \nabla \cdot i_l \tag{2.4.4-2}$$

Within the electrolyte, a mass balance is also applied for the Lithium Ions. This is given by Equations 2.4.4-3. Here, the electrolyte porosity, ε_l , is related to the electrolyte's flux of lithium ions, N_I [mol \cdot m⁻² \cdot s⁻¹], and electrolyte's lithium ion source term, R_l [mol \cdot m⁻³ \cdot s⁻¹].

$$\varepsilon_l \frac{\partial c_l}{\partial t} + \nabla \cdot N_l = R_l \tag{2.4.4-3}$$

The flux of lithium ions within the electrolyte, N_I [mol \cdot m⁻² \cdot s⁻¹] is related to the electrolyte current, i_l [A/m²], the transport number, t_{Li^+} , the Faraday constant, F [C/mol], and the effective electrolyte salt diffusivity, $D_{l,\text{eff}}$ [m²/s]. This is shown in Equation 2.4.4-4.

$$N_{l} = -D_{l,\text{eff}} \nabla c_{l} + \frac{i_{l} t_{\text{Li}^{+}}}{F}$$
(2.4.4-4)

The lithium ion source term, R_l [mol \cdot m⁻³ \cdot s⁻¹], is related to the charge transfer reaction current, $i_{\nu,m}$ [A/m³], via Equation 2.4.4-5. As previously, $\nu_{\text{Li}^+,m} = -1$ and $n_m = 1$ for the lithium insertion reaction, and the double layer capacitance current is assumed to be zero, $i_{\text{dl},m}$ [A/m³] = 0. The additional term, $R_{l,\text{src}}$ [mol \cdot m⁻³ \cdot s⁻¹] is a placeholder for an additional reaction source but is not used in this model (assumed to be zero).

$$R_{l} = -\sum_{m} \frac{\nu_{\text{Li}^{+},m} i_{\nu,m}}{n_{m}F} - \frac{\nu_{\text{Li}^{+},m} i_{\text{dl},m}}{n_{m}F} + R_{l,\text{src}}$$
(2.4.4-5)

The electrolyte in the separator domain and MOF layer follow the same Equations 2.4.4-1 to 2.4.4-5, but the lithium ion source term is zero, $R_l = 0$.

The Bruggeman model was used to account for the porosity effect in the porous cathode. This gives rise to $D_{l,eff}$ [m²/s], the effective liquid-phase diffusivity, as in Equation 2.4.4-6. Here, β is the Bruggeman coefficient, and ε_l is the electrolyte porosity.

$$D_{l.\text{eff}} = D_l \varepsilon_l^{\beta} \tag{2.4.4-6}$$

Further, it gives rise to $\sigma_{l,eff}$ [S/m], the effective electrolyte conductivity, as in Equation 2.4.4-7. Here, β is the Bruggeman coefficient and ε_l is the electrolyte porosity.

$$\sigma_{l,\text{eff}} = \sigma_l \varepsilon_l^{\beta} \tag{2.4.4-7}$$

Lastly, it gives rise to $\sigma_{e^-,eff}$ [S/m], the effective electric conductivity, as in Equation 2.4.4-8. Here, ε_s is the solid porosity.

$$\sigma_{e^-,\text{eff}} = \sigma_{e^-} \varepsilon_s \tag{2.4.4-8}$$

The positive current collector next to the porous cathode cannot accept or donate any Lithium Ions, and therefore a no flux boundary condition exists. The no flux boundary condition is given by Equation 2.4.4-9.

$$-n \cdot N_I = 0 \tag{2.4.4-9}$$

The negative current collector would have a similar boundary condition if it were modeled, however the right most point of the geometry in this model is the lithium metal anode surface, and for this the boundary condition is given by Equation 2.4.3-3.

2.5 LMB COMSOL Model Setup – SOC OCV Curve

The State of Charge vs. Open Circuit Voltage (SOC-OCV) curve is used as another data input for the model.^{27,28} COMSOL Multiphysics Batteries and Fuel Cells Module provides this SOC-OCV curve for the Lithium Cobalt Oxide (LiCoO₂) cathode, and is shown in Figure 11.



Figure 11: State of Charge (SOC) vs. Open Circuit Voltage (OCV) Curve for LiCoO₂ in COMSOL Multiphysics.

Due to LiCoO₂ having irreversible damage to the electrode at high voltages, the theoretical capacity is not realistic, and so the SOC-OCV curve only operates over a commercial/realistic range of 3.0/3.5 - 4.35 V. Operating at a higher voltage than 4.35 V requires specially modified LiCoO₂ materials.^{8, 18} Therefore, while the theoretical max capacity is 274 [mAh/g], this corresponds to a peak voltage of 5.2V, which is not achievable in industry. Thus for this model, and in the COMSOL SOC-OCV curve, the SOC_{min} is limited to 0.4 and SOC_{max} to 0.98 in order to keep within realistic operating range. This corresponds to a real max capacity of around 145 – 180 [mAh/g].^{8, 18}

2.6 LMB COMSOL Model Setup – Assumptions List

In order to model the cell in COMSOL, a number of assumptions were made. These simplifications improve computation time and reduce complexity, while maintaining accuracy of the desired key electrochemical results produced by the model. If analyzing further aspects, such as the effect of temperature, or capacity fade, became desirable in future work, then some of these assumptions could be removed. The following Table 8 produced by A. Fortini summarizes the key assumptions made.²⁸

| # | Assumption |
|----|--|
| 1 | 1D Battery Model (no deviation in y or z directions) |
| 2 | Isothermal Model |
| 3 | No Dissolving-Depositing Species |
| 4 | No SEI Film Resistance |
| 5 | No Double-Layer Capacitance |
| 6 | No Stress or Strain |
| 7 | Bruggeman Effective Transport |
| 8 | All transport equations shown |
| 9 | All constant parameters shown |
| 10 | All parameter equations shown |
| 11 | OCV vs. SOC curve shown |

Table 8. List of Assumptions in COMSOL battery simulation.

3 Results and Discussion

3.1 Activity Dependence in Positive Electrode

In order to evaluate the electrochemical performance of the cell, it is necessary to first model the activity dependence, electrolyte conductivity, and electrolyte diffusivity in the positive electrode. The activity dependence is given by Equation 3.1-1, which gives the activity dependence expression as a function of lithium ion transport number, $t_{\rm Li^+}$, electrolyte concentration, c_l , and temperature, T.

$$\left(1 + \frac{\partial \ln f}{\partial \ln c_l}\right) = \frac{\alpha_{1,25^\circ \mathbb{C}} \cdot e^{\left(\frac{E_{a,\alpha_1}}{T} \left(\frac{1}{298 \text{ K}} - \frac{1}{T}\right)\right)} c_l^2 + \alpha_{2,25^\circ \mathbb{C}} \cdot e^{\left(\frac{E_{a,\alpha_2}}{T} \left(\frac{1}{298 \text{ K}} - \frac{1}{T}\right)\right)} c_l + \alpha_{3,25^\circ \mathbb{C}} \cdot e^{\left(\frac{E_{a,\alpha_3}}{T} \left(\frac{1}{298 \text{ K}} - \frac{1}{T}\right)\right)} (1 - t_{\text{Li}})}$$
(3.1-1)

In addition, there are a series of isothermal $T = 25^{\circ}C$ constants that are necessary to calculate the activity dependence, and these have been provided by Lundgren et al.: $\alpha_{1,25^{\circ}C} [dm^6 \cdot mol^{-2}], \alpha_{2,25^{\circ}C} [dm^3 \cdot mol^{-1}], and \alpha_{3,25^{\circ}C} [unitless].^{32}$ Finally, there are a number of corresponding activation energies, $E_{a,\alpha_1} [J/mol], E_{a,\alpha_2} [J/mol], and E_{a,\alpha_3} [J/mol],$ which allow the previous isothermal constant parameters to be scaled with temperature. A table of the values of these 6 parameters is given in Table 9.

| Parameter | Value |
|---------------------|--|
| α _{1,25°C} | $0.2731 dm^6 \cdot mol^{-2}$ |
| α _{2,25°C} | $0.6352 \mathrm{dm^3 \cdot mol^{-1}}$ |
| α _{3,25°C} | 0.4577 |
| E _{a,α1} | 8350 J/mol |
| E _{a,α2} | 9400 J/mol |
| E_{a,α_3} | 1750 J/mol |

 Table 9. Constant parameters used in Equation 3.1-1.

The anion transport number, $(1 - t_{Li^+})$, is used to scale the activity dependence, $(1 + \frac{\partial \ln f}{\partial \ln c_l})$ and the product of these two expressions is given on the z axis. The overall activity dependence expression is given as a function of the electrolyte concentration, $c_l \left[\frac{mol}{m^3}\right]$, on the x-axis and Temperature, T [K], on the y-axis in Figure 12. As expected, the surface plot shows positive relationships for both concentration, and temperature on the activity dependence. Within the variable ranges (250 to 400K, and 0 to 2000 mol/m³), it appears that they have an almost equal effect on the activity dependence. At the isothermal assumed operating temperature of 298K, the slope for the activity dependence is quite steep between 0 and 2000 mol/m³. This indicates that at the expected cell operating conditions, electrolyte concentration will have a large impact on electrochemical performance. The COMSOL 1D model was subsequently programmed to automatically solve for the activity dependence at every discretized node on the mesh while solving for other output parameters.



Figure 12. Product of activity dependence and the anion transport number as a function of concentration and temperature.

In addition, the positive electrode's solid-phase diffusivity, $[D_s]_{pos}$ [m²/s], is dependent on temperature as defined in Equations 3.1-2, and 3.1-3. This is not graphed because for this model, the conditions are assumed to be isothermal.

$$[D_s]_{\text{pos}} = [D_s]_{\text{pos},298\text{K}} \cdot \exp\left(\frac{E_{a,D_s}}{R}\left(\frac{1}{298.15\text{ K}} - \frac{1}{T}\right)\right)$$
(3.1-2)

$$E_{a,D_s} = 69025.7 \text{ J/mol}$$
 (3.1-3)

3.2 Electrolyte Conductivity in the Positive Electrode

Similarly, the ionic conductivity had to be calculated within the Positive Electrode in order to know its values across a range of electrolyte concentrations and temperatures. Lundgren et al. provide a formula to calculate the ionic conductivity specifically for 1:1 LiPF₆ in EC/DEC and this is given by Equation 3.2-1. Here, the subscript *i* is a placeholder for t, the total electrolyte conductivity, or either of its component parts' (a, the anion's or c, the cation's) conductivity.

$$\sigma_{l} = e^{\left(\frac{E_{a,A1}}{T}\left(\frac{1}{298.15 \text{ K}} - \frac{1}{T}\right)\right)} c_{i}^{3} + A2_{25^{\circ}\text{C}} \cdot e^{\left(\frac{E_{a,A2}}{T}\left(\frac{1}{298.15 \text{ K}} - \frac{1}{T}\right)\right)} c_{i}^{1.5} + A3_{25^{\circ}\text{C}} \cdot e^{\left(\frac{E_{a,A3}}{T}\left(\frac{1}{298.15 \text{ K}} - \frac{1}{T}\right)\right)} c_{i}$$
(3.2-1)

This equation was then normalized by the $c_l = 1M$, T = 298K value, and this allows the standard conductivity to be set at standard conditions, while the equation scales across a range of temperatures and concentrations. This normalized equation is given by Equation 3.2-2. Here *j* is a placeholder for s, the separator, or p, the porous cathode.

$$\sigma_{l} = [\sigma_{i}]_{j,1M,298K} \cdot \{e^{\left(\frac{E_{a,A1}}{T}\left(\frac{1}{298.15 \text{ K}} - \frac{1}{T}\right)\right)} c_{i}^{3} + A2_{25^{\circ}\text{C}} \cdot e^{\left(\frac{E_{a,A2}}{T}\left(\frac{1}{298.15 \text{ K}} - \frac{1}{T}\right)\right)} c_{i}^{1.5} + A3_{25^{\circ}\text{C}} \cdot e^{\left(\frac{E_{a,A3}}{T}\left(\frac{1}{298.15 \text{ K}} - \frac{1}{T}\right)\right)} c_{i}^{3} / (A1_{25^{\circ}\text{C}} + A2_{25^{\circ}\text{C}} + A3_{25^{\circ}\text{C}})$$
(3.2-2)

Similar to the activity dependence, there are a series of isothermal T = 25 °C constants that are necessary to calculate the electrolyte conductivity, and these have also been provided by Lundgren et al.³² Again, there are a series of corresponding activation energies which allow the previous isothermal constant parameters to be scaled with temperature. A table of the values of these 6 parameters is given in Table 10.

| Parameter | Value |
|--------------------|---|
| A _{1,25℃} | $1.147 \text{ dm}^8 \cdot \text{mol}^{-3}$ |
| A _{2,25℃} | $-22.38 \mathrm{dm^{3.5} \cdot mol^{-1.5}}$ |
| A _{3,25℃} | $29.15 \text{ dm}^2 \cdot \text{mol}^{-1}$ |
| E _{a,A1} | 520 J/mol |
| E _{a,A2} | 1010 J/mol |
| E_{a,A_3} | 1270 J/mol |

 Table 10. Constant parameters used in Equation 3.2-2.32

Equation 3.2-2 was used to create the 2D surface plot of porous cathode electrolyte conductivity, $[\sigma_l]_{pos}$ [S/m], as a function of the electrolyte concentration, c_l , and temperature, *T*, as shown in Figure 13. Between concentrations of ~750 and 1100 mol/m³, the electrolyte conductivity is seen to peak between ~0.6 and 0.9 S/m, the former being achieved close to T = 250 K, and latter close to T = 350 K. While the electrolyte conductivity has an almost linear positive relationship with temperature, the electrolyte conductivity has a horseshoe shaped relationship with the electrolyte concentration. This indicates that smaller deviations from the initial electrolyte concentration of 1000 mol/m³ are desirable. Similar to the activity dependence results, the COMSOL 1D model was subsequently programmed to automatically solve for the electrolyte conductivity at every discretized node on the mesh while solving for other output parameters.



Figure 13. Electrolyte conductivity in the positive electrode as a function of electrolyte concentration and temperature.

3.3 Electrolyte Diffusivity in Positive Electrode

The third and final positive electrode value which had to be evaluated is electrolyte diffusivity. Similar to the previous two properties, the electrolyte diffusivity, $[D_l]_{pos}$ [m²/s], is a function of the electrolyte concentration, c_l , and the temperature, T as shown in Figure 14. Chintapalli et al. (2016) provide this relationship in Equation 3.3-1.

$$[D_i]_j = [\sigma_i]_j \frac{\mathrm{RT}}{c_i F^2} \tag{3.3-1}$$

Just as for the electrolyte conductivity, here the subscript i is a placeholder for t, the total electrolyte conductivity, or either of its component parts' (a, the anion's or c, the cation's) conductivity. In addition, the j is a placeholder for s, the separator, or p, the porous cathode.



Figure 14. Electrolyte diffusivity in the positive electrode as a function of electrolyte concentration and temperature.

3.4 Voltage vs. Specific Capacity

The effect of the addition of a MOF layer to the Lithium Metal Battery cell's performance was investigated by a series of electrochemical performance simulations. Xu et al. (2020) previously demonstrated that the MOF layer was able to significantly improve cycling

stability, and suppress the growth of lithium dendrites. It is interesting to compare the performance of the MOF layer cell vs. a control cell at different C-rates over a charge/discharge cycle. The voltage window was selected in accordance with the literature described in section 2.5, and an 8 μm MOF layer was tested against a bare LMA vs. LCO cell with no MOF layer. The results for the voltage (V) vs. specific capacity (mAh/g) data are shown in Figure 15.



Figure 15. Voltage (V) vs. specific capacity (mAh/g) for LMA vs. LCO cell with and without an 8 μm MOF layer. Simulated in COMSOL Multiphysics.

The MOF layer cell shows an improvement even on a single charge/discharge cycle. This indicates that the increased lithium ion transport number, t_{Li^+} , has a large effect on the real capacity. In this model the σ_{Li^+} is actually lower for the MOF model because no standard SEI

film resistance is considered in the control. While σ_{Li^+} for the MOF layer is one order of magnitude lower than bulk electrolyte, it is 5 orders of magnitude faster than in a pristine SEI layer that can develop on the LMA surface, and 2 orders of magnitude faster than polymer or ceramic solid electrolyte solutions. This indicates that the lithium ion transport number, t_{Li^+} , has a large enough improvement to outweigh the lack of an SEI film resistance assumption.

The improvement in capacity is larger at higher C rates, indicating that MOF layers may be useful in higher C-rate applications as well. Finally, it is worth noting that, based on Wu et al. (2020)'s results, extended cycling would be expected to drastically increase the specific capacity gap between the MOF and no MOF cells over time.²⁰

3.5 Electrolyte Salt Concentration Profiles

The electrolyte concentration profiles for both the MOF and no MOF cells are shown in Figures 16 and 17 respectively. A full 0.1C charge/discharge cycle is shown, with a 12 hour rest in between discharging and charging. The electrolyte concentration is given on the y-axis, while the x-coordinate is given on the x-axis (with the porous cathode on the left hand side, and lithium metal anode on the right hand side). Each time step is represented by a curve, and these start at t = 0 from the bottom left quadrant, fanning upward to t = max originating from the top left quadrant.



Figure 16. Electrolyte salt concentration vs. x-coordinate during a 0.1C full charge/discharge cycle of LMB vs LCO cell with MOF layer.

In Fig 3.5-1, the electrolyte salt concentration of the MOF layer model deviates in a maximum range of ~910-1080 mol/m³. By contrast, the electrolyte salt concentration of the model with no MOF layer deviates in a significantly larger maximum range of ~830 to 1140 mol/m³. The COMSOL simulation has provided further evidence to support that the MOF layer successfully reduces the concentration polarization. As discussed in section 3.2, this will also lead to a lower electrolyte conductivity. Finally, this data reinforces one method through which the MOF layer indirectly suppresses Lithium dendrite growth.



Figure 17. Electrolyte salt concentration vs. x-coordinate during a 0.1C full charge/discharge cycle of LMB vs LCO cell – no MOF layer.

3.6 Electrolyte Salt Potential Profiles

Similarly, the electrolyte potential profiles for both the MOF and no MOF cells are shown in Figures 18 and 19 respectively. A full 0.1C charge/discharge cycle is shown, with a 12 hour rest in between discharging and charging. The electrolyte potential is given on the y-axis, while the x-coordinate is given on the x-axis (with the porous cathode on the left hand side, and lithium

metal anode on the right hand side). Each time step is represented by a curve, and these start at t = 0 from the bottom left quadrant, fanning upward to t = max originating from the top left quadrant.



Figure 18. Electrolyte salt concentration vs. x-coordinate during a 0.1C full charge/discharge cycle of LMB vs LCO cell with MOF layer.

In Fig 3.6-1, the electrolyte salt potential of the MOF layer model deviates in a maximum range of -0.0225 to 0.02 V. By contrast, the electrolyte salt concentration of the model with no MOF layer deviates in a significantly larger maximum range of -0.035 to 0.025 V. Here, the

COMSOL simulation provides evidence that the potential polarization is significantly reduced by the MOF layer, helping to suppress Lithium Ion dendrite growth and improve cycling capability.



Figure 19. Electrolyte salt concentration vs. x-coordinate during a 0.1C full charge/discharge cycle of LMB vs LCO cell with MOF layer.

4 Conclusion

In summary, the greatest advances in Lithium Ion Battery (LIB) research in the near future will come in the form of high specific capacity and energy density LIBs. In order to achieve these, the commercial challenges of high specific energy electrodes, such as the Lithium Metal Anode (LMA), will need to be overcome. The LMA MOF layer solution presented by Xu et al. $(2020)^{20}$ has shown extremely promising results in both lithium dendrite suppression and electrochemical performance of LMBs. The Finite Analysis Model created in COMSOL herein showed that, without the MOF layer, a standard LMB cell can exhibit, respectively, 80% and 40% higher polarization of the electrolyte concentration and potential. The MOF layer's ability to reduce electrolyte polarization so significantly, reinforces its unique ability to alter the electrochemical processes close to the LMA surface and suppress lithium dendrite growth. Furthermore, the charge/discharge cycling simulations showed that the MOF layer LMB exhibited greater specific capacities than without a MOF layer, especially at higher C rates thanks to the increased overall Lithium Ion Transport number, t_{Li^+} . This, coupled with the MOF layer's high electrolyte conductivity, σ_{Li^+} , relative to competitor dendrite suppressant layers render it a very promising avenue of research for funding. In future, it is anticipated that advanced finite analysis software such as COMSOL Multiphysics will be an increasingly powerful and prevalent tool guiding LIB research.

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