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Development and Analysis of Solid-State Batteries through Implementation of the COMSOL® Platform

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Abstract

This report explores the utilization of COMSOL® to investigate material properties and perform finite element analysis in solid-state batteries. Through the use of a numerical composition simulation software, researchers are investigating materials, prototypes, and projects before implementing new solutions in the lab. The COMSOL® platform provides the team with the ability to research underlying properties, such as, state of charge, charge capacity, and internal resistance, while also enabling more pointed material selection. Through its use, experimenters conduct theorized optimal adjustments using the various modules of COMSOL®, including: AC/DC, Semiconductor, Fluid Flow, Heat Transfer, Electrochemistry. The first stage in developing such impactful technology is designing a storage device that maximizes electrolyte potential, C-rates, and surface concentrations.

Introduction

Over the years, the increase of energy density in lithium-ion batteries has begun to plateau. The impact of mainstream consumer electronics alone has doubled lithium-ion battery production, making it clear that the need for more viable energy storage solutions is immediate.[3] Extensive research in material science coupled with advances in computer databases have allowed researchers access to powerful software tools that may be used for simulating the structural behaviour before performing any lab experiments. These program components allow for the specification of behaviours and interactions for materials tested. This is integral in the pursuit of developing solid-state batteries that function efficiently, safely, and sustainably, since the specifications of such parameters will enable fabrication of energy storage solutions that are less detrimental to the environment, but have higher energy densities than lithium-ion batteries.

Historical background

The concept of a solid-state battery was first introduced in the 1800s, with a solid-state battery showing potential for the first time in the 1950s.[2] Within this decade, many industries and universities such have been filing patents for this concept, some investing tens of millions for the research

The basic components of the solid-state battery are the electrodes, which consist of a positive cathode and negative anode, a solid electrolyte, and, usually, separators to prevent short circuits. Different material combinations of the anode, cathode, and electrolyte are constantly being tested to achieve the highest performance at a reasonable price.

Reasons for Solid-State Batteries

Beyond the crisis of the lithium-ion plateau, the trend towards solid-state is driven by efficiency on a variety of levels. Solid-state batteries have been proven to be a more eco-friendly alternative to their liquid counterpart. The use of solid electrolytes means batteries are both less flammable and more durable, since they are non-flammable and react much less frequently, hardly undergoing decomposition reactions at all. This results in safer, more durable, longer lasting batteries. Maximizing the power density of solid-state batteries to match or surpass that of lithium-ion batteries is integral to both the future of solid-state batteries as well as energy storage solutions and green energy practices. Designing an efficient system utilizing solid-state electrodes sets the foundation for fabricating this kind of efficient, green, durable batteries.[3]

Experimental Set-up

Research has shown that a large drawback of solid-state energy storage has been the low levels of conductivity, which is drastically different than that of liquid lithium-ion batteries. The means to mitigate this has been to rely on solid material on the micro and nano scales. Within the library of COMSOL simulation examples, a thin-film, one dimensional model of solid-state mechanics has been built evidencing the performance of such a device.[4] While this model provides insight into the functionality of solid-state batteries, it is only theoretical, as a one dimensional battery is not feasible for fabrication. It does, however, provide a basis from which to work in designing a multidimensional solid-state battery. Relying on the basis COMSOL provided, a two-dimensional rendering of a solid-state battery was crafted utilizing the same lithium-based components as the one-dimensional model. The aim was to verify that the functionality observed in one dimension carried over into the two dimensional variant and lead to future analysis of achievable battery structures. The two-dimensional variant would be considered valid so long as the behaviours exhibited through various interfacing techniques emulated those of the one-dimensional battery.

Reasons for using COMSOL

The COMSOL platform has the capacity to enable researchers to be more cost effective by allowing for design and material testing simulations before actual experimentation. This means more informed decisions about research materials and less funds spent testing different layouts and materials, while still gaining valuable insight into the impact of geometry and material types within the batteries. It is also important to note that the environmental impact of conducting research in this way is significantly less than other methods simply because the model is computer generated.

Simulation

Using COMSOL Multiphysics, electrochemical processes were tested in a geometric design portraying an electrolyte and positive electrode; the device's negative electrode was assumed to have high electric conductivity and therefore, was not included. Parameters were set outlining constant values throughout the simulation, such as the thickness of the electrolyte and electrode, initial lithium concentrations in both, and charge transfer coefficients. Initial values of lithium in the electrolyte and positive electrode were specified as well.

Use of Simulation Apps

Materials designated for use within both the two-dimensional and one-dimensional simulations involved lithium-based compounds for both the electrolyte and electrode - a solid Li_3PO_4 electrolyte and $LiCoO_2$ electrode. Multiple studies were conducted to calculate electrolyte potential, C-rates, and surface concentrations of both the electrode and the electrolyte. Both physics and electrochemical interfaces were utilized to perform calculations, specifically, Tertiary Current Distribution (TCD) in the positive electrode, and Transport of Diluted Species (TDS) in the electrolyte. To increase the accuracy of all simulations, extra fine and extremely fine mesh were used to further define the geometry and provide a higher quality device to extract data from. All simulations ran were time dependent and required time constraints; these constraints were modified to prevent test errors in which COMSOL showed a singularity. In the process of mitigating instances of singularity, it was discovered that the size of electrodes played a stabilizing role. This became a subsidiary research point. To further address the singularity issue, stop conditions were included to prevent the solver process from gathering calculations once the ion concentrations reached a maximum value of 23,300 mol/m^3 in the positive electrode.

Simulation Results

One-Dimensional Battery

The geometry of the solid-state battery shown in Figure 1 below, shows two domains and three boundaries, which represent specific components of the device - the negative electrode, the positive electrode, and the electrolyte between them. Each electrode is visualized by the COMSOL software as a dot along the one-dimensional electrolyte, which is visualised as a line.

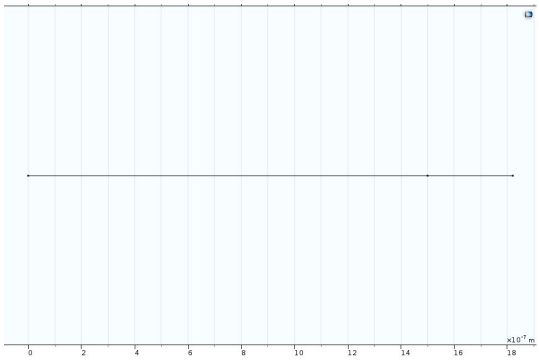

Figure 1. Geometric view of one-dimensional solid-state battery

Figure 2 depicts a comparison of various discharge rates. The data shows initial voltage at about 4.19 V, as the lithium ions and lithium species migrate, the voltage decreases over time. When the solid lithium concentration reaches its maximum activity value, the voltage drops rapidly.

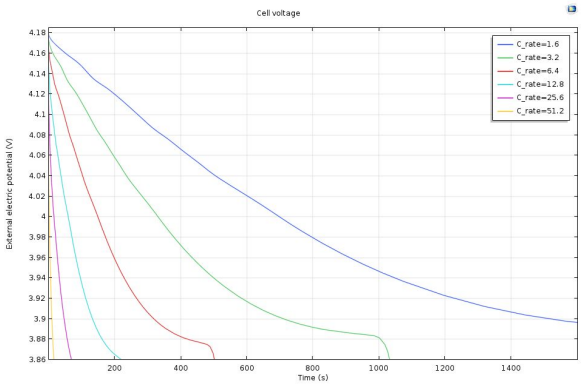

Figure 2. Cell voltage over time in one dimensional battery

Two-Dimensional Battery

The geometry of the two-dimensional solid-state battery shown in Figure 3 has two domains and three boundaries. The far left boundary is the negative electrode, the left domain is the electrolyte, and the right domain is the positive electrode. The sizes of the positive electrode and electrolyte vary from case to case, but the height stays constant at 1 nm^2.

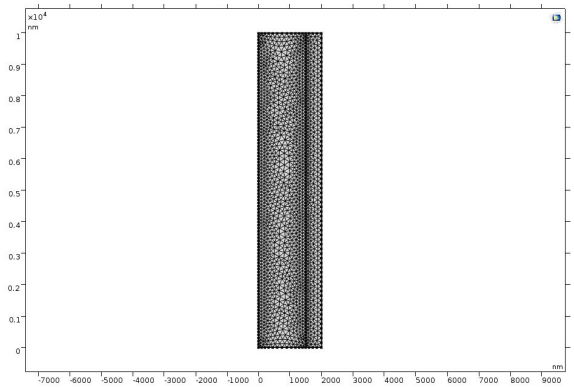

Figure 3. Geometric view of two-dimensional solid-state battery

Two-Dimensional Battery Case 1

The initial case created for the two-dimensional solid-state battery had a 1500 nm^2 area allotted to the electrolyte and 500 nm^2 for the electrode. The battery was tested at various discharge rates for external electric potential over time. As time progresses, the external electric potential gradually decreases. The different discharge rates affect how quickly potential is lost; the higher the discharge rate the quicker potential is lost.

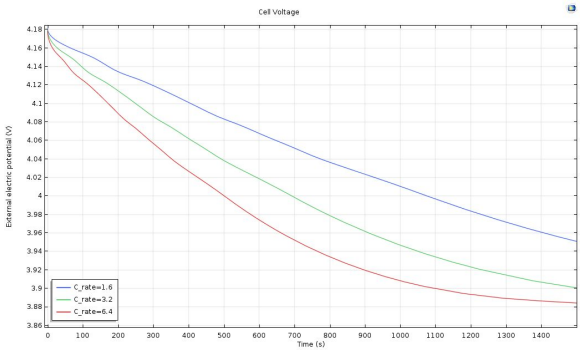

Figure 4. Case 1. Two-dimensional battery (1500 nm^2 Electrolyte and 500 nm^2 Electrode) cell voltage over time

Figure 5 shows the potential of lithium ions as it travels through the electrolyte in the first case of the 2-D variant; the potential decreases as it moves closer to the positive electrode. The figure depicts vectors of the current density within the electrolyte.

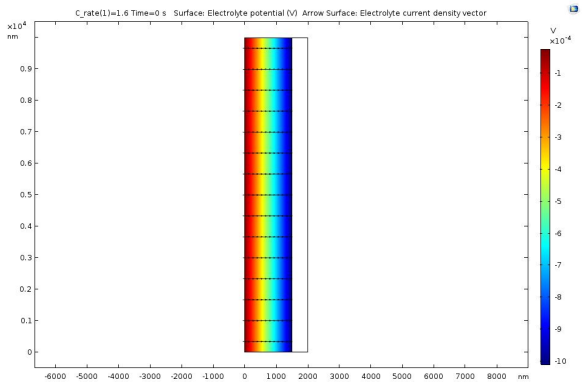

Figure 5. Case 1. Electrolyte surface concentration of lithium ions

Two-Dimensional Battery Case 2

Figure 6, below, shows a comparison of the same discharge rates as depicted previously in Case 1 with the geometry of both the electrolyte and the electrode altered to 900 nm^2 and 700 nm^2, respectively. The graph indicates that the lithium relocates causing voltage to decrease.

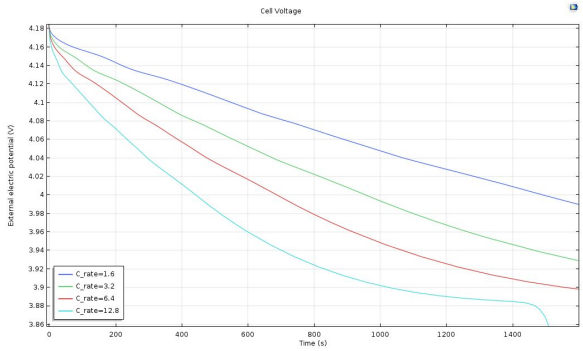

Figure 6. Case 2. Two-dimensional battery (900 nm^2 Electrolyte and 700 nm^2 Electrode) cell voltage over time

In Figure 7 the aforementioned the potential of lithium ions traveling through electrolyte is depicted; as in Case 1, the potential decreases nearer the positive electrode. This behaviour, while not identical to previous instances, emulates both the initial two-dimensional case as well as the one-dimensional control.

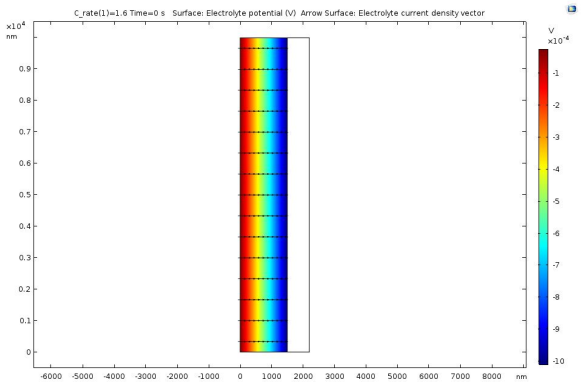

Figure 7. Case 2. Electrolyte surface concentration of lithium ions

Two-Dimensional Battery Case 3

The graph below, Figure 8, shows the effects of the discharge rates used in previous cases when altering the geometry of the electrolyte to 1500 nm^2, and the positive electrode to 700 nm^2.

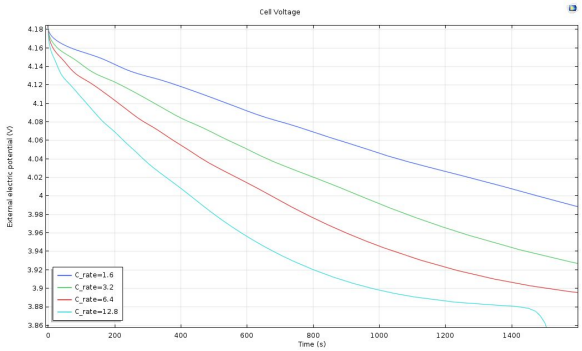

Figure 8. Case 3. Two-dimensional battery (1500 nm^2 Electrolyte and 700 nm^2 Electrode) cell voltage over time

Figure 9 shows the familiar delineation of lithium ions' potential on the path towards the 700 nm^2 electrode through a 1500 nm^2 electrolyte. As in all previous scenarios, the potential of the ions is less in areas closest to the positively charged electrode.

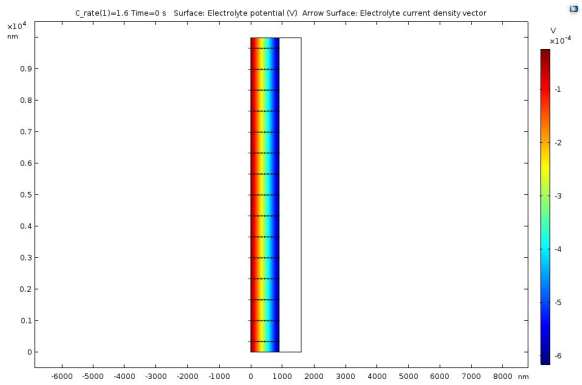

Figure 9. Case 3. Electrolyte surface concentration of lithium ions

Discussion

The results of the various one-dimensional and two-dimensional solid-state simulations exhibit similar, but still distinct behaviour. Analysis of the cell voltage data shows a much more gradual descent of the external electric potential in the two-dimensional batteries. The graphs of the one-dimensional battery, however, show discharge rates of 6.4 V and 3.2 V dropping suddenly as they approach 0 seconds, while 1.6 V continues past 3.919 seconds. The two-dimensional batteries, conversely, show discharge rates continuing past 1600 seconds for these potential measures, indicating that it holds external electric potential for longer than the one-dimensional battery. The electrolyte transfer data suggests there are slight differences between the cases of the two-dimensional batteries, the primary distinction being the initial and terminal values of voltage. A larger electrolyte generally correlates to a broader the range of voltages, which is a possible signifier that the battery has a larger capacitance. In each two-dimensional variant case the batteries' geometry was the sole variable. The effects of these slight changes were evidenced in discharge rate and the range of voltage, but were overall minimal and nondisruptive towards general performance.

Future Research

The findings of these simulations provide a basis to investigate two-dimensional devices utilizing other COMSOL modules, such as Corrosion, MEMS and Electrochemistry. Additionally, this work gives insight into the means necessary for the development of a three-dimensional solid-state battery. The corrosion module provides a platform for experimenting with how well the battery will fare under different conditions, giving insight into durability. The MEMS module allows for users to simulate thermal stresses placed upon an object, and the Electrochemistry module provides interfaces for the analysis of charge transfer coefficients current densities, and current distributions.

A design that would more accurately represent a solid-state battery that is both functional and feasible for fabrication. the most practical means to construct the battery model for such simulations would be using graphene in the electrolyte, as it is the only material that reaches two-dimensionality. Finite element analysis will be necessary to study the most effective materials to compose a solid-state battery, with graphene being a likely candidate; furthermore, materials can be synthesized using extrapolated data to produce a superior alternative to current solid-state batteries.

Conclusions

Using COMSOL, a two-dimensional model of a lithium-ion solid-state battery could be created and used to generate accurate simulations of battery physics. Three two-dimensional solid-state batteries, each with electrodes of different sizes, were analyzed to compare the cell voltage and electrolyte ionic surface concentration. The two-dimensional battery Case 2 reached its maximum activity value of solid lithium concentration at higher time compared to Case 1 and Case 3, suggesting that a solid-state battery with a smaller electrolyte layer may be best suited for future research, since the maximum activity value for solid lithium in the positive electrode is the maximum level of solid lithium the electrode is able to contain. A comparison of the electrolyte surface concentration indicates that the two-dimensional solid-state battery Case 3 with a 1500 nm^2 Electrolyte and 700 nm^2 Electrode has the greatest potential where the electrolyte and electrode meet. A solid-state battery matching these dimensions should be used for future research.

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