

# Study of LTO as Anode in Lithium-ion batteries Using a Theoretical Model

A DISSERTATION

SUBMITTED IN THE FULFILMENT OF THE  
REQUIREMENTS FOR THE AWARD OF DEGREE

*(Masters in Physics)*

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## DECLARATION

We hereby certify that this work which is presented in the Major Project-II entitled **Study of LTO as Anode in Lithium-ion batteries Using a Theoretical Model** in fulfilment of the requirement for the award of the Degree in **Masters in Physics** and submitted to the **Department of Applied Physics**, Delhi Technological University, Delhi is an authentic record of our own, carried out during a period from January to May 2022, under the supervision of **Dr. Sarita Baghel and Dr. Amrish K. Panwar**. We have not submitted the information in this report for the award of any other degree from this or any other Institute/University. The work has been published/accepted/communicated in **ICAPIE OR peer-reviewed Scopus indexed conference** with the following details:

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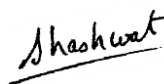
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Dear Authors,

Authors: Shashwat Sharma, Neelima Kawatra, Sarita Baghel, Amrish Panwar

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This is to enlighten you that the aforementioned paper is accepted for consideration for publication in **Advances in Transdisciplinary Engineering (ATDE)**, a Scopus Indexed Publication of IOS Press/ **International Journal of Electrical and Electronics Research (IJEER)**, a Scopus Indexed journal, subjected to presentation **during 7th International Conference on Advanced Production and Industrial Engineering ICAPIE'22** scheduled to be organized during **June 11-12, 2022**.

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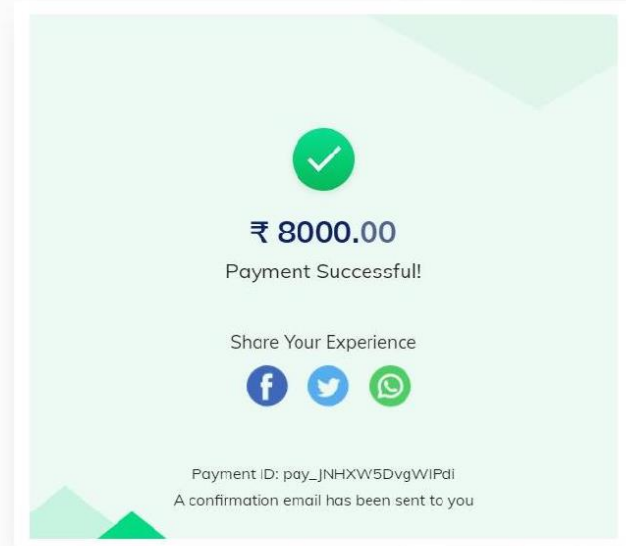
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*Shashwat*

**SHASHWAT SHARMA**

*Neelima Kawatra*

**NEELIMA KAWATRA**



## ABSTRACT

The performance of a battery is often determined by a number of factors and it is critical to tweak these factors in order to improve cell performance. In this study, parameters of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO)/  $\text{LiMn}_2\text{O}_4$  (LMO) materials made battery is modelled using 1-D cell geometry to obtain better electrochemical performance. The thicknesses of anode material, LTO has been adjusted as  $75\mu\text{m}$ ,  $100\mu\text{m}$ ,  $125\mu\text{m}$ , and  $150\mu\text{m}$  while the thickness of separator and cathode material, LMO is kept constant during simulation. The discharge curves of each of these variable thicknesses of LTO are plotted at lower to high C rates as 0.5C, 1C, 2C, & 4C, respectively. The discharge profile of these four full cells of varied anode thickness is also plotted at mentioned C Rates. Efforts are made to optimize anode thickness for better electrochemical performance. As a result, the outcomes could aid in the development of analytics for goods that have a lithium-ion battery as a component.

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# Chapter 1

## Introduction

### 1.1 Background

Wind and sunlight-based power stations are at present the developed innovation for exploitation of sustainable energy resources. Of the irregular idea of told resources, the requirement for excessive proficiency energy capacity systems emerges [1]. In the new past, the exceptionally poor or serious Air Quality Index (AQI) level in metro urban areas, requires a tough interest to diminish air contamination and one powerful arrangement is to utilize electric vehicles or hybrid electric vehicles rather than petroleum products vehicles. Petroleum derivative additionally turns out to be scant from now on [2].

### 1.2 Batteries

Batteries are an electrochemical device that can store and release energy, permitting the electrical network to be load levelled. A battery is called as a group of cells gathering associated in all parallel or all series or mixtures. An electrochemical unit comprise of an anode and a cathode both are isolated by the separator and electrolytes filled in the pores of the terminals. Other than power plant applications, rechargeable batteries are additionally viewed as encouraging power hotspot for the electric vehicle utilizations and then have been concentrated capably since first presented just about a long time back. There are a few necessities that a battery should meet with respect to costs, wellbeing, energy, and power to be a serious option in contrast to petroleum derivative-based impetus. Right now, the broadest battery frameworks for convenient electronic applications are involved graphite anodes and LiCoO<sub>2</sub> cathodes [1],[2].

### 1.3 Lithium-ion Batteries

Batteries of Li-ion, as quite possibly the most outstanding rechargeable battery, are thus attracting a lot of thought in the beyond hardly any numerous years. They are now of the overall portable power hotspot for flexible electronic contraptions, just used in mobiles and PCs. Li-ion batteries are seen as the force to be reckoned with for individual computerized electronic turmoil starting from about twenty years earlier, by and large at the similar time when the Li-ion batteries were promoted. As one would have proactively seen from his/her everyday presence, the rising utilization of flexible contraptions by and large demands better Li-molecule batteries. For example, charging the mobile phone of expanding functionalities less routinely than the continuous phone will deal with the idea of one's life. Electric and hybrid vehicles are another rapidly growing market for Li-ion batteries, which necessitate cutting-edge Li-ion batteries with high power, high charge rate, high cutoff, and long life, as well as increased security execution and reduced cost. [7].

## 1.4 Working of Li-ion batteries

Anode, which is the negative terminal, cathode, which is the positive terminal and electrolyte are the three parts of a battery. During the charging system, cations such as  $\text{Li}^+$  and anions such as  $\text{OH}^-$  are produced, as well as their transport across the terminals. These cations or anions attach to one another, attach to terminals, or are processed by them. Lithium particles reach the cathodes and anodes during charging and discharging cycles. Between the anode and the cathode, the electrolyte transmits Li particles. The development of  $\text{Li}^+$  particles through the electrolyte causes electron production in the outer circuit. As a result, electrons are generated during the charging and discharging process.

Intercalation-based technique, transformation response-based approach, and alloying reaction-based strategy are the methods used to make anode in Li particle batteries. Li particles are electrochemically intercalated into holes between the layers of the materials in the intercalation-based process. With fantastic release/charge proficiency, it enjoys a ton of benefits. The principal impediment of this method is that the time has come consuming. During the lithiation cycle, a few irreversible responses happen, bringing about the cathodic breakdown of various electrolyte parts similarly, in the event that graphite is utilized, absence of limit is the primary issue. Subsequently, the quest for elective carbonaceous materials is on for further developed execution.

The materials that are based on conversion reactions are mostly for faradic reactions. The capacity of the conversion reaction is remarkable. Pulverization and electric isolation are the two fundamental flaws. However, high surface area structures are used to improve volume change. The most well-known properties of these alloying reaction-based materials include their exceptional specific capacity. The first approach is to reduce volume expansion. Reducing size of the metal particle size is one way to achieve this [5],[22].

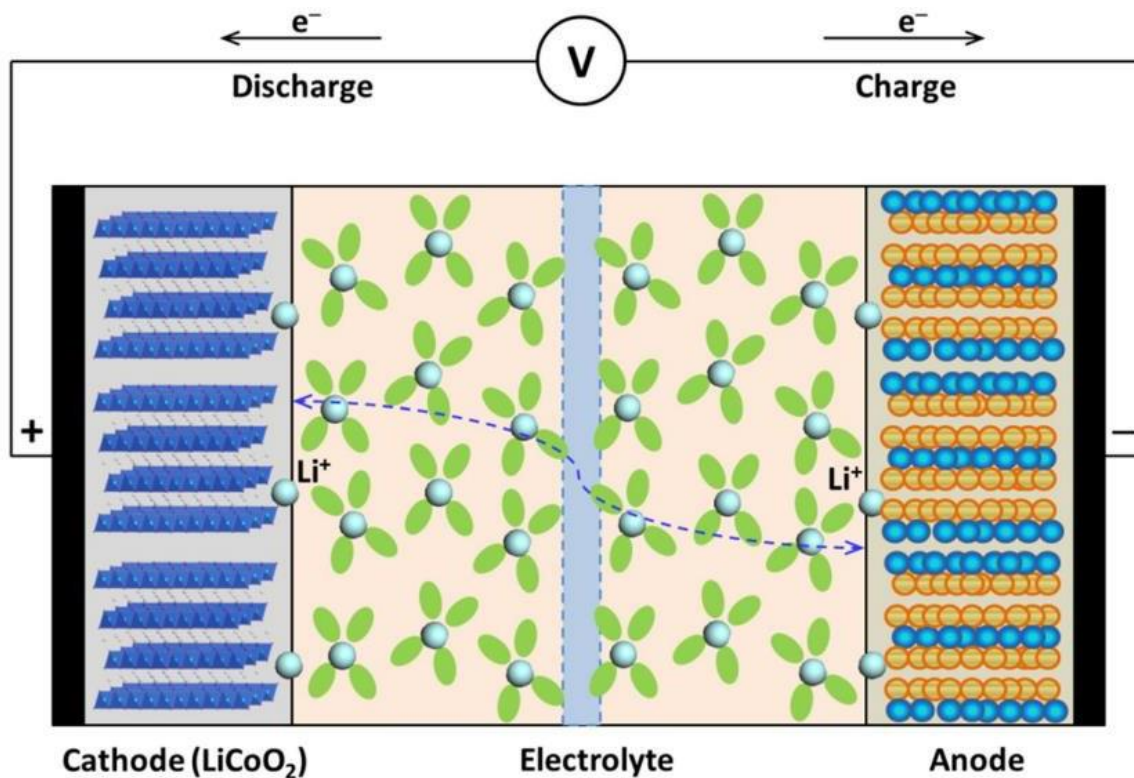


Fig. 1.4 Schematic of a common lithium-ion battery

## 1.5 Advantages and Disadvantages of Li-ion battery

Lithium-ion batteries are mostly popular as a result of the following benefits over competing technologies:

1. Contrasted with other rechargeable batteries, Li-ion batteries are lighter in weight for a similar size. Being a reactive component of lithium, it stores a lot of energy in the bonds of its nuclear design. Thus, these batteries have a high energy density. A nickel-metal hydride battery can hold 60-70 Wh/Kg of power and typical Li-ion battery stores 150 Wh/Kg.
2. The self-discharge rates of these batteries are less than that of Ni-MH and Ni-Cd batteries.
3. They do not suffer from memory effects, as a result, they need not be fully discharged before charge again.
4. Lithium-ion batteries can charge much quickly and also possess higher open-circuit voltage than other secondary batteries.

Despite several advantages, lithium-ion batteries are associated with a few disadvantages as well:

1. Lithium-ion batteries are costly to make contrasted with other secondary batteries.

2. Lithium-ion batteries also suffer from aging effect, which means it starts degrading as soon as it leaves the factory. This implies that even with longer charge/discharge cycles, they are not quite durable.
3. When overcharged or overheated, lithium-ion batteries tend to explode. Ignition of electrolyte and fire risks may occur due to overheating or internal short circuits.
4. Lithium-ion battery ruins if it is discharged completely and is also susceptible to high values of temperature [25].

## 1.6 The design of anode

Lithium metal, the lightest component in the whole periodic table, was utilized as the underlying negative terminal material. The use of lithium electrodes and polar aprotic electrolyte solvents will result in a thick surface layer, rendering passivation impossible. Lithium dendrites are shaped in the battery as it was charged and discharged, representing a danger and bringing about extreme lithium utilization. The current anode material is generally graphite, which has an unfortunate specific capacity and can't stay aware of the market interest for superior execution lithium batteries. Accordingly, researchers have performed significant investigation into the materials utilized in anodes. For the battery to maintain thermodynamic stability, the electrolyte's LUMO-HOMO energy gap must be greater than the possible energy between the cathode and anode. All in all, the capability of the terminal materials in lithium batteries should meet specific circumstances. The anode's potential energy should be less than the electrolyte's LUMO, while the cathode's potential energy should be greater than the electrolyte's HOMO. Such guidelines can safeguard the electrolyte while likewise broadening the battery's life.

Transfer of lithium ions and electrons is also an important factor to consider when designing an anode for LIBs. With regulated and diffusion systems, nano-scale terminal materials can expand the capacity sites of lithium ions and the known diffusion rate in anode materials. The high specific surface region of the negative terminal material allows it to consume more lithium ions in a given volume, extending the LIB limit. Nanomaterials' electrochemical performance will be worked on by an assortment of little size impacts brought about by their smaller size. Nonetheless, the material's size can't be diminished excessively. The battery's stability will be hurt by utilizing incredibly limited quantities of material, and the battery's duration and security will be imperiled during fast charging and discharging cycles. The utilization of novel crossover nanomaterials in LIBs has advanced altogether lately [22].

Due to the interaction between diverse components, hybrid heterostructures can take full benefit of each component of nanomaterial while also enhancing battery cycle stability and conductivity. However, when the hybrid terminal is set up, the strength of the point of engagement is an issue. Second, LIB performance is influenced by electrode arrangement. The current commercial anode is a few hundred micron thick sheet of cathode material powder, binder, and conductive additional chemicals. Adhesives and conductive additional chemicals are inconvenient because they reduce the energy density of the battery, but they are



required to meet conductivity standards. The electrode's design and shape significantly affect the unique dispersion of particles and electrons overstretched distances. The thickness, density and porosity of the terminal, for instance, straightforwardly affect the diffusion way. When the lithium ions in the electrolyte come into touch with the electrode's surface, the mixture of lithium ions and material compensates for the small shortage left by the dynamic material. The reduction in vacancies will prevent lithium ions from diffusing, lowering the battery limit. Accordingly, a thick and dense terminal will keep lithium ions from diffusing profoundly. An all around planned terminal construction can upgrade the contact region between the electrolyte and the electrode, subsequently further developing the battery's all out transmission rate. It's additionally intriguing contemplating how dynamic materials and conductive added substances are conveyed. To accomplish absolute ion exchange, the uniform appropriation of active material particles and the conductive carbon can conform to volume changes. Deformation is caused by the concentrated tension brought by the accumulation of active particles. The terminal materials will slip off the current collector because of the volume shift, or the ion channels will be obstructed, bringing about a sudden decrease in battery limit. Furthermore, as market demands for battery shape and flexibility grow, the condition of connection between the terminal and the current collector, as well as electrode adaptability, have become considerations in the electrode design. Conventional metal current collectors can't match the disfigurement demand, yet the making of unconventional electrodes and a deliberate format inside the counter terminals can assist with improving general adaptability. Adaptable electrodes could not just meet the market at any point of interest for electrode shape, yet in addition, accommodate internal terminal material distortion to guarantee the battery's safety. Three-layered permeable, exchanging layers, and arrays are a couple of the electrode structures that have been reported.

Finally, the anode material's performance in terms of the battery as a whole should be taken into account. The stability of interface, as well as integrity and security of the structure, should be assessed in order to meet the necessities of energy density and rate performance [23],[24].

## **1.7 Major anode materials used**

Phosphorous, Graphite, Germanium, Tin, metal nitrides, metal phosphides, nanostructured carbonaceous materials, silicon, Indium, metal sulphides, etc. [24].

## **1.8 Why LTO**

The lithium titanium oxide (LTO) anode is generally viewed as perhaps the best anode for future lithium-ion batteries utilized in electric vehicles (EVs), because of its very long cycle life. (8) Because of its rapid  $\text{Li}^+$  insertion and inexpensive cost, LTO has become a popular alternative anode material for graphite among all anode materials. Due to its voltage plateau at 1.55 V versus  $\text{Li}/\text{Li}^+$ , it has the great de-insertion ability, excellent cycle reversibility, strong thermodynamic stability, and a very undetectable volume change during the charging and discharge process, therefore, these materials are referred to as "zero strain" materials. The spinel LTO can prevent electrolyte decrease on the electrode surface, improving the safety of lithium-ion batteries. It's also an excellent contender for long-life battery electrodes. As a result, the

spinel LTO has surpassed graphite as one of the most used anode materials for lithium-ion batteries. (7) Because of its zero-strain property, nanosized molecule, no SEI film arrangement, no lithium plating while quick endlessly charging at low temperatures, and stability under high temperatures, the (LTO, generally  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) anode is viewed as a preferable decision over the customary graphite anode. Various authors have reported the capacity fading of graphite-based anode lithium-particle batteries, which as a rule observes a power regulation relationship with time. The deficiency of lithium ions because of the thickening of the SEI covering could make sense of this result. In any case, the aging mechanism of LTO-based anode lithium-ion batteries contrasts altogether with that of graphite anode lithium-ion batteries, and thus the capacity fading of LTO cells varies fundamentally [1],[4].

## Chapter 2

### Literature Review

**Zhang, Wei-Jun, 2010.** reviewed and studied the new advancement in figuring out the electrochemical execution of different alloy anodes. In this study, he sums up the various methodologies used to work on the performance of lithium-ion batteries and deliberates the reasons for the first-cycle irreversible limit loss. A correlation between irreversible limit loss and limit maintenance gives. In this review, he referenced that the multiphase carbon-framework nanocomposites displayed the best performance of alloy anode material. He likewise underscored that the utilization of binders and electrolytes additionally influences the cycle life and limits retention of the alloy anode material [16].

**Cai, Long, and Ralph E. White, 2011** The thermal behaviour of a lithium-ion battery was investigated during discharge with a fixed current through the electrode and a pulse. He did this by discharging the battery for 3000s at  $C/2$  and then for  $3C$  until the cell voltage dropped to 2.5V. In comparison to isothermal conditions, he determined that the cell under a considerably better environment for heat isolation, i.e., in adiabatic conditions, has a large discharge capacity. The reason for this is that with a 1 C discharge rate, the temperature of the cell rises faster because the diffusion coefficient of the binary electrode is large, lowering the diffusion limits under adiabatic conditions compared to isothermal conditions. He also concluded that as cells become hot as the discharge current increases rapid degradation of the cell may occur due to thermal runaway [17].

**M. Thunman, 2012** In this paper, the authors reviewed that introduction of thicker terminals would expand the energy thickness. In this manner, discharge performance examinations on  $\text{Li}_4\text{Ti}_5\text{O}_{12}(\text{s})|\text{LiPF}_6(\text{sol.})|\text{LiMn}_2\text{O}_4(\text{s})$  pocket cells containing terminals with 0.95, 1.90, 2.85, 3.80, and 4.75 mAh  $\text{cm}^{-2}$  stacking were finished. The results indicated that thicker electrodes give a larger discharge capacity at current densities (lower) ( $<13 \text{ mA cm}^{-2}$ ). The discharge capacity, on the other hand, appears to become practically free of the terminal thickness as the current thickness increases. This extreme cut-off maintenance could be linked to polarisation in the electrolyte and cathodes following discharge. The battery discharge characteristics were simulated using the COMSOL multiphysics software, using the Newman model for microporous electrodes. [8].

**Jung-Hyun Kim, 2014** They remembered the widespread use of lithium-ion batteries in electric vehicles, including entirely electric vehicles, and began to halt plug-in hybrid electric vehicles in this study due to their high energy and power density. They researched difficulties and solutions for high voltage spinel lithium-ion batteries in order to increase energy density, increase driving distance, and reduce costs. They pick the high-voltage cathode material as spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO) because of its high working voltage of around 4.75 V versus Li, less expensive, and remarkable rate capacity. They surveyed that the high-voltage Li-particle batteries are not popularized at this point. Because of the disintegration of electrolytes and synchronous degradative reactions at the electrode-electrolyte interface, outcomes, it degrades quickly with an increase in the quantity of cycle life (charging-releasing) for full cells (LNMO/graphite). In an eminent electrolyte, such as (solute) Lithium salt  $\text{LiPF}_6$  in a carbonate-based dissolvable, the rationale for electrolyte decay in LNMO/graphite complete cells, functional voltage range

becomes more noteworthy than electrochemical soundness window. The debasement in the limit is because of the deficiency of  $\text{Li}^+$  ions in the cells, as the consequence of parasitic reactions at the connection point of electrolyte/graphite. They likewise explored different issues like corrosion of the cell parts like conductive carbon, the separator, binder & stainless steel which can be tackled by involving the steadier high-level electrolytes instead of regular electrolytes. They discussed a variety of methods for extending the cycle life of LNMO/graphite full cells, including electrolyte additions, electrode covering, and LNMO compositional changes. While none of these methods were completely effective in extending the cycle life, their legitimate blend could address the issue of high voltage spinel Li-ion batteries. [18].

**Rahul Deb Pal, 2015** In this paper, the authors optimized a few parameters of the battery model and validated the results with the charge-discharge curve by experimental result. Their research studies are beneficial to find the condition at which the battery usage is maximum. In this experiment, the battery charged and discharges five times with a slow rate of 0.04C at room temperature to achieve a stable capacity. Followed by galvanostatic charging and discharging at a 1C rate with a voltage range of 2.8 V-3.8V at 10°C, 30°C, and 40°C. Compare these results with the full-cell model of the one-dimensional isothermal lithium-ion battery model available in COMSOL Multiphysics 5.0. This may use utilized in designing electronic devices and management systems of batteries [19].

**Yemeserach Mekonnen, 2016** Reviewed the various types of batteries and found that lithium-ion battery has the highest power density and efficiency, lowest weight, size, and cost. The cell performance of the battery was observed by measuring the charge capacity, energy density, and cell voltage which depends on the electrode materials. The various types of anodes and cathode material with their advantages and disadvantages are discussed. The author also reviews the applications and market of lithium-ion batteries. High energy density and power density make it useful for powered Electric Vehicles (EVs) such as Tesla Model S and start to stop plug-in Hybrid EVs like Chevrolet Volt. The other applications of batteries in laptops, mobile phones, tablets, and aeronautics. There are so many advantages of lithium-ion batteries high open-circuit voltage, no memory effect, low discharge rate when not in use, and do not affect the environment when thrown away. However, it has safety issues due to the flammable nature of lithium. The author tries to review a new electrode material and electrolytes to solve the safety issues of the batteries. The two-anode material which is mostly used is a carbon (graphite) due to its porosity nature, and another is lithium alloyed metals such as  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , and Li-Al. There are metal collections like bismuth, cadmium, magnesium, aluminum, magnesium, and Antimony that can alloy with lithium metal and some other intermetallic elements such as Tin-copper (Sn-Cu), Aluminium-Nickel alloy ( $\text{Al}_3\text{Ni}$ ), TinAntimony (Sn-Sb), and Iron-tin (Fe-Sn) can use as good anode material. Cathode materials choice depends upon the selection of anode material, if lithium metal is used as anode material then there is no need to take a lithiated positive electrode. When graphite is used as an anode material that doesn't have Li, so it is necessary to take a positive electrode that must act as a source of lithium such as  $\text{LiCoO}_2$ ,  $\text{LiFePO}_4$ , Li-Mn-O, and lithium layered metal oxides. Two types of electrolytes can use polymer bases such as Polyethylene oxide (PEO) and liquid electrolytes. The main criteria for the selection of electrolytes depended upon the high ionic conduction. The ionic conduction decides by the specific dielectric and viscosity constant of the liquid electrolyte. Finally, the author concludes that battery performance can be

improved in the future by the nano approach with CNT as an anode and nanoparticles of the material that can use as a cathode [20].

**Ian S. Huber, 2017** In this paper, the authors assembled a one-dimensional model of lithium-ion battery utilizing a multiphysics program called COMSOL. This model produces charts of electrolyte concentration, voltage, and release rates of the battery over the long haul. To additionally figure out the model, they changed the volumetric division (closely resembling porosity) of the positive and negative terminals, the electric conductivity of the positive and negative cathodes, the dispersion coefficient of the battery separator, and release flow to notice their consequences for concentration, voltage, and release rates. They tracked down that the volumetric part of the two anodes, the electric conductivity of the positive anode, and release current essentially affect focus and voltage, while dissemination altogether affects release rates. The electric conductivity of the negative terminal didn't fundamentally affect any of the reliant factors. With these outcomes, further comprehension of battery models can be acquired in anticipation of the possible development of effective lithium-particle batteries for commercial use [5].

**Xiaoyuan Shi, 2020** Lithium Titanate Oxide ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) uses as an anode material in lithium-ion batteries that has more attention because of its good stability & also high safety. Nevertheless, LTO has a low maximum potential plateau at 1.5V vs. Li/L+, which is the barrier to its advanced use. In this paper, the author approaches a configuration called dual-ion batteries (DIBs) to increase the maximum working potential of LTO as an anode, for this graphite as cathode use for high potential. Thus they achieved a working voltage of up to 3.5V. In DIB configuration - ve ions PF-6 intercalated in graphite with high potential and cation  $\text{Li}^+$  intercalated in LTO, the high potential of LTO achieved when its potential measured from the graphite potential, this provides a high value of specific energy around 140Wh/Kg corresponding to 35W/Kg specific power and with the remaining 11Wh/kg specific energy corresponding specific power 2933W/Kg. The author concluded that the DIB configuration with the above electrode material batteries has good energy-power performance than commercial LIB configuration batteries [21].

**A. Rozenblit, 2021** In light of the permeable terminal hypothesis, the researchers used Comsol Multiphysics to run simulations for different atom sizes of  $\text{LiMn}_2\text{O}_4$  cathode material in  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO)- (LMO) batteries. Due to compensating greater dynamic surface area/unit volume, which reduced the local current thickness at the LMO crystal interface with known electrolyte, the findings show that greater populations of small particles at consistent cathode material burden and reliable current density over electroactive area can consider greater flows to be applied. The importance of microstructure and PS in battery designs, particularly in the LTO-LMO architecture, is highlighted by these findings. [1].

**Zeyang Geng, 2021** This study looked at a new implementation of the widely used pseudo-two-layered (P2D) model for the simulation of lithium-ion batteries with transmission line circuit architectures. This execution approach alternates between physical and indistinguishable circuit representations often. The discharge cycles of graphite in a lithium-ion battery are modeled using multiple streams, and the results

from the circuit model match those from a real-world simulation using the COMSOL Multiphysics toolkit, which includes both terminal voltage and fixing apportionments. Finally, they illustrated how the circuit model might improve knowledge of cell electrochemistry by evaluating the overpotential responsibilities of various processes. [3].

# Chapter 3

## Model Development and Simulation

### 3.1 COMSOL

COMSOL is a modelling software for limited components used to address various PDEs with incredible application in a liquid stream, acoustics, and solid mechanics. It is a commercial limited component programming bundle intended to address a wide scope of actual peculiarities. Noticing the expanded utilization of this item in insightful electrochemistry, the creators expect to review its importance and practical use in this field. The software is adequately adaptable to oblige numerous PDEs in a single area model. Furthermore, to sum up PDEs that can be modified for explicit issues, COMSOL accompanies a basic library of predefined PDEs for specific applications (heat, liquid elements, diffusion, and so on), in expansion to sum up PDEs that can be redone for explicit applications. COMSOL (prior known as FEMLAB) can settle numerous material science issues used in designing purposes, especially Multiphysics issues. This incorporates an extensive displaying climate for portraying all physical phenomena utilizing PDEs [19],[20].

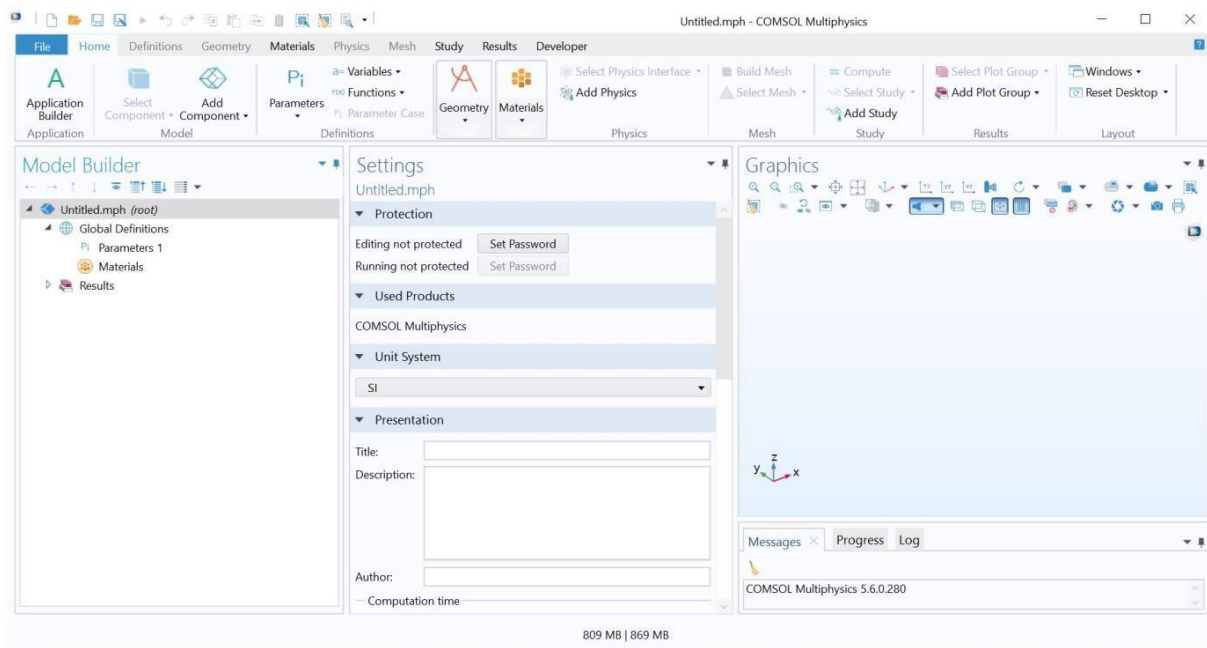


Fig. 3.1.1: COMSOL Multiphysics Software Layout.

## 3.2 Our Model

In this study, a full cell 1-D model is considered for lithium battery using COMSOL Multi-physics software.  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) has been used as an anode material with 75m, 100m, 125m, and 150m dimensions. A cathode material of lithium manganese oxide,  $\text{LiMn}_2\text{O}_4$  (LMO), with a diameter of 183m and a separator of 56m dimensions has been employed in a configuration as indicated in figure 1. Electrons and lithium ions are lost at the negative terminal. The lithium ions travel over the separator to meet at the positive terminal of the battery, while the electrons travel across the circuit. It is a one-layered, isothermal framework that models electronic current conduction in the cathode and anode, particle transport across the battery, material transport in the electrolyte, and Butler-Volmer terminal energy utilizing measured discharge curves for the equilibrium potential [4]. For testing the batteries at different C rates we have taken 0.01 gram of anode material (LTO) per  $\text{cm}^2$  of configuration.

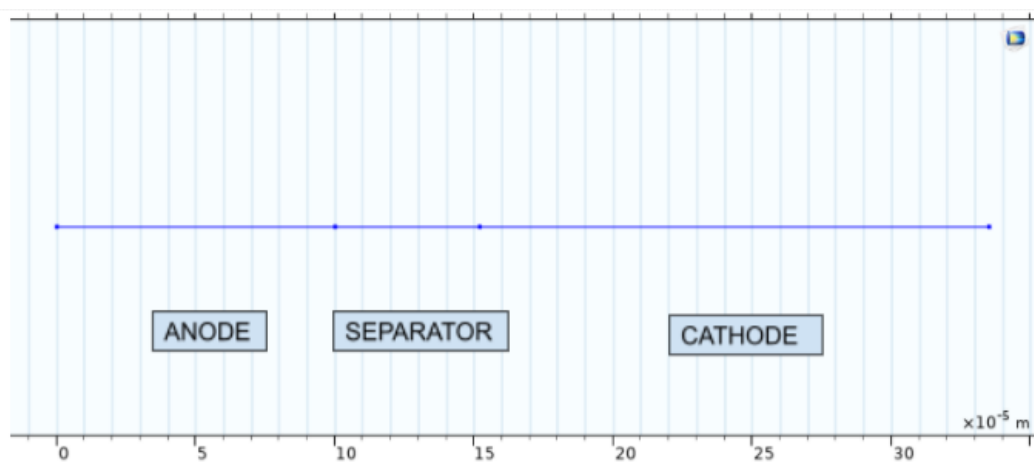


Figure 3.2.1: Model constructed to depict the three components of a battery.

### 3.2.1 Steps to create a 1D model of lithium-ion battery in COMSOL Multiphysics Software.

1. Create a one-dimensional geometry of lithium-ion battery, one for positive electrode with current collector and second for separator filled with electrolyte, and the last one for negative electrode with current feeder, and then click on the build all button.
2. Choose appropriate material for anode, cathode, and electrolyte.
3. Input material properties in the model.
4. Create a Domain for each component
5. Boundary conditions are applied for each domain.
6. The mesh has been created.



7. Run the model for simulation.
8. Process the results to obtain desired information from the simulation.

### 3.2.2 Parameters

Following parameters are used to run the present model at 298 K.

**Table 3.2.2.1 Parameters used for the optimization of anode thickness modelling.**

NAME	VALUE	DESCRIPTION
T	298[K]	Temperature
L_neg	(75,100,125,150)e-6[m]	Negative electrode length
L_sep	52e-6[m]	Separator length
L_pos	183e-6[m]	Positive electrode length
C	0.5,1,2,4	C-rate factor for the parametric study
brugg	3.3	Bruggeman coefficient

### 3.2.4 Equations used in Lithium-ion Cell Modelling

#### Current Balance

In COMSOL, the lithium-ion battery interface allows you to examine the cell potential and current distribution pattern in a lithium-ion battery. The current balance in the electrolyte, the current balances in the electrodes, the mass balance for the lithium salt, and the mass balance of lithium-ion batteries are all defined by this battery and COMSOL interface. The electrolyte in the battery should be binary, containing lithium cations (Li+) and anion (An-) in a single salt solution [19],[20].

The physics interface in COMSOL mainly solves for five dependent variables.

- i.  $\Phi_s$  – the electrodes electric potential (the electron conductor)
- ii.  $\Phi_l$  – the electrolyte potential (the ion conductor)
- iii.  $\Delta\Phi_{s, \text{film}}$  – the potential losses due to a solid -electrolyte interface (SEI), the film forming on electrode particle.
- iv.  $c_s$ – the porous electrode particle contains solid Li concentration.
- v.  $c_l$ – the binary electrolyte salt concentration.

### Electrolyte Charge balance in pores

Current conduction in the electrodes and electrolytes is explained jointly by the charge balance and Ohm's law.

In the porous electrode, the lithium salt phase current density,  $I_l$

$$I_l = (-\sigma_l \nabla \Phi_l) + 2\sigma_l RT/F (1 + \partial \ln f / \partial \ln c_l) (1 - t_+) \nabla \ln c_l$$

Here,  $f$  is electrolyte activity coefficient,  $t_+$ , the transport number of  $\text{Li}^+$  (also called transference number),  $\sigma_l$  denotes the electrolyte conductivity. The first term in the equation expressed the current due to the migration of ions influenced by the electric field, whereas the second term represents the concentration over-potential.

In the porous electrode, charge balance for the Lithium salt phase, remember here lithium salt express the electrolyte

$$\nabla \cdot I_l = a_i j_s$$

So, total charge balance is given by

$$\nabla \cdot I_s + \nabla \cdot I_l = 0$$

Current density of the cell is given by

$$I_s + I_l = I_{\text{cell}}$$

### Electrolyte Mass Balance in pores

The electrolyte the ionic flux is given by:

$$N_l = -D_l \nabla c_l + i t_+ / F$$

Here  $D_l$  is the electrolyte salt diffusivity in the electrode. Ionic flux due to gradient of concentration

represent by the first term on the right-hand side of the equation, and the second term is due to the electric field.

### Electrode Kinetics Equations

For an electrode reaction, the activation over-potential is denoted by  $\eta$  and defined as follows:

$$\eta = \Phi_s - \Phi_l - E_{eq}$$

where,  $E_{eq}$  denotes the equilibrium potential.

### Butler-Volmer equation:

The processes of charge and mass transport in solid and solution phase included in the model constitute the electronic conduction and charge transport of ions in the electrodes and also in the electrolyte, the kinetics of Butler-Volmer electrode employing the use of practically measured discharge curves intended for potential achieved at the time of equilibrium, and material transport within the spherical particles. The most general expression is of Butler-Volmer Equation which designates the rate of reaction at the electrode surface.

$$i_{oc} = i_0 (\exp(\alpha_a F \eta / RT) - \exp(-\alpha_c F \eta / RT))$$

where  $\alpha_c$  and  $\alpha_a$  denote the cathodic and anodic charge transfer coefficient.

### Limiting Current Density

Electrode reaction's steady-state rate never goes beyond the rate of transport of products and reactants from and to the surface of the electrode. When transport of mass includes in the model, this dependence is defined by a concentration-dependent kinetics expression as given below:

$$i_{oc} = i_0 (C_r \exp(\alpha_a F \eta / RT))$$

where,  $E_{eq}$  denotes the equilibrium potential and  $C_r$  is a dimensional-less expression, and it depends upon oxidized & reduced species in the reaction.

### Nernst-Planck Equation

In salt electrolyte, the mass balance for diluted species is given by

$$\partial c_i / \partial t + \nabla \cdot N_i = R_{i,tot}$$

Here,  $R_i$ , the reaction rate for ions (mol/m<sup>3</sup> s) ;  $c_i$  ions concentration (mol/ m<sup>3</sup> )

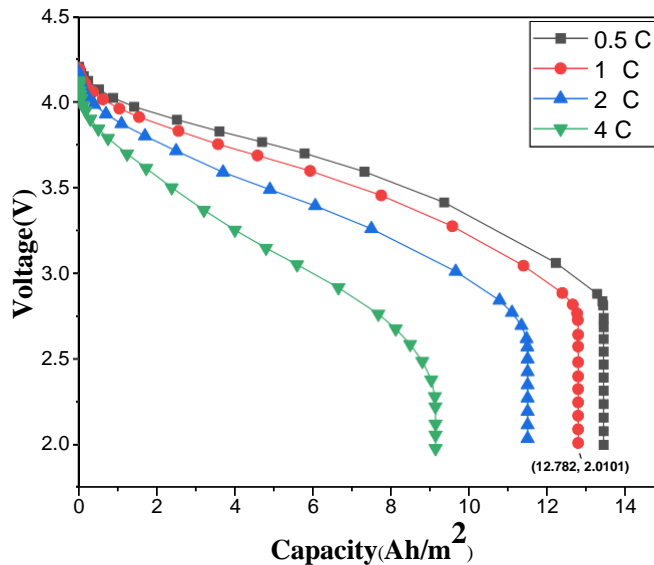
## Chapter -4

### Results and Discussion

We at first have set the battery as described in the model builder section. All the equations justifying the flow of charges and charge balancing are made into use. Then the creation of mesh insured the application of equations to small sections of the battery, compiling it up to the entire cell. Then the battery was fully charged initially. Then discharged as described in the modeling.

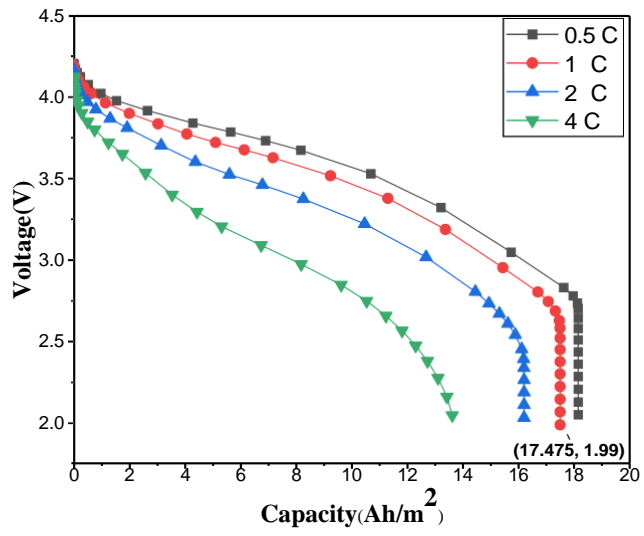
**4.1:** To complete the aim of comparing the different discharge rates for cells with varied thickness, simulations has been carried out to see the discharges. Keeping the thickness of the cell constant, we used different current densities to plot the curves i.e. four cells with thickness of  $75\ \mu\text{m}$ ,  $100\ \mu\text{m}$ ,  $125\ \mu\text{m}$ , &  $150\ \mu\text{m}$  were constructed one after another. Each thickness were then simulated at 0.5C, 1C, 2C & 4C. These plots from these simulations are:

*Plot 1: Anode thickness: 0.075mm\_ (C Rates 0.5, 1, 2, 4)*



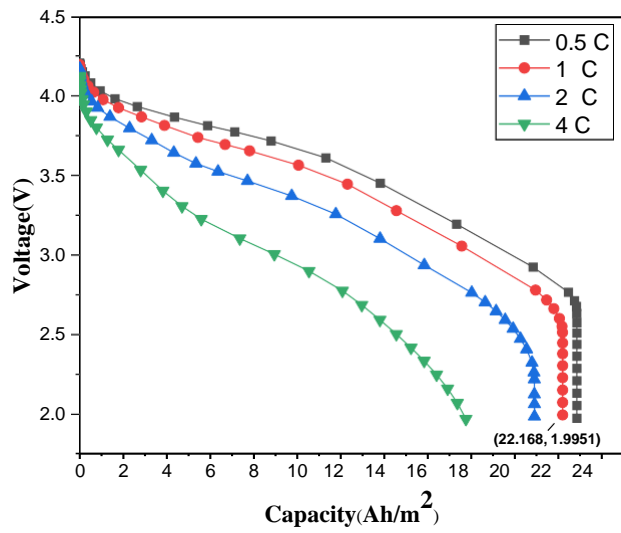
**Fig. 4.1** Discharge curve of 0.75mm thickness anode at 0.5,1,2 & 4 C Rates

*Plot 2: Anode thickness: 0.100mm\_(C Rates 0.5, 1, 2, 4)*



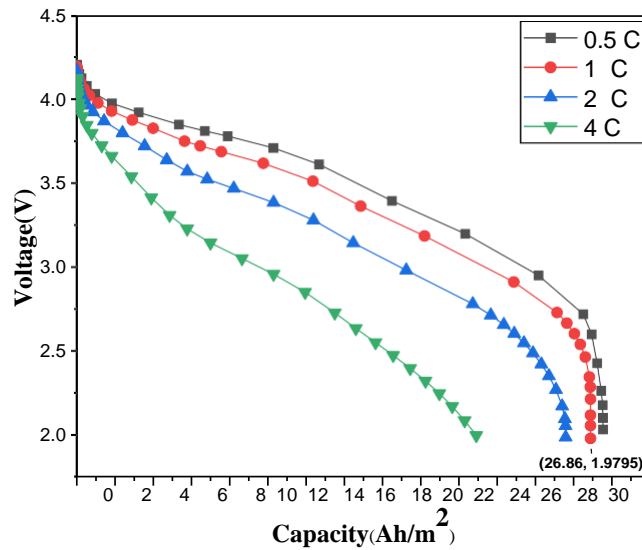
**Fig. 4.2** Discharge curve of 0.1mm thickness anode at 0.5,1,2 & 4 C Rates

*Plot 3: Anode thickness: 0.125mm\_(C Rates 0.5, 1, 2, 4)*



**Fig. 4.3** Discharge curve of 0.125mm thickness anode at 0.5,1,2 & 4 C Rates

**Plot 4: Anode thickness: 0.150mm\_(C Rates 0.5, 1, 2, 4)**



**Fig. 4.4** Discharge curve of 0.15mm thickness anode at 0.5,1,2 & 4 C Rates

Figure (4.1-4.4) shows the outcome of the discharge capacity of the battery at the low, 0.5C to high, 4.0C discharge rates relating to variable thicknesses of LTO anode as 75  $\mu\text{m}$ , 100  $\mu\text{m}$ , 125  $\mu\text{m}$  & 150  $\mu\text{m}$ . To compare the highest discharge capacity, we choose 1C rate and marked the corresponding points in the plots. The points are further constructed in the table for better comparison.

*Table 4.1: Discharge capacities for variable thicknesses at the discharge rate 1C*

<b>Thickness</b>	<b>Highest Discharge Capacity (1C) (Ah/m<sup>2</sup>)</b>
75 $\mu\text{m}$	12.782
100 $\mu\text{m}$	17.475
125 $\mu\text{m}$	22.168
150 $\mu\text{m}$	26.86

As shown by the data in Table 4.1, the discharge capacity of anode material LTO is increasing from 12.782 Ah/m<sup>2</sup> to 26.86Ah/m<sup>2</sup> as the thickness increases from 75 $\mu\text{m}$  to 150 $\mu\text{m}$  at 1C. Considering the mass loading of 0.01gm per cm<sup>2</sup> of configuration, the corresponding capacity would be 127.82 mAh/g to 268.6 mAh/g with respect to the thicknesses 75  $\mu\text{m}$  to 150  $\mu\text{m}$ , respectively.

If we tabulate the points for other C rates, a similar trend of increase in discharge capacity is observed. Hence, it reveals that discharge capacity is increased with the increase of anode thicknesses. It can likewise be seen that the 3 V discharge capacity diminishes somewhat while applying a 1C discharge current and

drastically while going over that. At 4C, the battery conveys around half of the ideal capacity before the cell reaches a voltage of 3V.

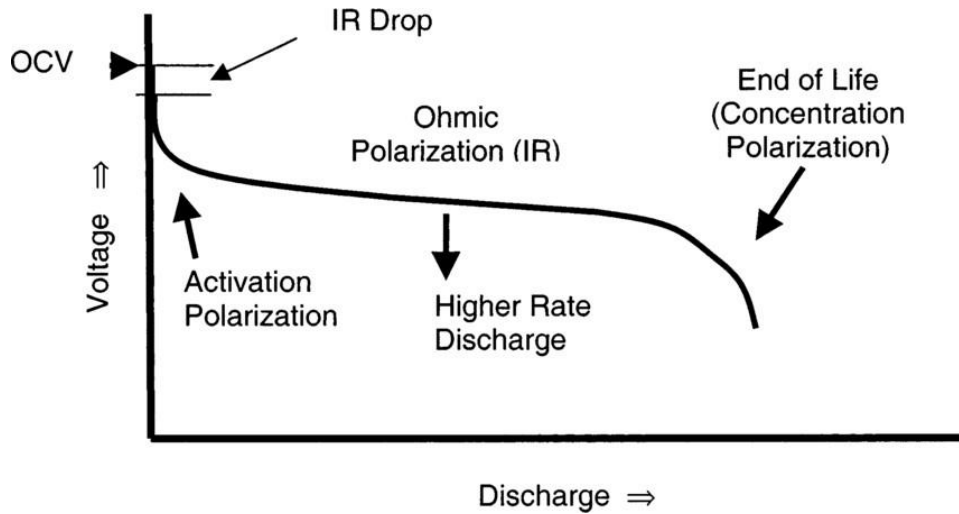


Figure 4.5 Polarization plots

To understand the discharge curves further. We studied and compared the polarization status of the battery as shown in figure 4.5 . The analysis of our plots lead us to varied conclusions and choosing one optimized battery thickness.

It has been observed that due to the migration of the Li-ions to cathode by means of the electrolytic medium, the region of Ohmic polarization rises. Moreover, IR drop refers to the internal resistance to this known ionic diffusion process. Every chemical reaction has an activation barrier which must be get over with to progress, and the energy required to do so causes the activation polarization voltage drop. In this study, the cell/battery, however, does not demonstrate any trend for growing thickness at activation polarization after reaching this activation polarization. Furthermore, the concentration polarization zone shrinks, owing to the fact that the electrochemical reaction consumes the reactants early comparing to the reactant diffuses to the porous electrode, and change in the composition of the bulk flow. Here the consumption of Li-ion leads to the drop in the overall concentration within the cell, between electrodes, resulting in drop in the local potential close to the cathode [2]. As a result, we see essentially constant activation polarization, increase in Ohmic polarization, and decreasing concentration polarization as the thickness increases. This investigation prefers the figure 4.2 i.e., at 100  $\mu\text{m}$  thickness because a flat discharge bend signals consistent voltage throughout the battery discharge.

**Modelling 4.2: Up next,** By keeping the C rate constant at a time, we tried to experiment with the varied thicknesses. The simulated flat-voltage profiles of four full cells made by LTO-LMO as an anode and cathode material with respect to capacity ( $\text{Ah}/\text{m}^2$ ) for variable anode thicknesses of 75  $\mu\text{m}$ , 100  $\mu\text{m}$ , 125  $\mu\text{m}$  & 150  $\mu\text{m}$  were modelled. So, four different discharges have been carried out and the discharge rates starting from small to high are estimated as 0.5C, 1C, 2C, and 4C.

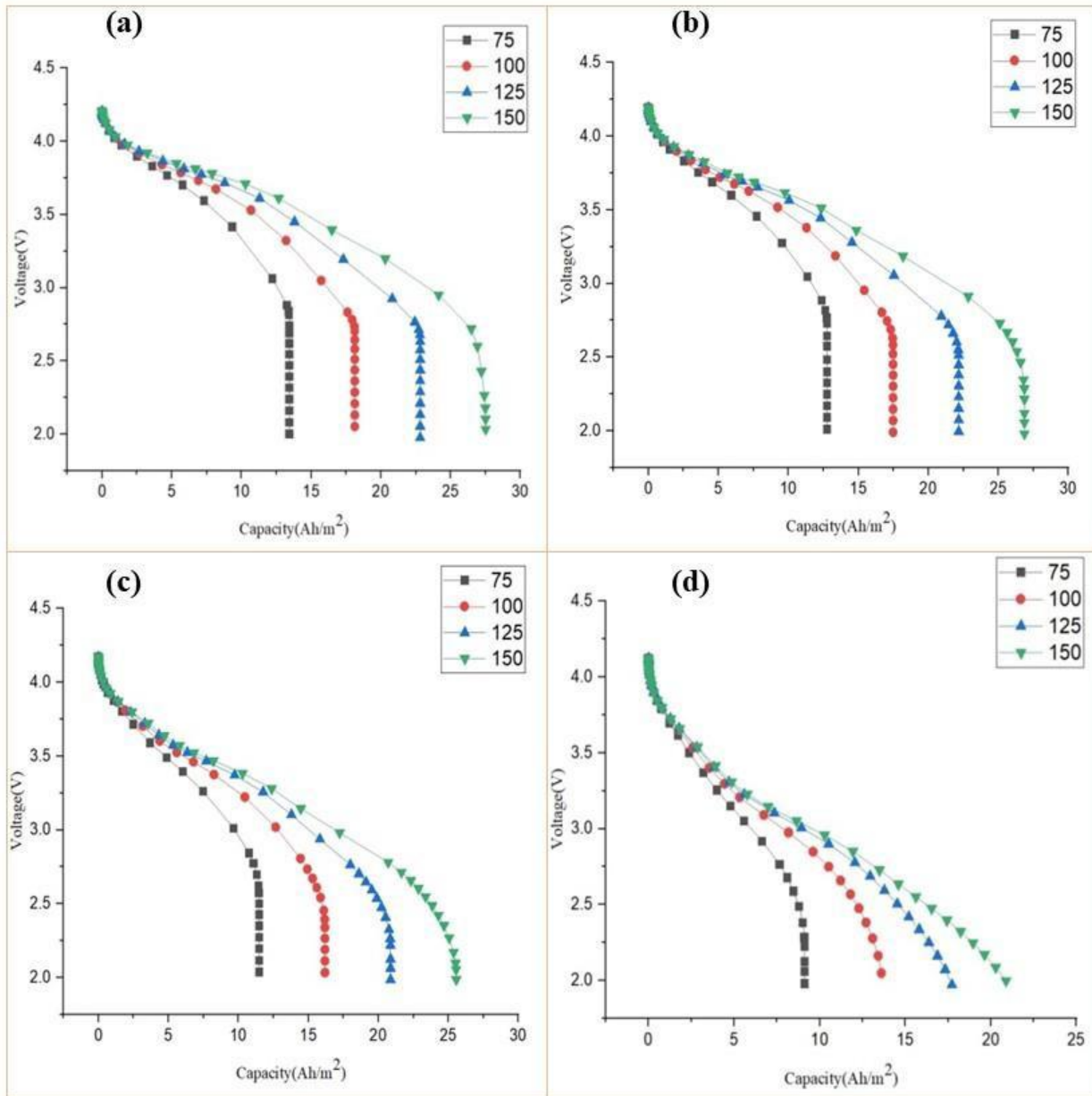


Figure 4.6 Discharge profile of four full cells made at different anode thicknesses of 75  $\mu\text{m}$ , 100  $\mu\text{m}$ , 125  $\mu\text{m}$ , & 150  $\mu\text{m}$  at discharge rates: (a) 0.5C (b) 1C (c) 2C & (d) 4C.

It has been noticed that at different discharge rates from figure 4.6, the nominal voltage provided by all the four cells is around 4.2V, but there is a significant change in their flat-voltage plateau. The reason behind this effect is the polarization and mass transport process. As the thinner electrode (0.075mm) has less polarization and a fast mass transport kinetics than the thicker one (0.150mm), because thickness that affects the diffusion path length of lithium-ion.



## Chapter 5

# CONCLUSIONS

This study included discharge curves of the lithium-ion battery plotted against voltage and discharge capacity. Aim was to construct flat discharge bend since it implies consistent voltage all through the battery discharge. Because the battery voltage remains generally consistent throughout the discharge cycle, a flat discharge bend may simplify certain application designs. A sloping curve, on the other hand, can make estimating SoC easier because the battery voltage is directly tied to the remaining charge in the cell. For Li-ion cells with flat discharge curves, however, more complex approaches are required, such as Coulomb counting, which analyses the battery's discharging current and integrates the current over time to estimate SoC. Furthermore, the power output of cells having a downward sloping discharge curve decreases over time. To handle high-power applications toward the finish of the discharge cycle, it may be essential to "oversize" batteries. When using a battery with a steeply sloping discharge curve, a boost voltage regulator is frequently required to power sensitive devices and systems. The discharge curves for a Li-ion battery below illustrate that if the cell is depleted at very high rates, the effective capacity is diminished (or conversely increased with low discharge rates). The phenomenon is known as the capacity offset, and it happens in most cell chemistries. Also, the study of electrochemistry directs that bring down the C-Rate of a charge, more energy can be stored in the battery. In other words, bring down the C-Rate of charge, more energy can convey from the battery. Consequently, charging and discharging the battery uniquely in contrast to the standard consistent charge current and standard consistent discharge current referenced in the cell datasheet can yield various outcomes for the energy stored and energy conveyed in the cell.

In our study we found out that;

- The voltage profile of the cells at different C-rate with varying anode thickness of the cell shows the different polarization status.
- As the thickness of LTO is increased, the ohmic part of the polarization curve showed an increase whereas the concentration part of polarization is decreased.

The pattern of lithium distribution on the electrodes at the same discharge rate but varying anode thickness has been observed that a thicker anode has more concentration of lithium on the cathode when compare with the thinner anode cell. It also has been observed the concentration of lithium on the cathode decreases as the discharge rate increase due to the increase of electronic and ionic flux and most of the active material is unreachable at end of discharge at a high C-rate.

We also found out that:

- The galvanostatic discharge at 0.5C, 1C, 2C, and 4C of four cells with varying anode thickness, shows a somewhat similar trend in that the thinner electrode provides high operating voltage around 4.2V
- But thicker electrode provides higher capacity but low operating voltage which is because of their higher polarization and longer diffusion path length .This leads to flat voltage plateau in their discharge profiles.

## REFERENES

- [1] Rozenblit, A., Torres, W.R., Tesio, A.Y. and Calvo, E.J., 2021. Effect of particle size in Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO)-LiMn<sub>2</sub>O<sub>4</sub> (LMO) batteries: a numerical simulation study. *Journal of Solid State Electrochemistry*, 25(8), pp.2395-2408.
- [2] Samina Siddiqui ,Amrish K. Panwar , (2021 ), International Journal of Advances in Science, Engineering and Technology(IJASEAT) , pp. 68-72, Volume-9,Issue-2.
- [3] Geng, Z., Wang, S., Lacey, M.J., Brandell, D. and Thiringer, T., 2021. Bridging physics-based and equivalent circuit models for lithium-ion batteries. *Electrochimica Acta*, 372, p.137829.
- [4] Ghosh, A. and Ghamouss, F., 2020. Role of electrolytes in the stability and safety of lithium titanate-based batteries. *Frontiers in Materials*, 7, p.186.
- [5] Huber, Ian S. Diss. College of William and Mary, 2017.
- [6] Pal, R.D. and Paul, A.K., 2015. Charge-discharge studies of lithium-ion batteries. In *Proceedings of the COMSOL Conference*.
- [7] Deng, D., 2015. Li-ion batteries: basics, progress, and challenges. *Energy Science & Engineering*, 3(5), pp.385-418.
- [8] Thunman, Mikael, et al. "Discharge performance dependence on electrode thickness for li<sub>4</sub>ti<sub>5</sub>o<sub>12</sub>/limn<sub>2</sub>o<sub>4</sub> cells for application in wafer-integrated microbatteries." *Ecs Transactions* 41.41 (2012): 147.
- [9] Cai, L. and White, R.E., 2011. Mathematical modeling of a lithium ion battery with thermal effects in COMSOL Inc. Multiphysics (MP) software. *Journal of Power Sources*, 196(14), pp.5985-5989.
- [10] Dusastre, V. ed., 2010. *Materials for sustainable energy: a collection of peer-reviewed research and review articles from Nature Publishing Group*. World Scientific.
- [11] Doyle, M. and Newman, J., 1996. AS Gozdz, CN Schmutz, and J.-M. Tarascon. *J. Electrochem. Soc*, 143, p.1890.
- [12] Doyle, M., Fuller, T.F. and Newman, J., 1993. Modeling of galvanostatic charge and discharge of the lithium/polymer/insertion cell. *Journal of the Electrochemical society*, 140(6), p.1526.
- [13] Honkura, K., Honbo, H., Koishikawa, Y. and Horiba, T., 2008. State analysis of lithium-ion batteries using discharge curves. *ECS Transactions*, 13(19), p.61.
- [14] Zhang, L., Wang, S.L., Chen, L., Wang, Y. and SU, J., 2018. Study on the charging and discharging characteristics of the lithium-ion battery pack. *Transactions on Computer Science and Engineering*.
- [15] Mei, W., Chen, H., Sun, J. and Wang, Q., 2019. The effect of electrode design parameters on battery performance and optimization of electrode thickness based on the electrochemical–thermal coupling model. *Sustainable energy & fuels*, 3(1), pp.148-165.
- [16] Park, M., Zhang, X., Chung, M., Less, G.B. and Sastry, A.M., 2010. A review of conduction phenomena in Li-ion batteries. *Journal of power sources*, 195(24), pp.7904-7929.

- [17] Cai, L. and White, R.E., 2011. Mathematical modeling of a lithium ion battery with thermal effects in COMSOL Inc. Multiphysics (MP) software. *Journal of Power Sources*, 196(14), pp.5985-5989.
- [18] J. H. Kim, N. P. W. Pieczonka, and L. Yang, "Challenges and approaches for highvoltage spinel lithium-ion batteries," *ChemPhysChem*, vol. 15, no. 10, pp. 1940–1954, 2014, doi: 10.1002/cphc.201400052.
- [19] R. D. Pal and A. K. R. Paul, "Charge-discharge studies of lithium-ion batteries," pp. 1– 4, 2015.
- [20] Y. Mekonnen, A. Sundararajan, and A. I. Sarwat, "A review of cathode and anode materials for lithium-ion batteries," *Conf. Proc. - IEEE SOUTHEASTCON*, vol. 2016- July, no. 1541108, pp. 2–7, 2016, doi: 10.1109/SECON.2016.7506639.
- [21] X. Shi, S. Yu, T. Deng, W. Zhang, and W. Zheng, "Unlock the potential of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> for high-voltage/long-cycling-life and high-safety batteries: Dual-ion architecture superior to lithium-ion storage," *J. Energy Chem.*, vol. 44, pp. 13–18, 2020, doi: 10.1016/j.jechem.2019.09.015.
- [22] Lu, J., Chen, Z., Pan, F., Cui, Y. and Amine, K., 2018. High-performance anode materials for rechargeable lithium-ion batteries. *Electrochemical Energy Reviews*, 1(1), pp.35-53.
- [23] Mekonnen, Y., Sundararajan, A. and Sarwat, A.I., 2016. A review of cathode and anode materials for lithium-ion batteries. *SoutheastCon 2016*, pp.1-6.
- [24] Pradeep, N., Sivasenthil, E., Janarthanan, B. and Sharmila, S., 2019, November. A review of anode material for lithium ion batteries. In *Journal of Physics: Conference Series* (Vol. 1362, No. 1, p. 012026). IOP Publishing.

## RESEARCH PAPER

# Electrochemical Study of Variable LTO Thicknesses as Anode Material Using a Theoretical Model

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**Abstract:** The performance of a battery is often determined by a number of factors and it is critical to tweak these factors in order to improve cell performance. In this study, parameters of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO)/  $\text{LiMn}_2\text{O}_4$  (LMO) materials made battery is modelled using 1-D cell geometry to obtain better electrochemical performance. The thicknesses of anode material, LTO has been adjusted as  $75\mu\text{m}$ ,  $100\mu\text{m}$ ,  $125\mu\text{m}$ , and  $150\mu\text{m}$  while the thickness of separator and cathode material, LMO is kept constant during simulation. The discharge curves of each of these variable thicknesses of LTO are plotted at lower to high C rates as 0.5C, 1C, 2C, and 4C, respectively. The discharge profile of these four full cells of varied anode thickness is also plotted at mentioned C Rates. Efforts are made to optimize anode thickness for better electrochemical performance. As a result, the outcomes could aid in the development of analytics for goods that have a lithium-ion battery as a component.

**Keywords:** Battery; LTO; LMO; Discharge Curve

## 1. INTRODUCTION

Researchers are aware of the extent of the damage caused by the combustion of natural energy sources, which in general are the problems of global warming that led to the trend for lithium-ion batteries (LIBs). Years of study and contributions from many outstanding scientists and engineers went into the commercial success of Li-ion batteries in the 1990s. Then, considerable efforts were made to improve Li-ion battery performance, and significant progress was accomplished. To meet the growing demand for energy storage, particularly from increasingly popular electric vehicles, more research is needed to bring up next-generation Li-ion batteries with improved performance, improved specific energy, cyclability, volumetric energy density, charging rate, stability, and most importantly safety. [7]. Resulting which LIBs is now considered the backbone of portable electronics which is one of the most important components of the industrial renaissance today. It also came out as the most popular energy storage device for generation of ours. It currently surpasses all other battery technologies over volumetric, gravimetric energy, and power densities [8]. Due to their high energy with minimum memory effect, low weight, high-power density, and low self-discharge, lithium-ion batteries are valuable battery systems among many types of secondary/ rechargeable batteries. Due to their high power and energy density to weight proportion, lithium-ion batteries are being utilized in heavy-duty

applications like electric vehicles, hybrid electric vehicles, and module electric vehicles [10].

The increase in the demand for portable electronics led to the search for a basic material available and cheap to be used in preparing the anode, so carbon was the focus of the researchers' attention with the continuation of the search for an alternative material that has a high capacity and a long life, due to the low voltage, which leads to the lack of resiliency of electrons. LTO was chosen as an alternative anode because it has a minimal volume change during lithiation and de-lithiation, enabling it to withstand more revolutions before mechanical failure. Furthermore, LTO's thermodynamic stability against most carbonate-based electrolyte solvents virtually eliminates problems associated with the supposed Solid Electrolyte Interface SEI; thermodynamic stability ensures that SEI does not form, which would otherwise consume active materials continuously over the battery's lifetime [4]. However, LTO has a lesser capacity ( $175 \text{ mAh g}^{-1}$ ) than other anode materials such as graphite ( $372 \text{ mAh g}^{-1}$ ). Usually, the anode used in batteries is of low atomic weight, but for thermal and ionic conductivity it is relatively high. One of the most important alternative materials for

the anode is spinel lithium titanate LTO, which has achieved a low cost and long life, as it works at a voltage of 1.5 volts so it can eliminate the dendrites that synchronized with the graphite anode. Also, LTO operates at a relatively low voltage, which makes it higher than the electrolyte decomposition capabilities with negligible size changes during intercalation operations, which increases the stability of the battery. With all these advantages that accompany the use of LTO, there is instability that arises from the different interactions with the electrolyte, which leads to the process of instability. Since the surface of LTO is highly reactive with the electrolyte, limits must be set for this reaction. In a previous study conducted by the scientist that the layers of SEI are two parts, the organic part arises from the oxidation of the two solvents at the cathode side, while the inorganic part (LiF) occurs on the surface of the anode as a result of the decomposition of  $\text{LiPF}_6$ . The intercalation potential available in LTO causes a loss in the potential of the cell which leads to a loss in energy density [1,5]. To overcome such a loss, high-voltage cathodes are used, which enables the cell to recover some of its lost energy. However, the anode based on LTO is the candidate to work, as it is not without defects such as low diffusion of lithium as well as low electrical conductivity, which negatively affects the electrochemical performance of the battery. Conductive coating such as carbon, CNT, and graphene, is one of the methods used to overcome these disadvantages. As well as doping and substitution with metal cations instead of lithium and titanium increased the rate capacity and cycling capacity of LTO while non-metal anions have improved electrochemical execution of the LTO anode. Barium, chlorine, and fluoride were added as doping elements to the LTO anode and the results showed high discharge capacities with good electrochemical performance. So with all these advantages and disadvantages, we are moving a step forward in this research by taking LTO as our anode material. In comparison to  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$  was chosen primarily because of its reduced cost and toxicity [2]. Because of its lower cost, high disintegration temperature, high oxygen discharge

temperature, low harmfulness, and safe activity LMO has shown to be an exceptionally cutthroat option in contrast to  $\text{LiCoO}_2$  cathodes [10]. LMO cathodes were given a renewed perspective when LTO addition anodes for Li-particle batteries became well known, in light of the fact that they had a more extended cycle life when matched with LTO than when matched with graphite anodes [10]. Thus, LMO is our chosen cathode material.

Optimizing battery design to obtain its best performance for actual application is very time-consuming and needs experimental hard work and expenditure. The computer simulations model of batteries is helpful to reduce the time and cost. Therefore, a mathematical model is required to obtain simulation results that are sufficient enough to properly describe the battery system and its electrochemical analysis. The simulation explains the charging/discharging behaviour of batteries and predicts some significant boundary dispersion inside the battery like potential ion concentration [9,6]. Hence, the impact of thickness variation of LTO on electrochemical performance, such as discharge capacity and discharging rates has been studied by this simulation work.

The first-principles-based lithium-ion battery model created by Newman, Doyle, and Fuller that is included in a lot of commercial software packages is an example of a physics-based approach that we considered. The Pseudo-two-Dimensional model created by Newman consisted of a set of partial differential equations. For solving partial differential equations, the finite element method or the finite volume method are widely utilised, resulting in a large computing load. Because of the long processing time, the partial differential equations model has been further simplified into single particle models or also called reduced equations which considers polynomial approximations. These simplifications increase calculation efficiency while restricting the scenarios in which the models can thus be utilized. In order to work on our model, we followed the same method..[12]

## 2. MODEL DEVELOPMENT

In this study, a full cell 1-D model is considered for lithium battery using COMSOL Multi-physics software.  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) has been used as anode material with variable dimensions of  $75\mu\text{m}$ ,  $100\mu\text{m}$ ,  $125\mu\text{m}$ , and  $150\mu\text{m}$ . Lithium manganese oxide,  $\text{LiMn}_2\text{O}_4$  (LMO) is used as a cathode material with a dimension of  $183\mu\text{m}$ , and separator of  $56\mu\text{m}$  dimensions has been used in a geometry as shown in figure 1. The negative terminal loses electrons and lithium ions. The electrons navigate across the circuit while the lithium ions go across the separator to meet at the positive terminal of the battery. It is a one-layered, isothermal framework that models electronic current conduction in the cathode and anode, particle transport across the battery, material transport in the electrolyte, and Butler-Volmer terminal energy utilizing measured discharge curves for the

equilibrium potential [5]. For testing the batteries at different C rates we have taken 0.01 gram of anode material (LTO) per  $\text{cm}^2$  of configuration. An image of the model as it shows up in the program is visible in Figure 1. The parameters used in the modeling are given in table 1.

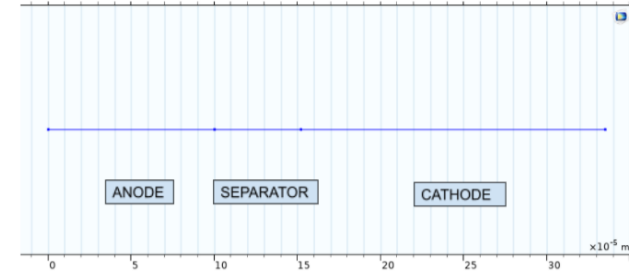


Figure 1. Model constructed to depict the three components of a battery

Table 1. Modelling input parameters used for

1-D simulation of LTO anode

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NAME	VALUE	DESCRIPTION
T	298[K]	Temperature
L_neg	(75,100,125,150) $\mu\text{m}$	Negative electrode length
L_sep	$52\mu\text{m}$	Separator length
L_pos	$183\mu\text{m}$	Positive electrode length
C	0.5,1,2,4	C-rate factor for the parametric study

## 3. RESULT AND DISCUSSION

Initially, the battery is in a completely charged state. To see the behavior of cells at different discharge rates, a simulation has been carried out to see the discharge at different current densities. Figure 2(a)-(d) show the outcome of the discharge capacity of the battery at the low, 0.5C to high, 4.0C discharge rates relating to variable thicknesses of LTO anode as  $75\mu\text{m}$ ,  $100\mu\text{m}$ ,  $125\mu\text{m}$ , and  $150\mu\text{m}$ . The comparison has been made for variable thicknesses using 1C rate data as marked in the respective plots. Figure 2 (a) indicates the discharging characteristic of full cell (LTO/LMO) made by  $75\mu\text{m}$  of LTO as anode from 0.5C to 4C rates.

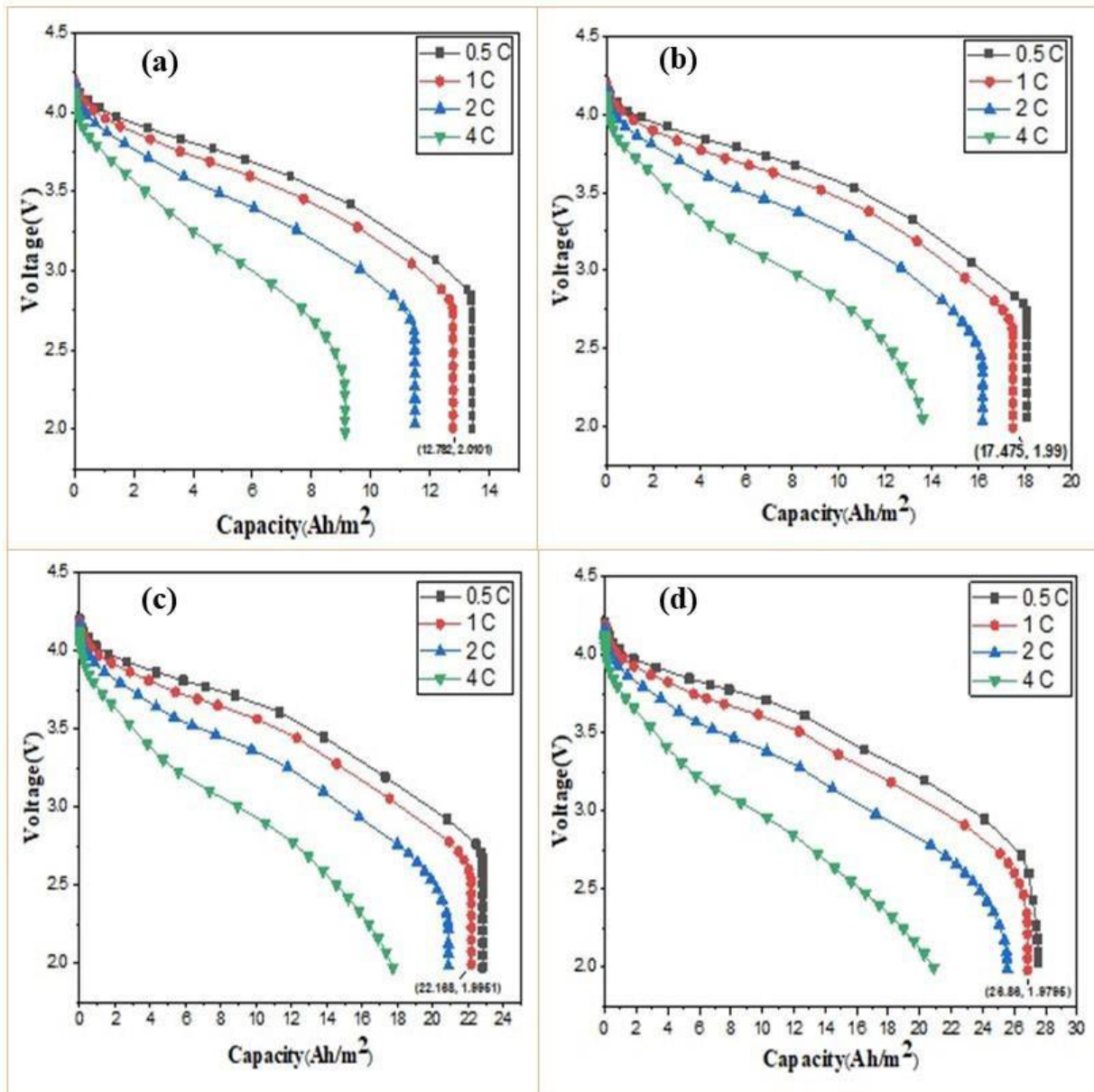


Figure 2. Discharge curve of (a) 75 µm (b) 100 µm (c) 125 µm (d) 150 µm thickness anode at 0.5, 1, 2, 4 C Rates



Table 2: Discharge capacities for variable thicknesses at the discharge rate 1C

Thickness	Highest Discharge Capacity (1C) (Ah/m <sup>2</sup> )
75μm	12.782
100μm	17.475
125μm	22.168
150μm	26.86

As shown by the data in Table 2, the discharge capacity of anode material LTO is increasing from 12.782 Ah/m<sup>2</sup> to 26.86Ah/m<sup>2</sup> as the thickness increases from 75μm to 150μm at 1C, and the variation of voltage with these increased capacities is shown in Fig. (a) – (d) at this C rate. Considering the mass loading of 0.01gm per cm<sup>2</sup> of configuration, the corresponding capacity would be 127.82 mAh/g to 268.6 mAh/g with respect to the thicknesses 75 μm to 150 μm, respectively. A similar trend of increase in discharge capacity is observed for other C. Hence, it reveals that discharge capacity is increased with the increase of anode thicknesses. It can likewise be seen that the 3 V discharge capacity diminishes somewhat while applying a 1C discharge current and drastically while going over that. At 4C, the battery conveys around half of the ideal capacity before the cell reaches a voltage of 3V.

Furthermore, it has been observed that due to the migration of Li-ions to the cathode by means of the electrolytic medium, the region of Ohmic polarization rises. Moreover, IR drop refers to the internal resistance to this ionic diffusion process. Every chemical reaction has an activation barrier which must be get over with to progress, and the energy required to do so causes the activation polarization voltage drop. In this study, the

cell/battery, however, does not demonstrate any trend for growing thickness at activation polarization after reaching this activation polarization. Furthermore, the concentration polarization zone shrinks, owing to the fact that the electrochemical reaction consumes the reactants early comparing to the reactant diffuses to the porous electrode, and change in the composition of the bulk flow. Here the consumption of Li-ion leads to the drop in concentration along the cell, between the electrodes, resulting in a drop in the local potential close to the cathode [2]. As a result, we see essentially constant activation polarization, increase in Ohmic polarization, and decreasing concentration polarization as the thickness increases. This investigation prefers the figure 1(b) i.e., at 100 μm thickness because a flat discharge bend signals consistent voltage throughout the battery discharge.

The simulated flat-voltage profiles of four full cells made by LTO-LMO as an anode and cathode material with respect to capacity (Ah/m<sup>2</sup>) for variable anode thicknesses of 75 μm, 100 μm, 125 μm and 150 μm are shown. Here, four different discharges have been carried out and the discharge rates starting from small to high are estimated as 0.5C, 1C, 2C, and 4C.

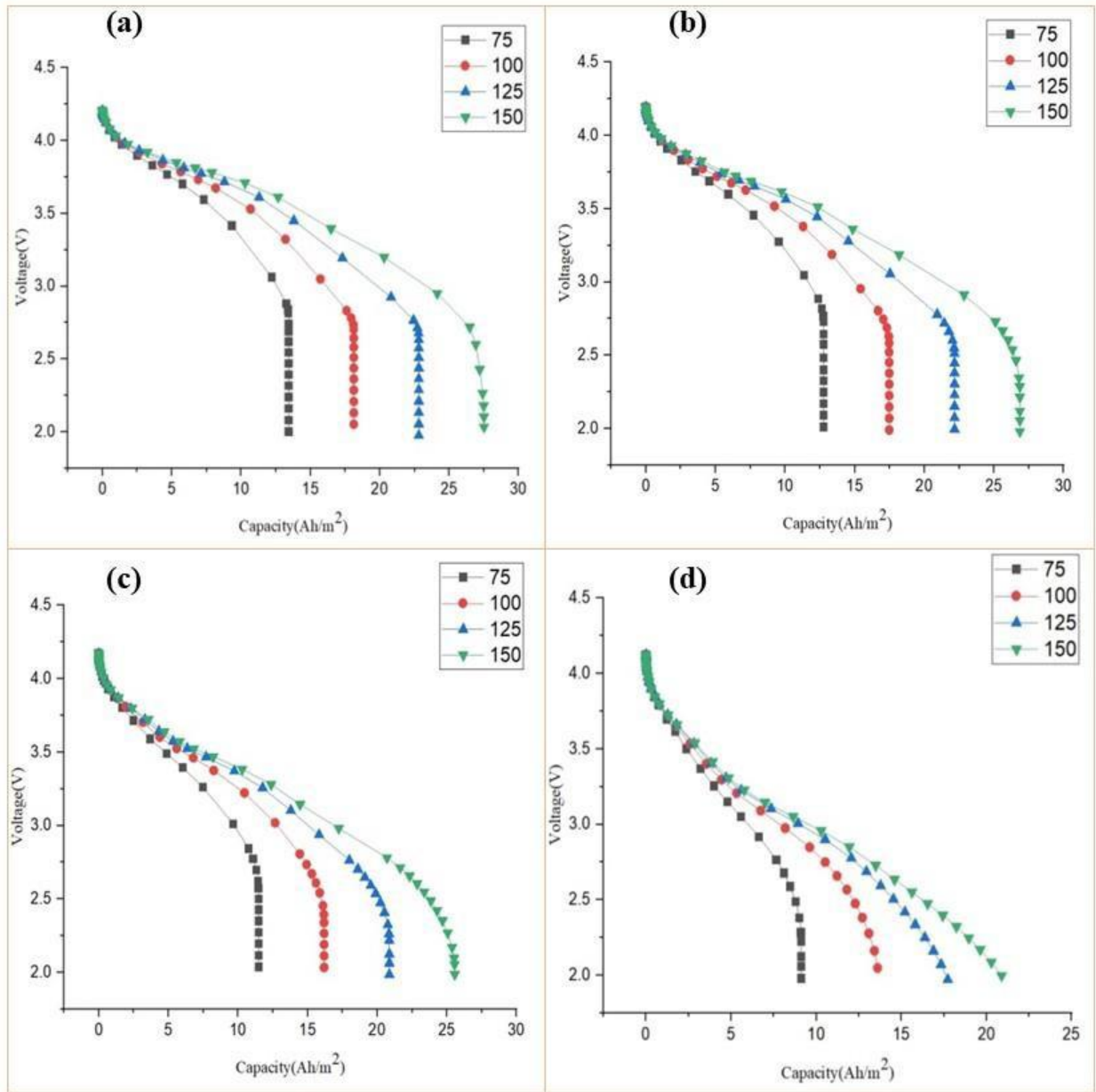


Figure 3. Discharge profile of four full cells made at different anode thicknesses of 75  $\mu\text{m}$ , 100  $\mu\text{m}$ , 125  $\mu\text{m}$ , and 150  $\mu\text{m}$  at discharge rates: (a) 0.5C (b) 1C (c) 2C (d) 4C.

It has been noticed that at different discharge rates from figure 3(a)-(d), the nominal voltage provided by all the four cells is around 4.2V, but there is a significant change in their flat-voltages plateau. The reason behind this effect is the polarization and mass transport process. As the thinner electrode has less polarization and a fast mass transport kinetics than the thicker one because thickness affects the diffusion path length of the lithium-ion.

#### 4. CONCLUSION

The voltage profile of the cells at C-rates of 0.5C, 1C, 2C, and 4C with varying anode thickness of the cell shows the different polarization status. As the thickness of LTO is increased, the ohmic part of the polarization curve showed an increase whereas the concentration part of polarization is decreased.

- The galvanostatic discharge at different C rates of four cells with varying anode thickness (75  $\mu\text{m}$ , 100  $\mu\text{m}$ , 125  $\mu\text{m}$  and 150  $\mu\text{m}$ ), shows a somewhat similar trend of high operating voltage of around 4.2V. But as seen there is a significant change in their flat-voltages plateau. The reason is due to polarization and mass transport process.

#### 5. ACKNOWLEDGEMENT

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#### 6. REFERENCES

- [1] Rozenblit, A., Torres, W.R., Tesio, A.Y. and Calvo, E.J., 2021. Effect of particle size in Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO)-LiMn<sub>2</sub>O<sub>4</sub> (LMO) batteries: a numerical simulation study. *Journal of Solid State Electrochemistry*, 25(8), pp.2395-2408.
- [2] Samina Siddiqui, Amrisha K. Panwar, (2021), International Journal of Advances in Science, Engineering and Technology (IJASEAT), pp. 68-72, Volume-9, Issue-2.
- [3] Geng, Z., Wang, S., Lacey, M.J., Brandell, D. and Thiringer, T., 2021. Bridging physics-based and equivalent circuit models for lithium-ion batteries. *Electrochimica Acta*, 372, p.137829.

[4] Ghosh, A. and Ghamouss, F., 2020. Role of electrolytes in the stability and safety of lithium titanate-based batteries. *Frontiers in Materials*, 7, p.186.

[5] Huber, Ian S. Diss. College of William and Mary, 2017.

[6] Pal, R.D. and Paul, A.K., 2015. Charge-discharge studies of lithium-ion batteries. In *Proceedings of the COMSOL Conference*.

[7] Deng, D., 2015. Li-ion batteries: basics, progress, and challenges. *Energy Science & Engineering*, 3(5), pp.385-418.

[8] Thunman, Mikael, et al. "Discharge performance dependence on electrode thickness for Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/LiMn<sub>2</sub>O<sub>4</sub> cells for application in wafer-integrated microbatteries." *Ecs Transactions* 41.41 (2012): 147.

[9] Cai, L. and White, R.E., 2011. Mathematical modeling of a lithium ion battery with thermal effects in COMSOL Inc. Multiphysics (MP) software. *Journal of Power Sources*, 196(14), pp.5985-5989.

[10] Dusastre, V. ed., 2010. *Materials for sustainable energy: a collection of peer-reviewed research and review articles from Nature Publishing Group*. World Scientific.

[11] Doyle, M. and Newman, J., 1996. AS Gozdz, CN Schmutz, and J.-M. Tarascon. *J. Electrochem. Soc.*, 143, p.1890.

[12] Doyle, M., Fuller, T.F. and Newman, J., 1993. Modeling of galvanostatic charge and discharge of the lithium/polymer/insertion cell. *Journal of the Electrochemical society*, 140(6), p.1526.