

Effect of Sulfur - Porous Carbon Cathode Morphology on
the Discharge Process in Lithium-Sulfur Battery

By

Sabarinathan Pushparaj Subramaniyan

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Supervising Committee:

Dr. Kenneth Reifsnider, Advisor

Dr. Ye Cao, Co-Advisor

Dr. Md. Rassel Raihan, Supervising Committee Member

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Abstract

In the present era, Lithium-ion (Li-ion) batteries are most commonly used in all electronic devices, but the demand for alternative energy increases rapidly due to the catastrophic climate caused by excess use of fossil fuels in automobiles. Li-ion batteries cannot fully satisfy the need as its theoretical capacity is low, and the cathode cost is high. On the other hand, Lithium-Sulfur (Li-S) battery meets the requirement with the highest theoretical capacity of Sulfur 1672 mAh/g. Lithium anode and Sulfur cathode together form to be having the highest energy density. The highest energy capacity of Sulfur is achieved by the conversion of Elemental Sulfur to Lithium Sulfide. Even-though Li-S cell shows the highest theoretical capacity, and the experimental results show much less capacity due to various challenges, which include low cathode conductivity, polysulfide dissolution in the electrolyte and shuttle effect. Although different methods have been developed both experimentally and mathematically to increase the capacity of the cell, further understanding of the mechanism of the Li-S cell is necessary. Hence in this research work, a mathematical framework has been developed in continuum scale to demonstrate the reaction mechanism of the Li-S cell along with all the electrochemical reactions and chemical reactions that include the precipitation and dissolution during the discharge condition. As active surface area loss caused by Li_2S (insulator) precipitation in Li-S cell has a significant impact on the capacity of the cell, the effect of the active surface area of the cathode during discharge condition was studied. Studies on the effects of initial porosity and its effects on the capacity of the Li-S cell are explained.

Later, a pore-scale model of Li-S cell was developed considering the electrochemical reactions (without precipitation and dissolution) and by applying the insulating nature of Sulfur in the Li-S cell, and the results are compared with the continuum scale modelling.

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CHAPTER 1 - INTRODUCTION

The need for alternative energy increases day by day with an ever-growing population, pollution and climatic changes lead to extensive research in the alternative energy systems like solar energy, Wind energy, Electrochemical energy etc. Batteries come under electrochemical energy system, which is considered to be one of the promising alternatives for fossil fuels. Specifically Lithium-ion batteries are widely used in all areas in our life like mobile phones, cars, etc. The increase in demand for energy needs an alternative battery with the highest energy density.

The First electrochemical battery was built by Alessandro Volta in 1800, and He made a zinc and copper electrodes, which is known as the voltaic pile. The development in the area of battery research is slow while compared with other electronic equipment. One of the main reason for this is understanding of battery dynamics and mechanism of reactions that take place inside the electrochemical system.

1.1 Fundamentals of Battery:

The battery is considered to be the heart of electric vehicle system, and it converts the electrical energy to chemical energy and vice versa. There are two types of battery primary and secondary, where the primary batteries are single-use batteries whereas the secondary batteries are rechargeable. In the primary batteries the electrochemical reactions are not reversible, whereas the electrochemical reactions are reversible in the secondary batteries. The average voltage of the battery is a combination of active chemical used in the cell.

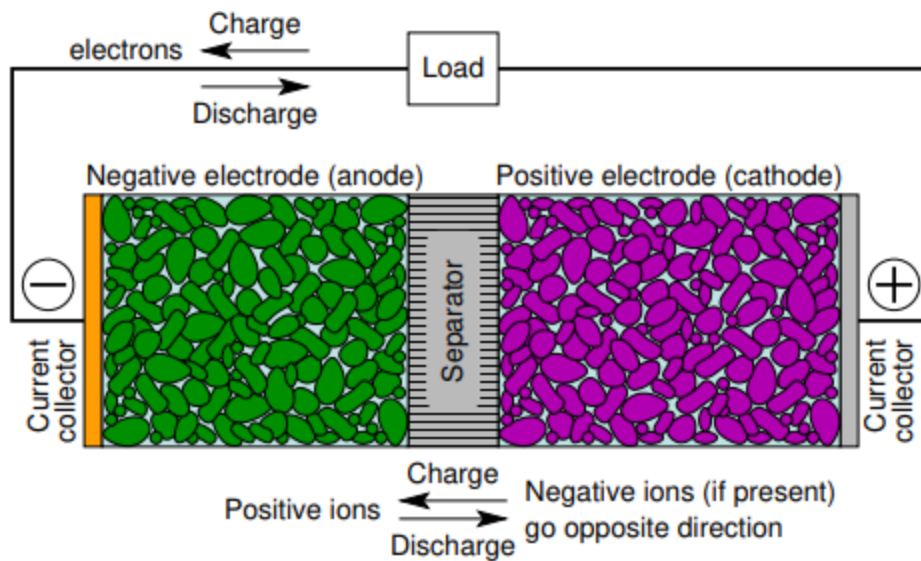


Figure 1:- Schematic representation of an electrochemical cell. [1]

The negative electrode is made up of either metal or an alloy, whereas the positive electrode is often metallic oxide, sulfide etc. During discharge the negative electrode loses electron by oxidation, whereas the positive electrode by a reduction reaction, and vice versa for the charging condition. The electrolyte which is then dissolved salts that levitates the ionic conductivity inside the cell. The separator is used to avoid the self-discharge of the cell.

The lithium-ion battery is the most prominent over the last two decades, especially for all the portable electronic devices. However the ever-increasing energy storage demand needs another rechargeable energy system with higher energy density than the current Lithium-ion batteries in the market. This further energy density can be achieved by increasing the charge storage capacity of anode, cathode or increasing the cell voltage. To overcome the charge storage capacity limitations there should be a need for an electrode material that can accommodate more ions with conversion reactions, In that case Li-O₂ and Li-S batteries are having highest energy density with more challenges in it.

1.1.1 Why Lithium-Sulfur Battery:

Sulfur is one of the cheap and most abundant material in the earth crust with the highest theoretical capacity of 1672 mAh g^{-1} . The highest capacity of the Sulfur is achieved by the conversion of the active sulfur into lithium sulfide (Li_2S), which is the end product of Lithium-Sulfur cell during the discharge process.

How does Lithium-Sulfur Cell work?

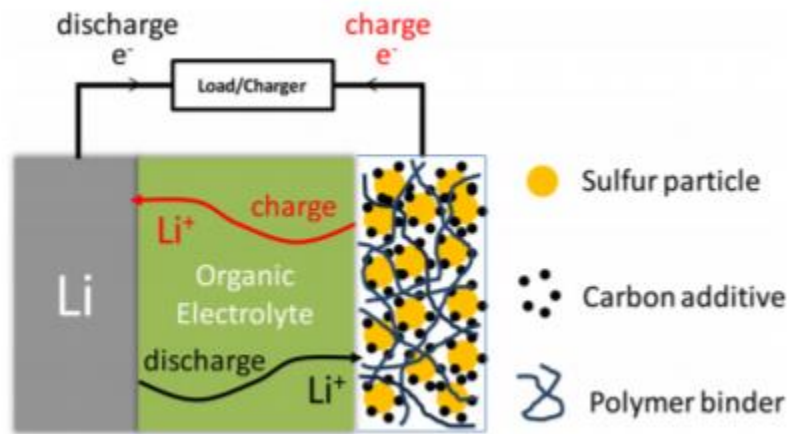


Figure 2:- Schematic representation of the Li-S cell during charge and discharge. [2]

Lithium-Sulfur cell consists of Lithium metal anode and sulfur porous carbon composites as a cathode, with the organic electrolyte/separator. During Discharge the Lithium metal is oxidised to form the Li^+ ions and an electron. The produced lithium ions move towards the cathode where they precipitate to form Lithium Sulfide (Li_2S), which includes numerous Intermediate chemical reactions and intermediate chemical compounds.

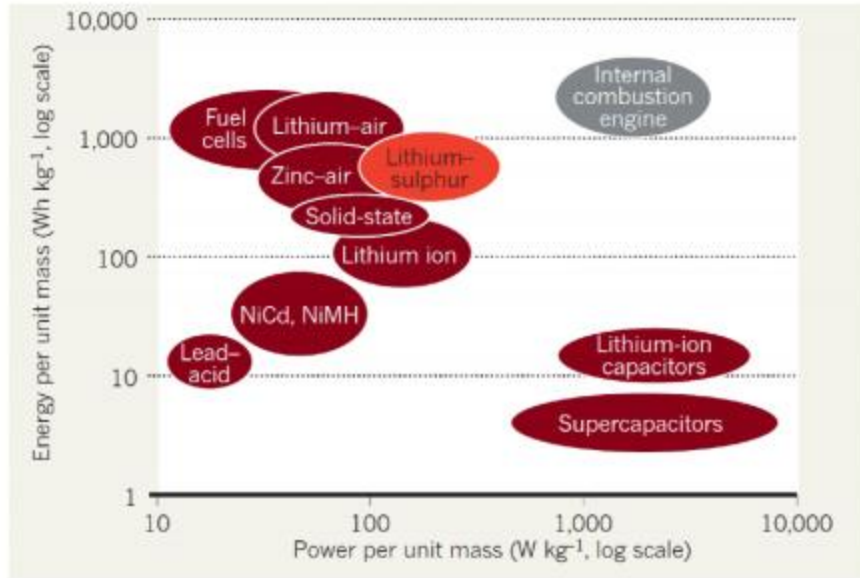
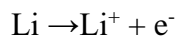


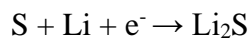
Figure 3:- Energy density Vs power density of Different energy storage systems.[8]

Basic reactions that are occurring in Lithium-sulfur cell during discharge,

Negative electrode:



Positive electrode:



The Theoretical capacity of the lithium is 3861 mAh g⁻¹, and Sulfur is 1672 mAh g⁻¹ when both are combined to give a theoretical capacity of 1167 mAh g⁻¹. The discharge reaction has a nominal cell voltage of 2.15 V.

1.1.2 Reaction mechanism of Lithium-Sulfur cell:

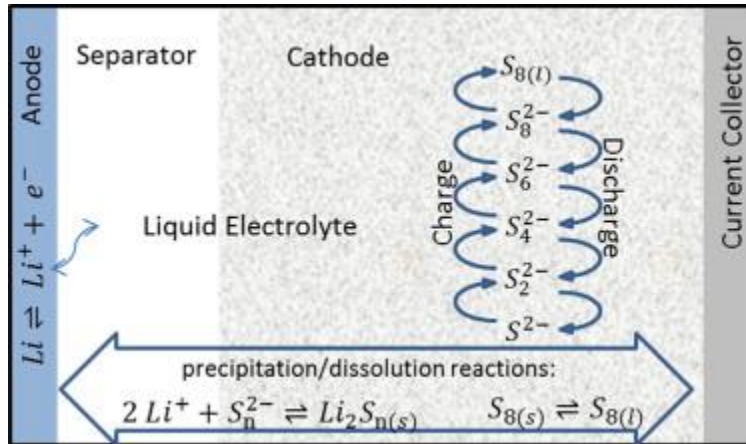


Figure 4:- Schematic of Li-S cell with various intermediate reactions. [7]

Over the last decade, there is intensive research in this field of Lithium-sulfur cell, but it's not yet commercialised due to the unsolved challenges like insulating nature of Lithium poly-sulfides that is formed after the discharge and also the morphological changes that are occurring in the cell during the charge and discharge of the cell.

So it is essential for one to know about the underlying reaction mechanisms that are taking place in the lithium-sulfur cell. One must take the morphology of cathode into account because the sulfur batteries are mostly depended upon the morphology of cell [9] shuttle phenomenon.

The Lithium-Sulfur cell consists of two voltage plateau one is upper voltage plateau, which ranges from 2.4 to 2.0, and another one is lower voltage plateau, which is approximately around 2V. Even though much experimental research is being done in this field of Lithium-sulfur battery there is a need for theoretical understanding in this mechanism of Lithium-Sulfur cell.

During discharge the elemental Sulfur S_8 is reduced to $S_8^{2-} \rightarrow S_6^{2-} \rightarrow S_4^{2-} \rightarrow S_2^{2-} \rightarrow S^{2-}$, this multi-reduction step also includes the Precipitation as a side reaction where Li^+ that is migrating from

the anode reacts with reduced sulfur to form the Lithium poly-sulfides, and this is not the exact reduction mechanism, The research is still going on to understand the mechanism.

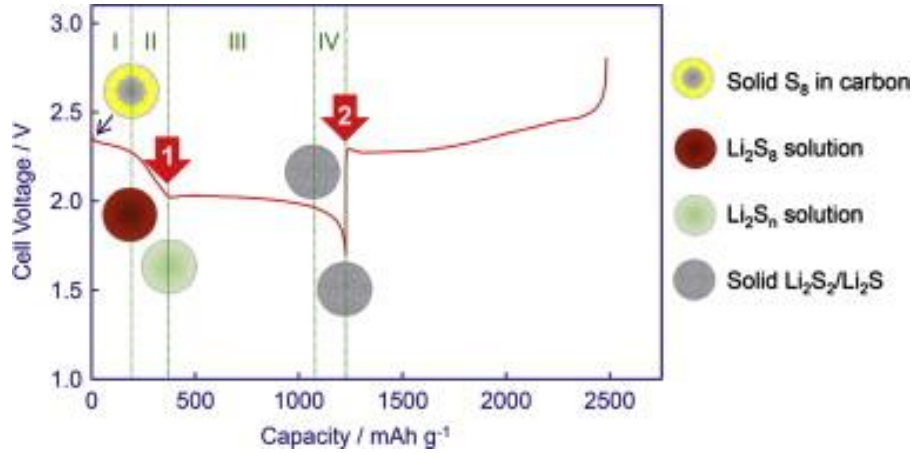
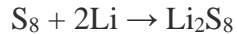
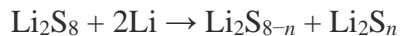


Figure 5:- discharge and charge voltage profile of Li-S cells. [13]

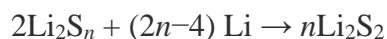
Stage 1: this is the upper voltage plateau of 2.2 – 2.3 V, Here there Elemental Sulfur is Reduced to S_8^{2-} and reacts with Lithium-ion to form Li_2S_8 , Then the formed Li_2S_8 dissolves in the electrolyte.

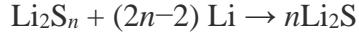


Stage 2: In this dissolved Li_2S_8 is further reduced to lower-order lithium-poly-sulfides, and also we could find a sharp declination in the cell voltage and also the viscosity of the electrolyte solution increases with the increase in the concentration of the lithium poly-sulfides.



Stage 3: In this region, the dissolved lower-order lithium poly-sulfides are further reduced to produce the Insoluble Li_2S_2 and Li_2S where the Lower voltage plateau ranges from 1.9-2.1 V, and it defines the capacity of the entire Lithium-Sulfur cell.





Stage 4: In this solid to a solid reduction reaction takes place where the insoluble Li_2S_2 reacts with the lithium ions to form insoluble Li_2S , which is the end discharge product of the Lithium-Sulfur cell.[13].



1.1.2 Challenges in Lithium-Sulfur cell:

Despite having the highest energy density, Low cost, etc. the Lithium-sulfur cell has so many challenges.

The Insulating nature of sulfur active material ($5 \times 10^{-30} \text{ S/cm}$) [3] and Lithium Sulfide (10^{-13} S/cm)[4] which are the intermediate compounds that are formed during the electrochemical reactions, for an electrochemical reaction it is necessary that the material needs to be conductive so there where so many research going on in making Sulfur/Carbon cathode. However, the Lithium sulfide that is formed during the electrochemical reaction will make structural and morphological changes in the cathode, which leads to less utilisation of the active sulfur material.

Another critical issue is the polysulfide shuttle, the Higher-order polysulfide that is formed will migrate to anode and react with the Lithium to form Lower order poly-sulfides and then migrate back again to cathode to form an Higher-order poly-sulfides in cathode which leads to poor charge efficiency[5].

1.1.3 Sulfur/Carbon Cathode:

The solution to the problem of High resistance of the cathode is found by adding appropriate electrical conductors like conductive carbon and carbon additives, Among the conductive carbon,

the porous carbon has received more attention due to its high conductivity and ability to hold the insulating sulfur in to its pore structure with good electrical contact between active material, so it helps in high sulfur utilization and thereby increasing the efficiency of the cell. There are various types of porous carbon matrix-like engineered pore structure, mesopore, micro-pore everything enhances the electrolyte transport and charge transport. However, the challenge over here is increasing the carbon leads to less capacity, due to less carbon while increasing the sulfur will leads to poor utilisation due to less carbon content, so it is necessary to employ the optimum range of Sulfur and Carbon in the Cathode. However, the manufacturing process of these porous structures is tedious. During dissolution and precipitation there is a change in volume of cathode and separator, and the porous carbon need to be made in way to withstand this volume changes during the charging and discharging cycle and also the chemical surface properties of the carbon affects the polysulfide retention, over the past decade there was extensive research in this cathode design [6].

Barai.et al. developed a computation model to quantify the effect of precipitation in the volume change and pore morphology where they found smaller pore tends to attain lesser volume changes compared to larger pores and also concluded that non-uniform Precipitation of Li_2S might cause micro-crack formation in the pore walls. [12]

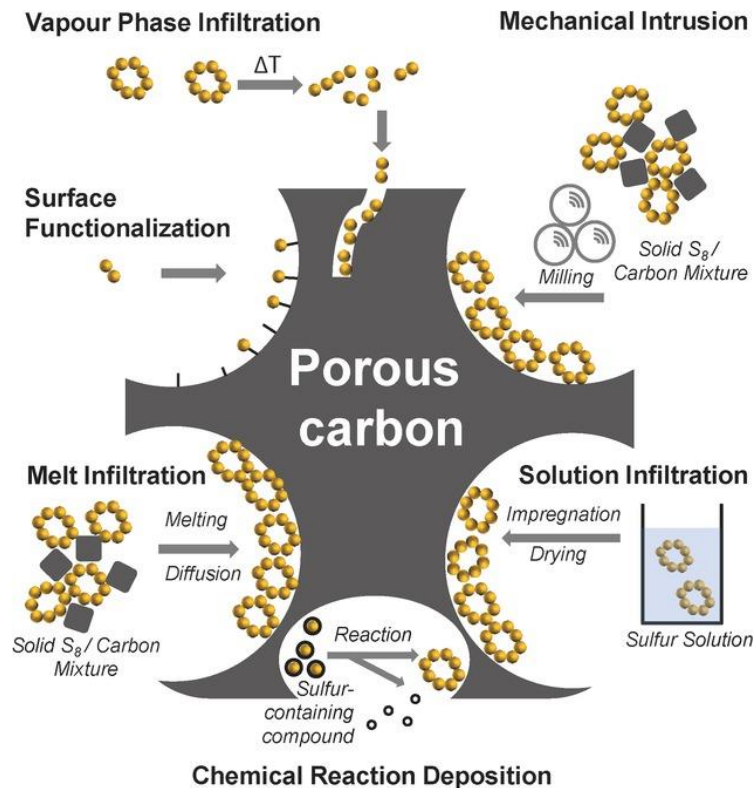


Figure 6:- Various approaches for Introducing sulfur into the Porous carbon [6]

1.1.4 Development in Mathematical modelling of Lithium-Sulfur cell:

Apart from the other experimental researches the numerical modelling of Lithium-Sulfur cell also shows a significant improvement in the field of this research, Kumeresan.et.al created a mathematical model for a Lithium-Sulfur cell where they included transport of ionic species, electrochemical reaction due to Butler-Volmer equation, precipitation reaction and also pore volume change due to precipitation, they have assumed all the parameters, and how they affect the discharge of cell. [11]

To analyse the sensitivity of Kumeresan.et.al[11] model to the physical parameters Chen.et.al [14,15,16] and found that the Kumeresan.et.al model is so sensitive to the parameters that are governing the precipitation and dissolution, Chen et al. have analysed the different rate constants

for the precipitation reactions. The model showed highly non-linear behaviour where a small change in the rate constants produced a significant difference in the model. They also reported that the model failed to work under the charge condition due to low saturation concentration of Li_2S , which limits the re-dissolution of Li_2S upon charging. They also increased the sulfur content per volume of the cathode, but they did not include the insulating nature of sulfur and poly-sulfides and assumed the active surface area does not change with increase in the sulfur content [14]. They have also done a sensitivity analysis of Lithium-Sulfur cell by varying the applied discharge current rate, and the electronic conductivity and found that minimum electronic conductivity of the cathode to activate the cell ranges from 1 to 10^{-4} S m^{-1} but their model predicts very flat second plateau that is different from the results of many experiments because they have assumed all the surface in the cathode facilitates electrons from the electrochemical reaction which is not same experimentally [15]. Chen et al. also done a parameter analysis of Mathematical model framework created by Kumerasan et al with different electrochemical reaction kinetics where the change in the exchange current densities of $\text{S}_{8(l)}$ and S_2^{2-} reduction reaction showed a capacity loss. They have also analysed the Different diffusion coefficient, which helps us to understand the viscosity effect of electrolyte. At low diffusion coefficients we could find non-uniform usage of active sulfur and uneven distribution of Precipitate. Which leads to stress in the cathode; they also modelled for charging condition by increasing the solubility of Li_2S to a larger value [16].

Numerical model by Zhang et al. showed the importance of electrolyte resistance and precipitation kinetics in Voltage loss of Li-S cells, here they have produced the concentration-dependent electrolyte conductivity with variation in the ionic concentration due to the precipitation also the activation over-potential increase in lower plateau is explained with reduced active surface area of cathode [10]. Hofmann et al modelled Lithium-sulfur cell where they have used Four-step sulfur

reduction mechanism and also simple representation of Polysulfide shuttle where the results match with their experimental data and also they could see the polysulfide shuttle that is mostly visible in liquid-electrolyte Li-S batteries and also Infinite charging at low constant current densities, Low Coulombic efficiency and capacity fading due to loss of active material from cathode to anode. But they haven't considered the nucleation and growth of the Lithium sulfides [17].

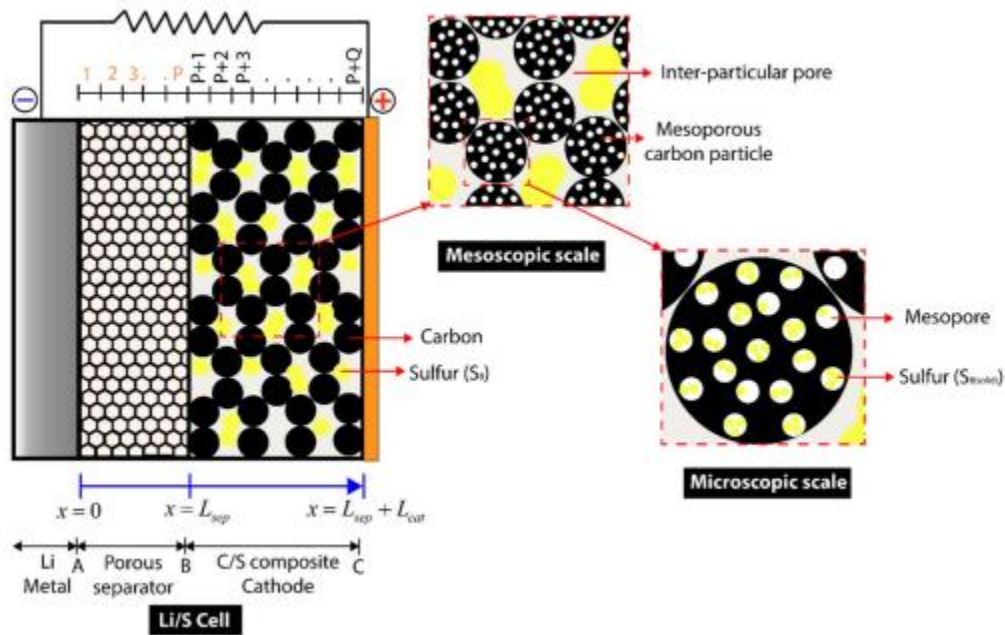


Figure 7:- Schematic representation of Lithium-Sulfur cell at Multi-scales.[18]

Thangavel.et.al introduced microstructurally resolved Lithium-sulfur model in which they have introduces inter-particle porosity and mesopores separately, and this model is not solved for the particle size dimension; instead, they used lumped approach to define the mass balance inside the particles.

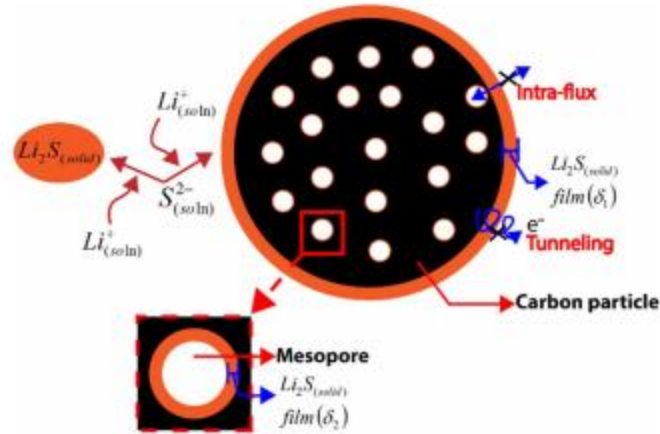


Figure 8:- Schematic representation of the route of Li_2S Precipitation. [18]

They also introduced the Li_2S precipitation in the carbon causes the surface passivation, and it is solved by taking the Li_2S precipitate thickness as a function of ionic flux between the bulk electrolyte and the particle. This model can predict the optimal carbon/sulfur ratio, porosity distribution in Li-S cell. [18]. Yoo.et.al modified the existing mathematical kinetic model for precipitation by adding an additional term to improve numerical stability. They also included the reduction reaction of Higher-order poly-sulfides on Lithium anode to model and investigated the polysulfide shuttling problem, and they modeled the charging behaviour of Lithium-Sulfur cell at various reaction rate constant of Poly-sulfides reduction on Lithium anode and they compared it with the experimental results of Lithium-Sulfur cell and found that overcharge problem is more with higher reaction rate constant of poly-sulfide reduction reaction in lithium anode [19]

Moreover As a summary of development in the mathematical model still we are not able to predict the behaviour of Lithium-Sulfur cell accurately. All the model did not investigate the loss of active surface area of the cathode including the insulation nature of Sulfur and Lithium Sulfide and its impact on the lithium-sulfur cell, They do consider the active surface area change but they

considered it to be a phenomenological expressions where the whole change in the porosity changes the active surface area of the cathode.

1.2 Thesis summary and objectives:

This thesis work employs the continuum modelling and Pore-scale modelling of Lithium-sulfur cell, in which the Continuum modelling involves all the precipitation and dissolution reaction whereas the 2D modelling will consider only the electrochemical reaction and doesn't take precipitation and dissolution into an account.

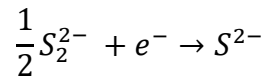
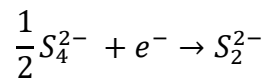
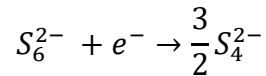
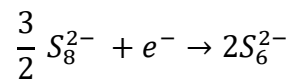
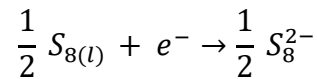
The main objectives are

- Employ continuum modelling of Lithium-Sulfur cell
- To analyse the effect of Specific surface area of the cathode In Lithium-Sulfur cell in the continuum model.
- To analyse the effect of Pore Volume Fraction in the Continuum model.
- To analyse the effect of including the insulating nature of Sulfur in the 2D modelling and changing the Surface length of Carbon/electrolyte interface.

Chapter 2 - MODEL DEVELOPMENT

2.1 Continuum model development

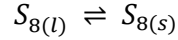
Mathematical modelling is found to be an important tool in our day to day life to predict the performance; here, we are going to use the mathematical framework developed by Kumaresan.et.al [11]. In Lithium-Sulfur cell, the discharge is based on the dissolution of elemental sulfur and precipitation of Lithium Sulfide, and There are multiple species along with multiple electrochemical and chemical reactions involved in this discharge of Lithium-Sulfur cell.



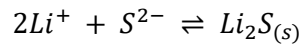
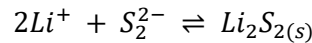
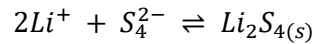
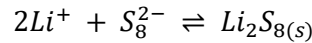
The above equations are the electrochemical reactions that take place in the cathode where the dissolved sulfur is reduced to S^{2-} finally. The Lithium oxidation reaction below is happening at the surface of the anode.



In addition to all the electrochemical reaction mentioned above, there is a chemical reaction which involves the dissolution of Elemental Solid Sulfur in the cathode to dissolved sulfur, which then undergoes sequence of reduction reaction.



Apart from the dissolution chemical reaction, the precipitation reaction also takes place in the cathode, where the Lithium-ion migrates from anode to cathode react with the several Sulfur ions that are being reduced in the cathode to form the Lithium poly-sulfides, and the end product of the discharge of Lithium-Sulfur cell is the Li_2S . So the Solid S_8 and Li_2S determine the capacity of the cell. The higher-order poly-sulfides are soluble in the electrolyte, whereas the Li_2S is insoluble.



2.1.1 Governing Equations:

All the electrochemical reactions, chemical reactions, transport of ions, current conservation in solid phases and liquid phases are governed by a set of governing equations which helps us to define and analyze the physics of cell with appropriate parameters and boundary conditions.

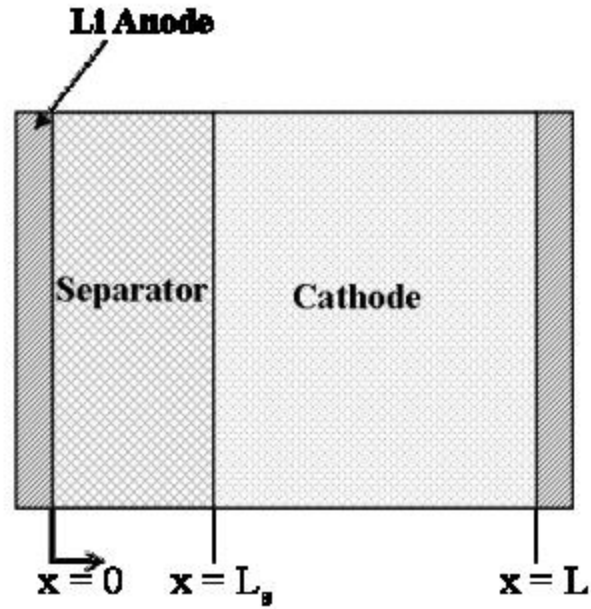


Figure 9:- Schematic of Lithium-Sulfur cell [11]

The material balance equation in the porous media is governed by

$$\frac{\partial \varepsilon C_i}{\partial t} = -\nabla \cdot N_i + r_i - R_i$$

Where $i = Li^+, S_{8(l)}, S_8^{2-}, S_6^{2-}, S_4^{2-}, S_2^{2-}, S^{2-}, A^-$

The flux of the species is due to both the diffusion and migration in the dilute solution is

$$\frac{N_i}{\varepsilon} = -D_i \nabla C_i - z_i \frac{D_i}{RT} F C_i \nabla \Phi_2$$

Where $D_i = D_{i,o} \varepsilon^b$

$D_{i,o}$ is the diffusion coefficient in the bulk medium, b is the Bruggeman coefficient, D_i is the effective diffusion coefficient considering the tortuosity and porosity.

z_i is the charge number of the species,

R is the gas constant

T is the temperature

F is the Faraday's constant

Φ_2 is the liquid potential

The second term in the right-hand side of the material balance equation is the electrochemical reaction term through which the species is either produced or consumed during the reaction if the r_i is negative then there is the consumption of the species, and if it is positive then there is the production of the species.

$$r_i = -a \sum_j \frac{s_{i,j} i_j}{n_j F}$$

$$i = Li^+, S_{8(l)}, S_8^{2-}, S_6^{2-}, S_4^{2-}, S_2^{2-}, S^{2-}, A^-$$

a is the active surface area of the cathode,

$s_{i,j}$ is the stoichiometric coefficient of the species i in the reaction j

i_j Denotes the butler Volmer equation for the reaction j

The active surface area decreases with precipitation of the Li_2S , which causes a decrease in the porosity hence the phenomenological expression is introduced below.

$$a = a_o \left(\frac{\varepsilon}{\varepsilon_{initial}} \right)^\xi$$

The over-potential for the reaction j is given by the equation below,

$$\eta_j = \phi_1 - \phi_2 - U_{j,ref}$$

Where ϕ_1 refers to the solid phase potential

$U_{j,ref}$ refers to the open circuit potential.

$$U_{j,ref} = U_j^\theta - \frac{RT}{n_j F} \sum_i s_{i,j} \ln\left[\frac{C_{i,ref}}{1000}\right]$$

The chemical reaction is governed by the equation below which considered the precipitation and dissolution,

$$R_i = \sum_k \gamma_{i,k} R'_k$$

$$i = Li^+, S_{8(l)}, S_8^{2-}, S_6^{2-}, S_4^{2-}, S_2^{2-}, S^{2-}, A^-$$

Where k denotes the solid precipitate that is formed during the reactions.

$$k = S_{8(s)}, Li_2S_{8(s)}, Li_2S_{4(s)}, Li_2S_{2(s)}, Li_2S_{(s)}$$

$\gamma_{i,k}$ is the number of moles of ionic species i

The Rate of precipitation of the solid precipitates is governed by the equation below

$$R'_k = k_k \varepsilon_k \left(\prod_i C_i^{\gamma_{i,k}} - K_{sp,k} \right)$$

Where k_k is the rate constant for precipitation and dissolution reaction.

ε_k is the volume fraction of the solid precipitates.

$K_{sp,k}$ is the solubility product.

Electric potential in Cathode,

$$\nabla \cdot [(1 - \varepsilon)^{1.5} \sigma \nabla \phi_1] = a(i_2 + i_3 + i_4 + i_5 + i_6)$$

Where σ is electric conductivity.

Electric potential in the electrolyte

$$\nabla \cdot (\varepsilon^{1.5} \lambda \nabla \phi_2) = -\nabla \cdot [F \sum (Z_i \varepsilon^{1.5} Z D_i \nabla C_i)] - a(i_2 + i_3 + i_4 + i_5 + i_6)$$

2.1.2 BOUNDARY CONDITIONS:

Anode-Electrolyte interface:

$$N_{Li^+} = \frac{i_{load}}{F}$$

$$N_i = 0 \text{ for other ions}$$

Separator-Cathode interface:

$$\nabla \phi_1 = 0$$

Cathode-Current collector interface:

$$N_i = 0$$

$$\nabla \phi_2 = 0$$

$$\sigma \nabla \phi_1 = -i_{load}$$

Table 1:- Stoichiometric coefficients, $s_{(i,j)}$ [11]

The reaction given by equation						
Species	1	2	3	4	5	6
Li ⁺	-1	0	0	0	0	0
S _{8(l)}	0	-1/2	0	0	0	0
S ₈ ²⁻	0	1/2	-3/2	0	0	0
S ₆ ²⁻	0	0	2	-1	0	0
S ₄ ²⁻	0	0	0	3/2	-1/2	0
S ₂ ²⁻	0	0	0	0	1	-1/2
S ²⁻	0	0	0	0	0	1
A ⁻	0	0	0	0	0	0

Table 2:- Thermodynamic and Kinetic Properties. [11]

Reaction (j)	i_j^{ref}	α_c	α_a	n_j	U_j^θ (V)
1	0.394	0.5	0.5	1	0
2	1.9719	0.5	0.5	1	2.39
3	0.019719	0.5	0.5	1	2.37
4	0.019719	0.5	0.5	1	2.24
5	1.972x10 ⁻⁴	0.5	0.5	1	2.04
6	1.972x10 ⁻⁷	0.5	0.5	1	2.01

Table 3 :- Transport properties and reference concentrations. [11]

Species(<i>i</i>)	z_i	$D_{i0}(m^2/s)$	$C_{i,ref}(mol/m^3)$
Li^+	+1	1×10^{-10}	1001.04
$S_{8(l)}$	0	1×10^{-9}	19.0
S_8^{2-}	-2	6×10^{-10}	0.178
S_6^{2-}	-2	6×10^{-10}	0.324
S_4^{2-}	-2	1×10^{-10}	0.020
S_2^{2-}	-2	1×10^{-10}	5.229×10^{-7}
S^{2-}	-2	1×10^{-10}	8.267×10^{-10}
A^-	-1	4×10^{-10}	1000.0

Table 4:- Cell dimensions and porosity of Cathode and separators. [11]

Parameters	Separator	cathode
Thickness(m)	9×10^{-6}	41×10^{-6}
$\epsilon_{initial}$	0.37	0.778
$\epsilon_{S8(s),initial}$	1×10^{-12}	0.160
$\epsilon_{Li2S8(s),initial}$	1×10^{-6}	1×10^{-6}
$\epsilon_{Li2S4(s),initial}$	1×10^{-6}	1×10^{-6}
$\epsilon_{Li2S2(s),initial}$	1×10^{-6}	1×10^{-6}
$\epsilon_{Li2S(s),initial}$	1×10^{-7}	1×10^{-7}
$a_0(m^2/m^3)$	-	132762
b	1.5	1.5

Table 5 :- Parameters for the precipitation reactions.[18]

Precipitate(k)	Rate constant(k_k) ($\text{mol}^2.\text{m}^{-6}.\text{s}^{-1}$)	Solubility product(K_k) ($\text{mol}^3.\text{m}^{-9}$)	Molar Volume(V_k) (m^3/mol)
$\text{S}_{8(s)}$	$35.0 (\text{s}^{-1})$	$19(\text{mol}/\text{m}^3)$	1.239×10^{-4}
Li_2S_2	10^{-9}	30	4.317×10^{-5}
LiS_2	5×10^{-7}	10	2.768×10^{-4}

2.2 Pore-scale model development

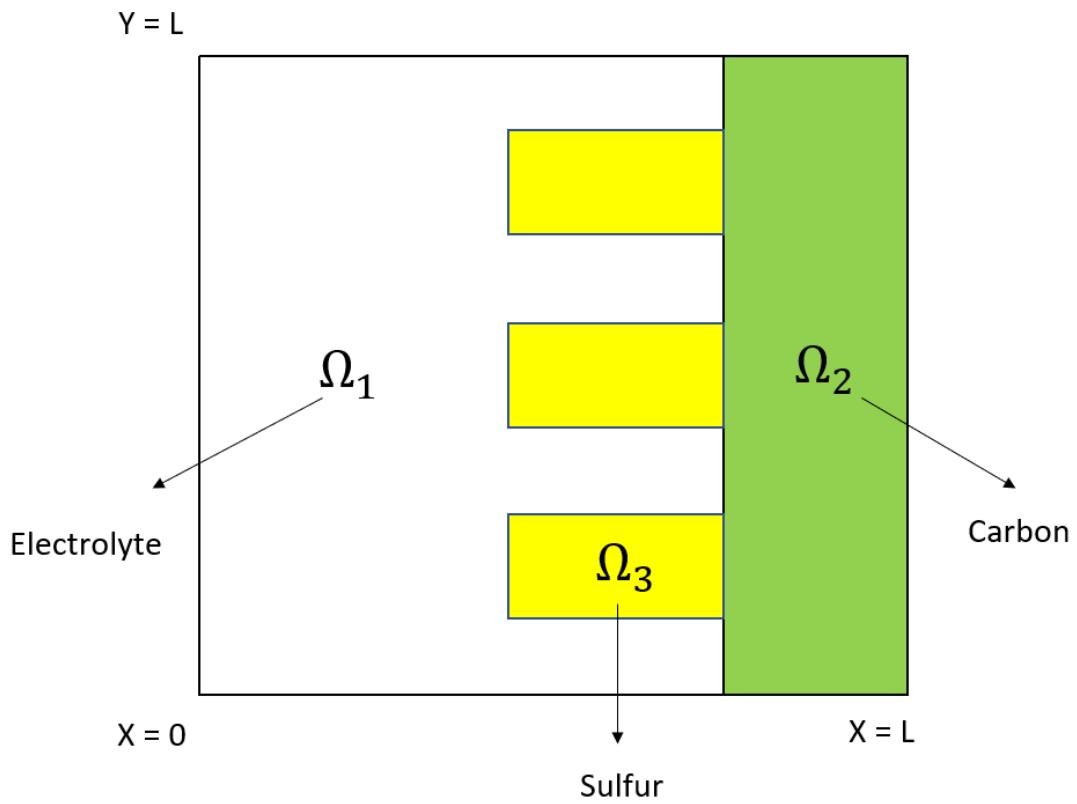


Figure 10:- Schematic representation of pore scale model of Lithium-Sulfur cell

2.2.1 Governing Equation

The governing equations for mass transport

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot N_i + r_i$$

The flux of each species is given by

$$N_i = -D_i \nabla C_i - z_i \frac{D_i}{RT} F C_i \nabla \Phi_2$$

$$i = Li^+, S_{8(l)}, S_8^{2-}, S_6^{2-}, S_4^{2-}, S_2^{2-}, S^{2-}, A^-$$

In this model, only the electrochemical reaction is considered, whereas the dissolution and precipitation reaction is not considered.

The electrochemical reaction is given by,

$$r_i = - \sum_j \frac{s_{i,j} \dot{i}_j}{n_j F}$$

The over-potential for the reaction j is given by the equation below,

$$\eta_j = \phi_1 - \phi_2 - U_{j,ref}$$

Where ϕ_1 refers to the solid phase potential

$U_{j,ref}$ refers to the open circuit potential.

$$U_{j,ref} = U_j^\theta - \frac{RT}{n_j F} \sum_i s_{i,j} \ln \left[\frac{C_{i,ref}}{1000} \right]$$

Electric potential in Cathode,

$$\nabla \cdot [\sigma \nabla \phi_1] = (i_2 + i_3 + i_4 + i_5 + i_6)$$

Where σ is electric conductivity.

Electric potential in the electrolyte

$$\nabla \cdot (\lambda \nabla \phi_2) = -\nabla \cdot [F \sum (Z_i D_i \nabla C_i)] - (i_2 + i_3 + i_4 + i_5 + i_6)$$

2.2.2 Boundary condition:

We use the same governing equations,

Domain notations:

Entire domain, $\Omega = \Omega_1 \cup \Omega_2 \cup \Omega_3$

Intersection of domains $\Gamma_{jk} = \Omega_j \cap \Omega_k$

Periodic boundary conditions are used along the Y-axis.

At $\Gamma_{12} \cup \Gamma_{13}$

Electrolyte potential, $k_1 \frac{\partial \phi_1}{\partial x} = i \cdot \hat{n}$

The solid-phase potential of carbon, $\sigma_2 \frac{\partial \phi_2}{\partial x} = -i \cdot \hat{n}$

The solid-phase potential of Sulfur, $\sigma_3 \frac{\partial \phi_3}{\partial x} = -i \cdot \hat{n}$

The electrical conductivity of the sulfur is 5×10^{-30} S/cm, and it is added to the model.

Chapter 3 - RESULTS AND DISCUSSION

3.1 Continuum modelling of Lithium-Sulfur cell:

Here we used the Mathematical framework used by Kumerasan.et.al[11] to build the continuum scale modelling of the Lithium-Sulfur cell where we studied the working mechanism of Lithium-Sulfur cell with the help of that model and validated the model with the results obtained using the same parameters.

It is important to study the behaviour of the cell using the voltage curve, and we are concentrating only on the discharge behaviour since our model only focuses on that. The discharge cell voltage profile of the Lithium-Sulfur cell is divided into four stages, from the discharge graph along with the average concentration profile of the Lithium-Sulfur cell we can understand the physics of it. Initially during the first stage we could see the drops from 2.4 V to 2.3 V which is the upper voltage plateau (i.e) when the discharge capacity is along **250(Ah/kg of S₈)** during which the Solid Sulfur that is being dissolved along with the formation S_x^{2-} ($x=2,4,6,8$) after that there is steep decrease in the cell voltage from 2.3 to 2.1 V which is considered to be the stage 2, in which the solid sulfur is being completely dissolved with the increase in the porosity, after stage 2 there is a slight dip in the cell voltage, (i.e) when the discharge capacity is along **400 (Ah/kg of S₈)** this dip is an evident for the nucleation of Li_2S because usually nucleation is the slow process, in-order to nucleate on the carbon substrate it needs to overcome a large energy barrier, the depth of the dip defines the energy required to overcome the barrier of the nucleation, once the nucleation is done, the growth happens simultaneously when there is already some amount Li_2S present in the cell then there will be no dip in the cell voltage, the precipitation starts to grow above that nucleated area in the carbon substrate.

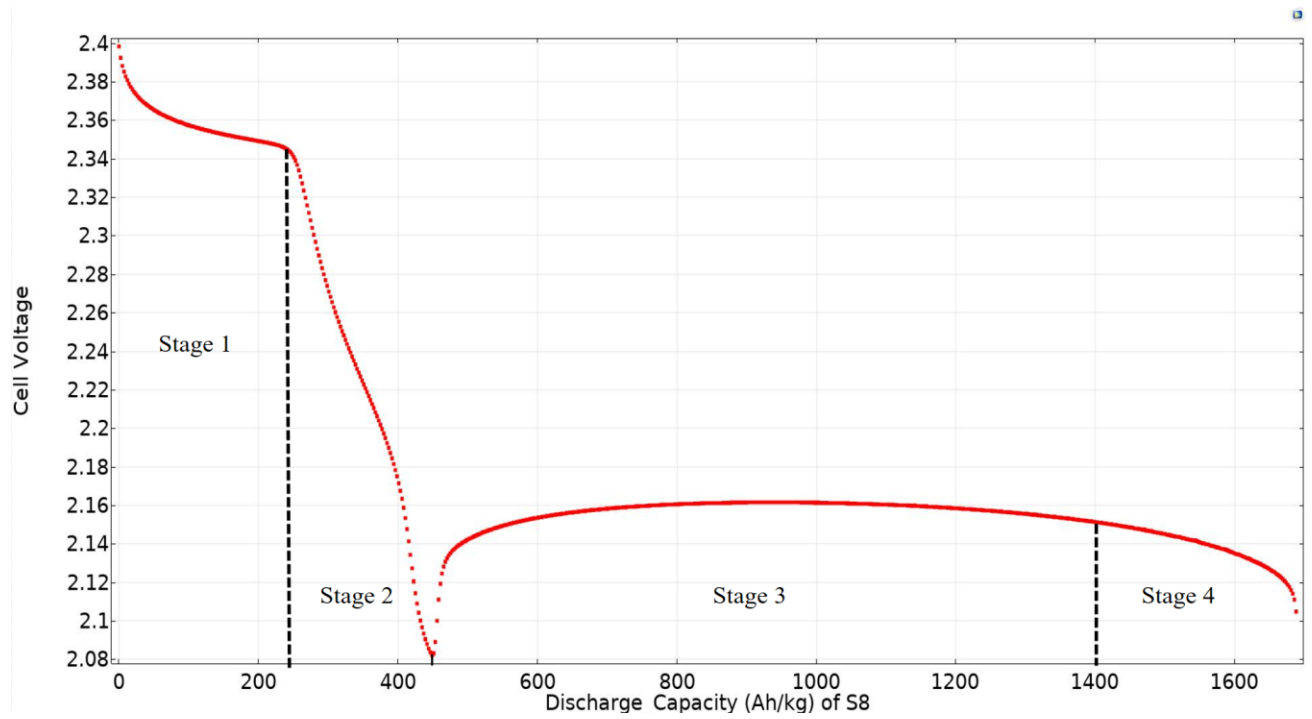


Figure 11:- Cell Voltage Vs. Discharge Capacity

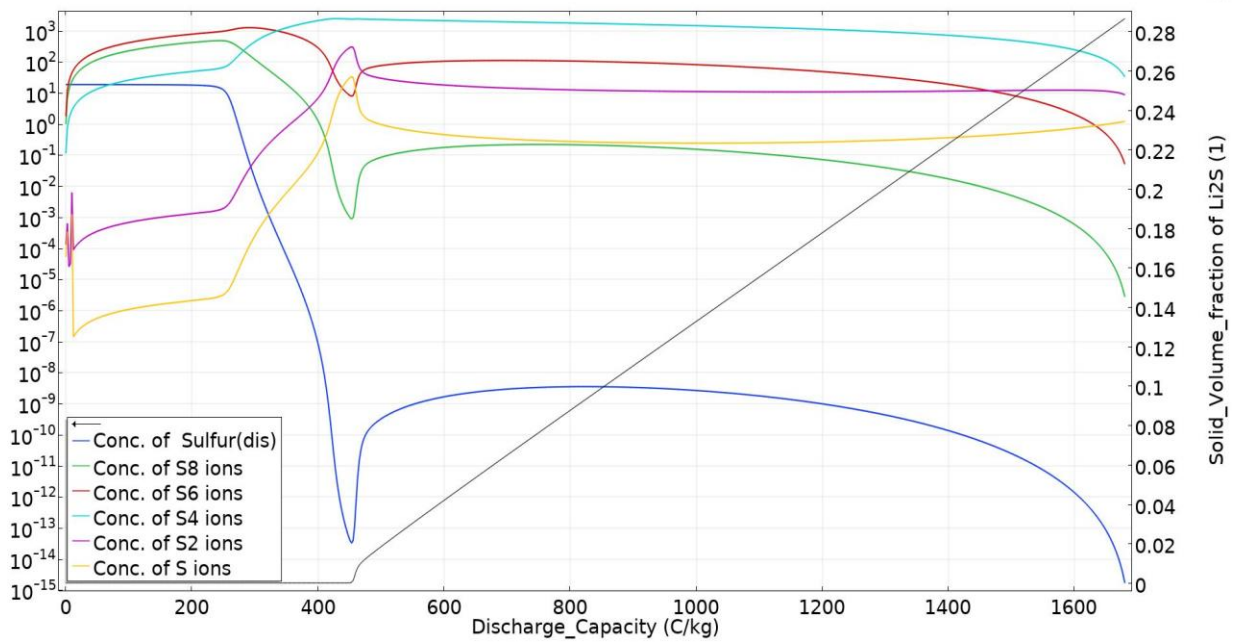


Figure 12 :- Average concentration (mol/m³) Vs. Discharge Capacity

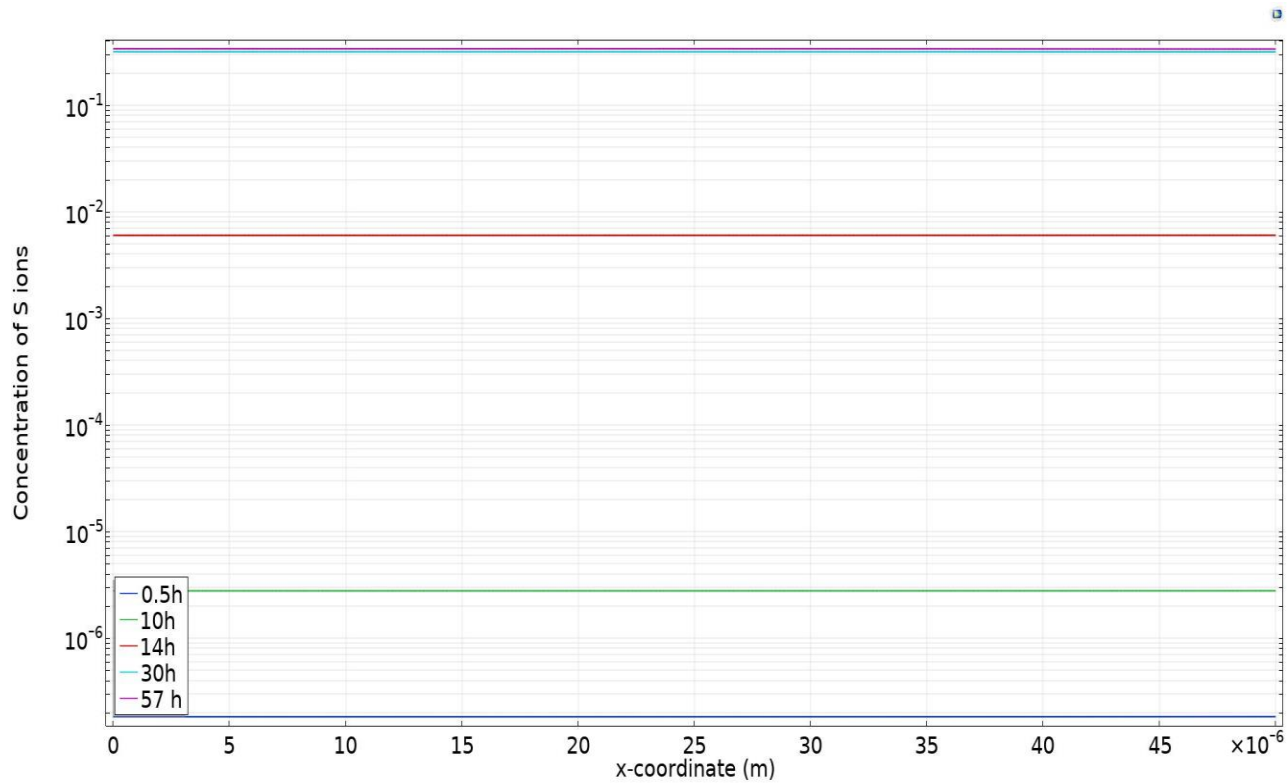


Figure 13:- Concentration of S^{2-} ions vs length of separator and cathode

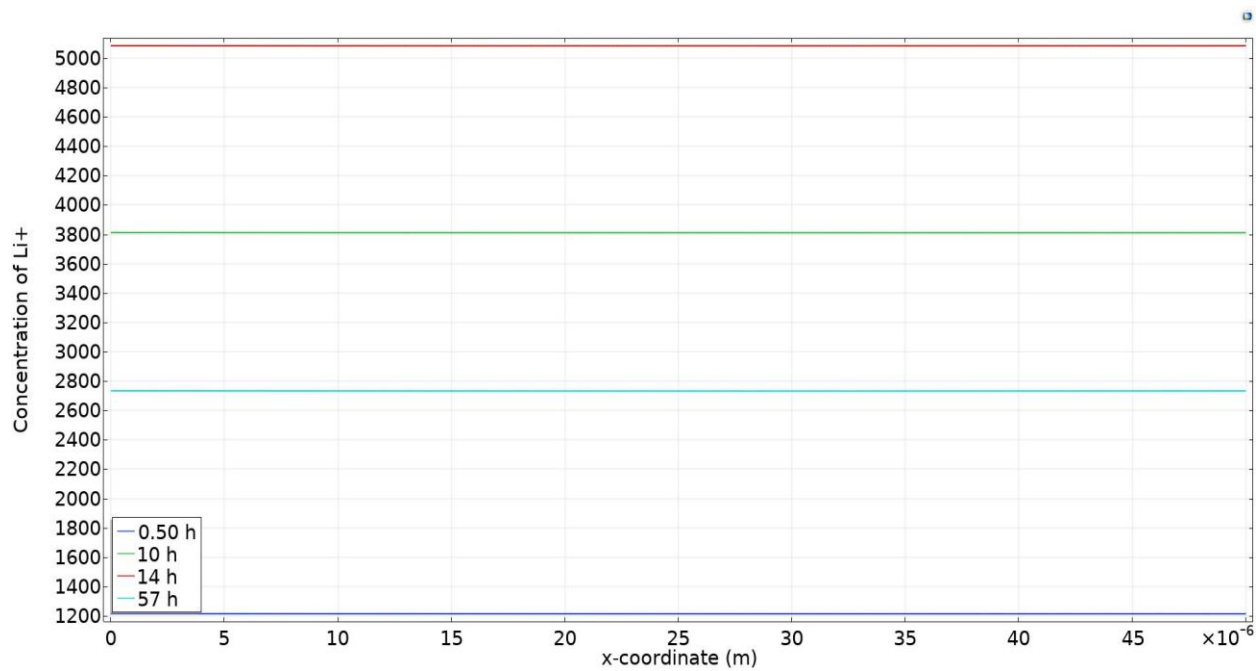


Figure 14:- Concentration of Li^+ ions vs length of separator and cathode

Here the concentration gradient along the cathode and separator is negligible, so we must take the average concentration of all the ions at various time in-order to see how it varies with the discharge profile. Which gives us a better understanding of reaction mechanism.

At the start of Stage 3, the ionic product of $[\text{Li}^+][\text{S}^{2-}]$ will become supersaturated that represents that its value is more than its solubility product which causes the precipitation of Li_2S on the carbon substrate, during this stage 3, all the S ions remains constant throughout and at the end of Stage 3, the porosity of the lithium Sulfur cell will decrease along with the precipitation of the Li_2S and all the S_x^{2-} will tend to decrease along with the decrease in the Cell Voltage. Depending upon the precipitation rate, the concentration of S^{2-} decreases.

3.2 Effect of Active Surface area in Sulfur Porous Carbon Composites

One of the key features in the porous electrode of batteries are active surface area, Active surface area is an area through which the current is being distributed throughout the cell, One of the main problem in the lithium Sulfur cell is the decrease in the active surface area after the discharge cycle, This decrease in the active surface area is mainly due to the Li_2S precipitation, that is happening on the surface of the cathode, so it blocks the carbon surface that is in direct contact with the electrolyte, Since Li_2S is an insulator with the electronic conductivity of 10^{-13} (S/cm^{-1}) because of this it reduces the rate of electrochemical reaction that is happening between the cathode and electrolyte.

In our study, we have done a parametric study to verify the effect of the change in the active surface area of the cathode in the Lithium-Sulfur cell using the Kumersan.et.al model [11].

In this present model, certain assumptions were made,

- We are using the phenomenological expression in which we are studying the Change in the initial active surface area a_0
- We consider the whole simulation is taking place in an isothermal condition.
- The porous separator and the cathode are the only computational domain in this continuum model because anode is made up of thin lithium foil, so it is considered as a source of Lithium ions.

We do consider this only for the discharge cycle.

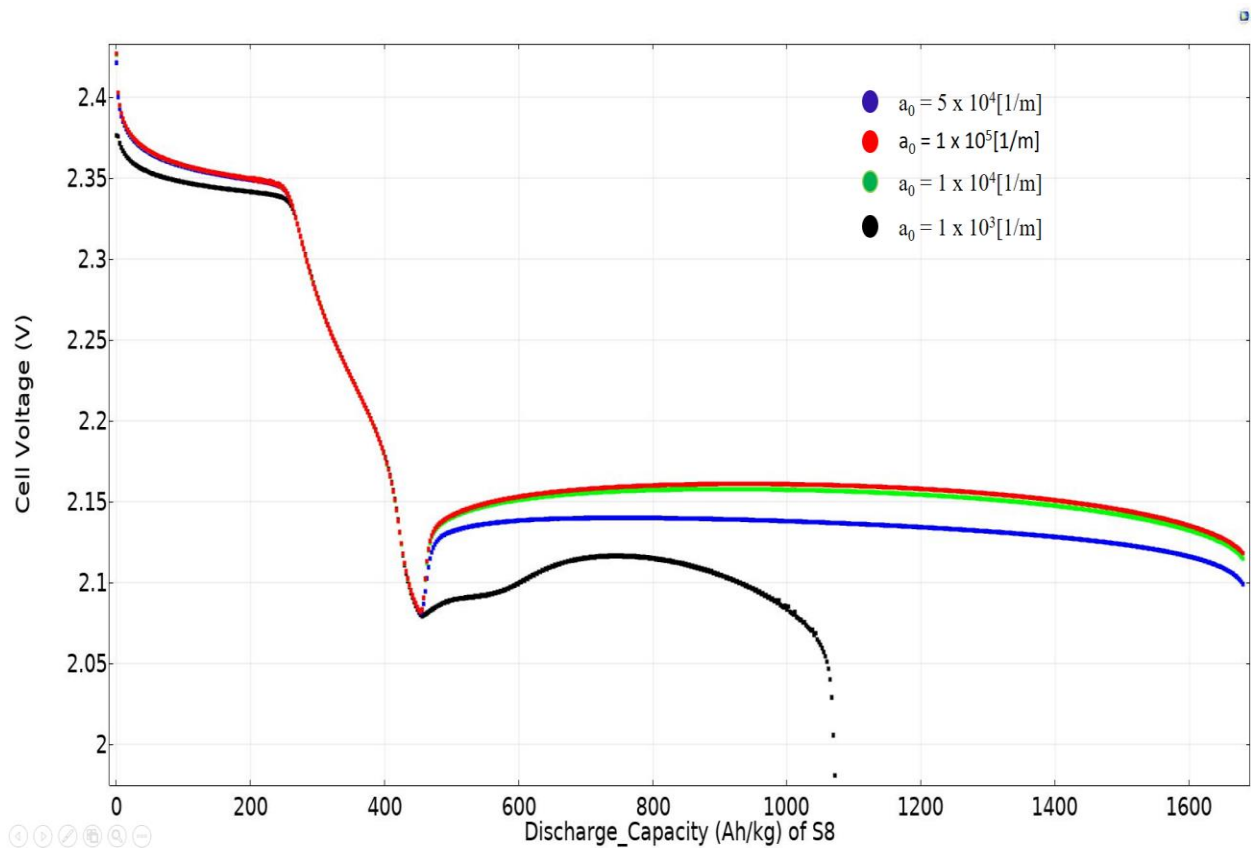


Figure 15:- Cell Voltage Vs Discharge Capacity for Different a_0 :

Here, the initial voltage is kept to be 2.45[V], we have simulated the test for four different initial active surface area value of $a = 5 \times 10^4$, 1×10^4 , 1×10^3 , 1×10^5 . The initial porosity is 0.778, and the above discharge is obtained by applying a constant current density of $0.324[\text{A}/\text{m}^2]$.

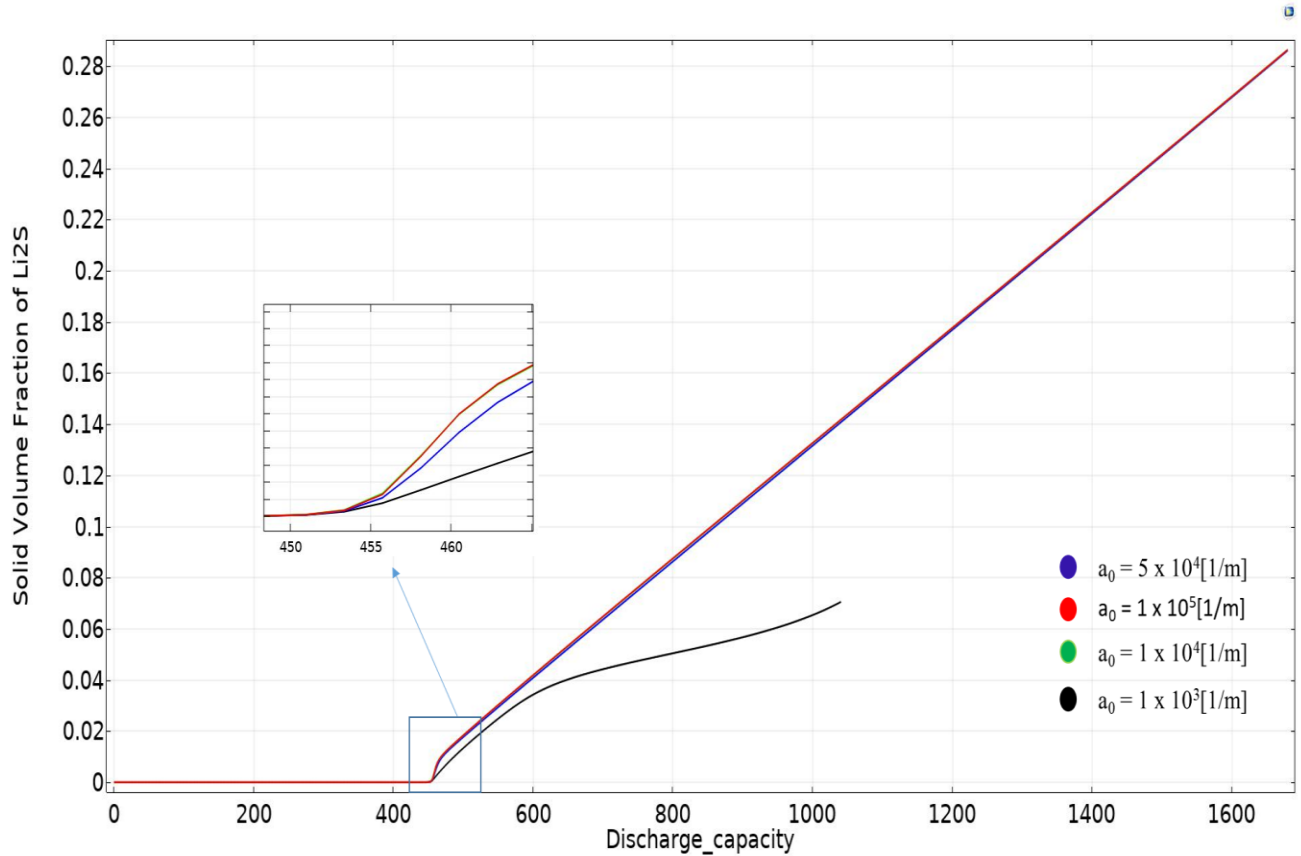


Figure 16:- Solid Volume Fraction of Li_2S Vs Discharge Capacity for different a_0

We know that change in free energy is related to the electrochemical reaction that is taking place in the cell. $\Delta G = \mu_{\text{Re}} - \mu_{\text{ox}} - \mu_e$, Where μ_{Re} and μ_{ox} is the electrochemical potential of reductant and oxidant respectively, whereas μ_e is the electrochemical potential of the electron.

When $\Delta G < 0$, the reduction reaction takes while $\Delta G > 0$, then oxidation reaction is taking place in the cell. The rate of reaction is related to the free energy change, when free energy change is far from the equilibrium, the reaction rate is faster to move forward towards the equilibrium, Consider the electrochemical potential increases for the species that is being produced whereas the electrochemical potential decreases for the species that is being consumed, Here in this process the electrochemical reactions are governed by the Butler-Volmer equation.

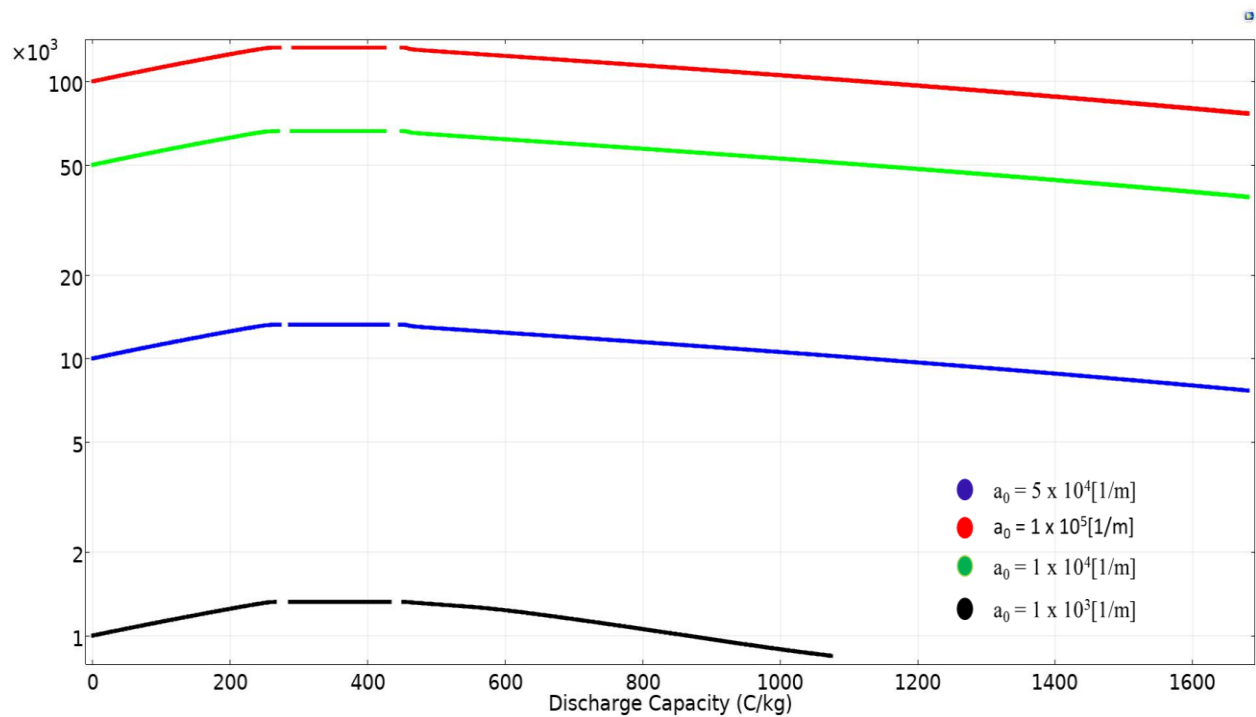


Figure 17 :- Active surface area(1/m) Vs. Discharge Capacity

When there is the higher active surface area of the cathode, change in free energy is closer to the equilibrium so the reaction takes place slowly and the amount of current density required at that point is also low, this makes the cell to operate in a higher voltage. This can be seen in our graph where the operating Voltage increases with the increase in the active surface area of the cathode.

Another one problem is when there is less active surface area of the cathode, the supply of the current increases the electrochemical potential of electron which in turn makes the change in free energy far from the equilibrium position in-order to bring back that to near the equilibrium position the remaining active surface need to increase the rate of reaction which causes the decrease in the cell voltage. This can be seen in our graph for initial active surface area 1×10^3 where the cell voltage is decreased to compensate with the rate of electrochemical reaction along with the degradation of the remaining active surface area of the cathode.

3.3 Effect of Change in Initial Porosity in Lithium-Sulfur Cell

Typically the discharge behaviour of the Lithium-Sulfur cell depends upon the various factor, but one of the important factor to be considered is the volume fraction of the conductive material that is found in the Cathode. So here we are doing a parametric study in which we are changing initial porosity without changing the volume fraction of the active material in the cell, and we are not changing the initial active surface area of cathode. We have done this simulation by applying constant current density of 0.324 A/m^2 .

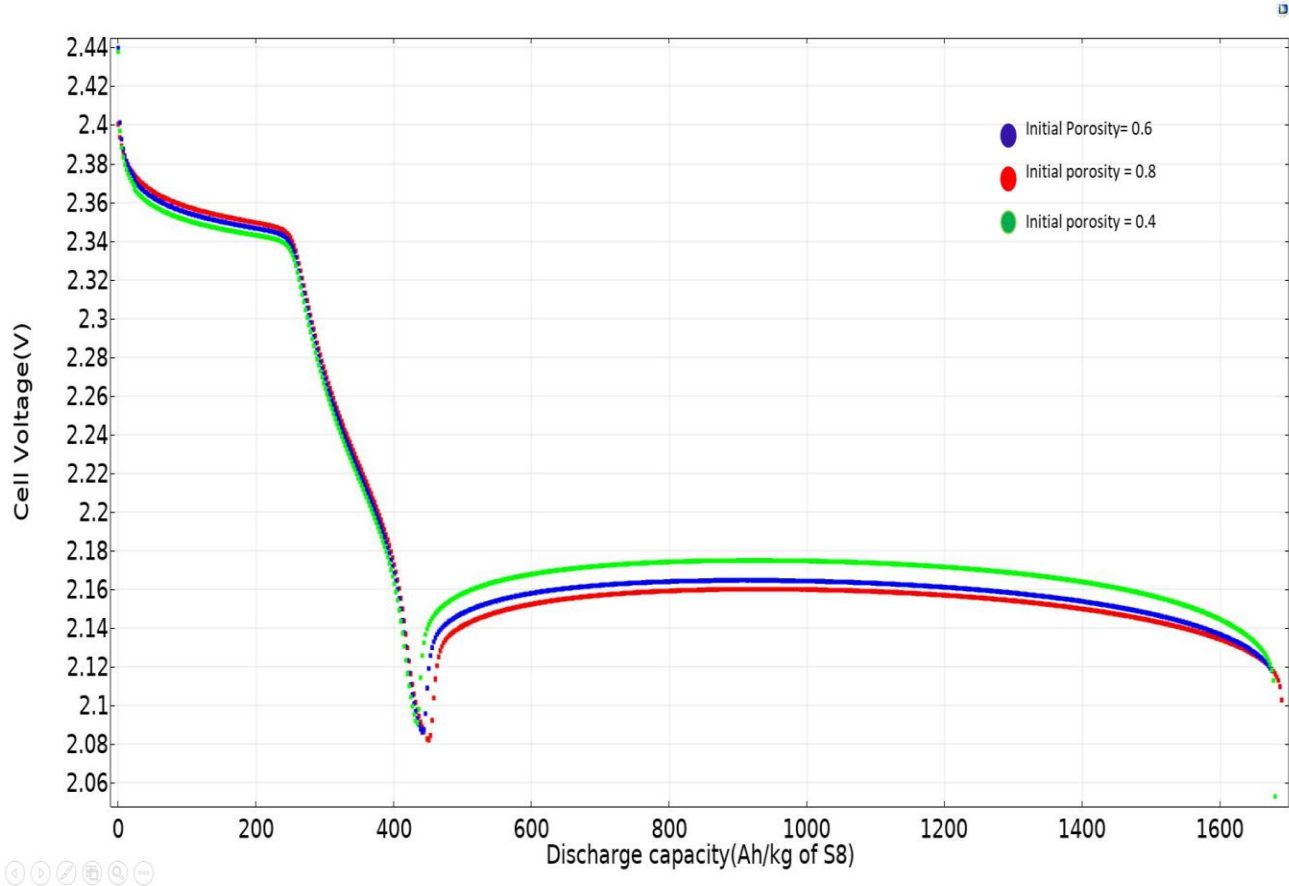


Figure 18:- Cell Voltage Vs. Discharge Capacity for different initial porosity

We have done simulation for different initial porosity of 0.4, 0.6, 0.8 In this we could see the result where the cell voltage of upper voltage plateau between 2.3 V to 2.4 V in which the voltage decreases with the decrease in initial porosity, and then after that there is a step decrease in voltage from 2.3 V to 2.1 V in which the active sulfur is entirely dissolved by increasing the porosity, the nucleation of Li_2S is the slow process, and the nucleation and growth of the Li_2S happens faster with a decrease in the initial porosity. From this simulation we can understand that the initial porosity has a direct influence of the phenomenological expression of the active surface area.

$$a = a_o \left(\frac{\varepsilon}{\varepsilon_{\text{initial}}} \right)^\xi$$

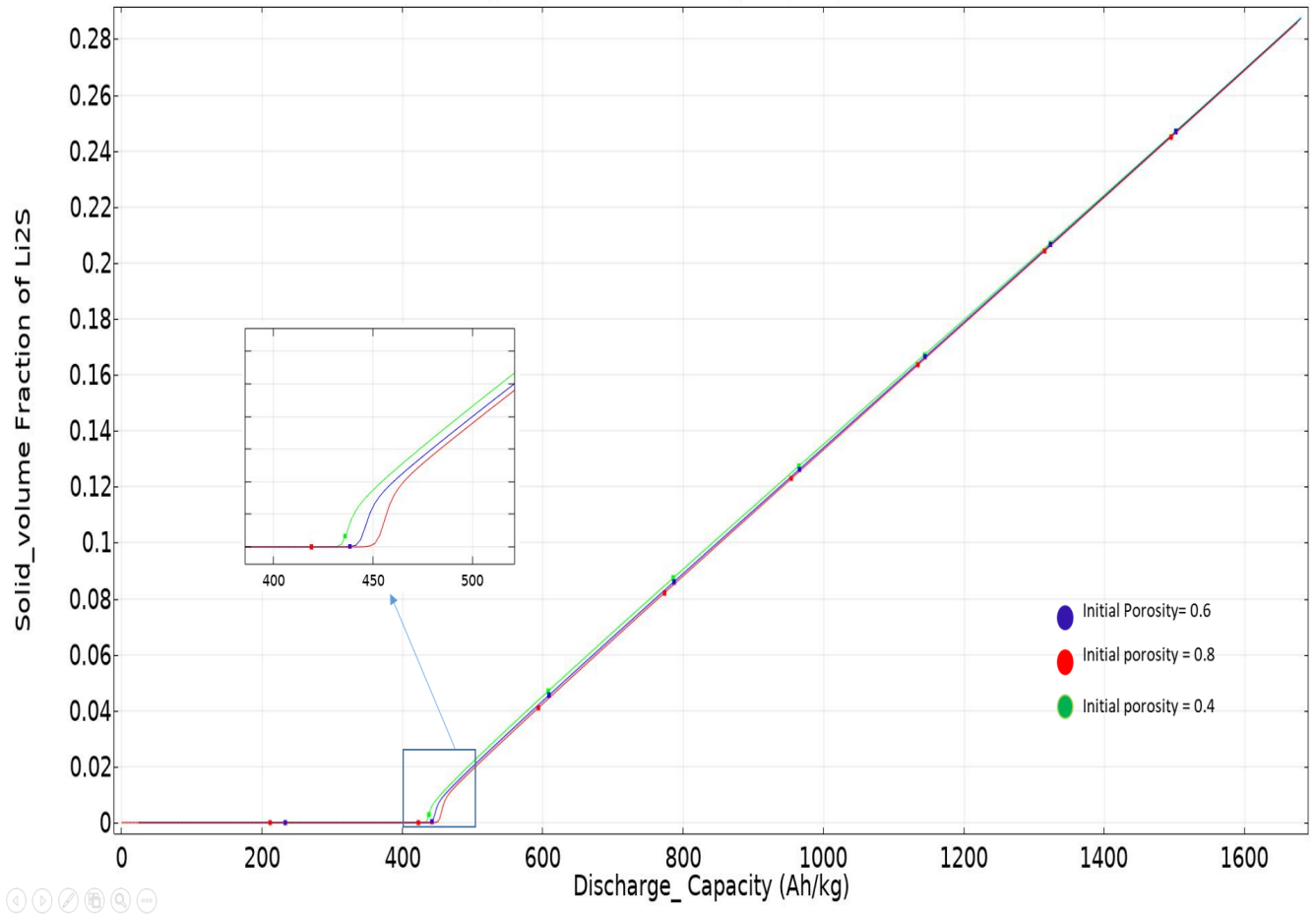


Figure 19:- Solid Volume Fraction of Li_2S Vs. Discharge Capacity

Here in this simulation after the end of the dissolution of the sulfur the active surface area is more for the initial volume fraction of pore to be 0.4, then followed by 0.6 and 0.8, the active surface area is less for the initial porosity of 0.8, That is the main reason for the increase in the operating cell voltage with the decrease in the initial porosity. This same trend is also found by Darren Law et al. in their thesis.[20]

Chapter 4 - 2D MODELLING OF Li-S CELL

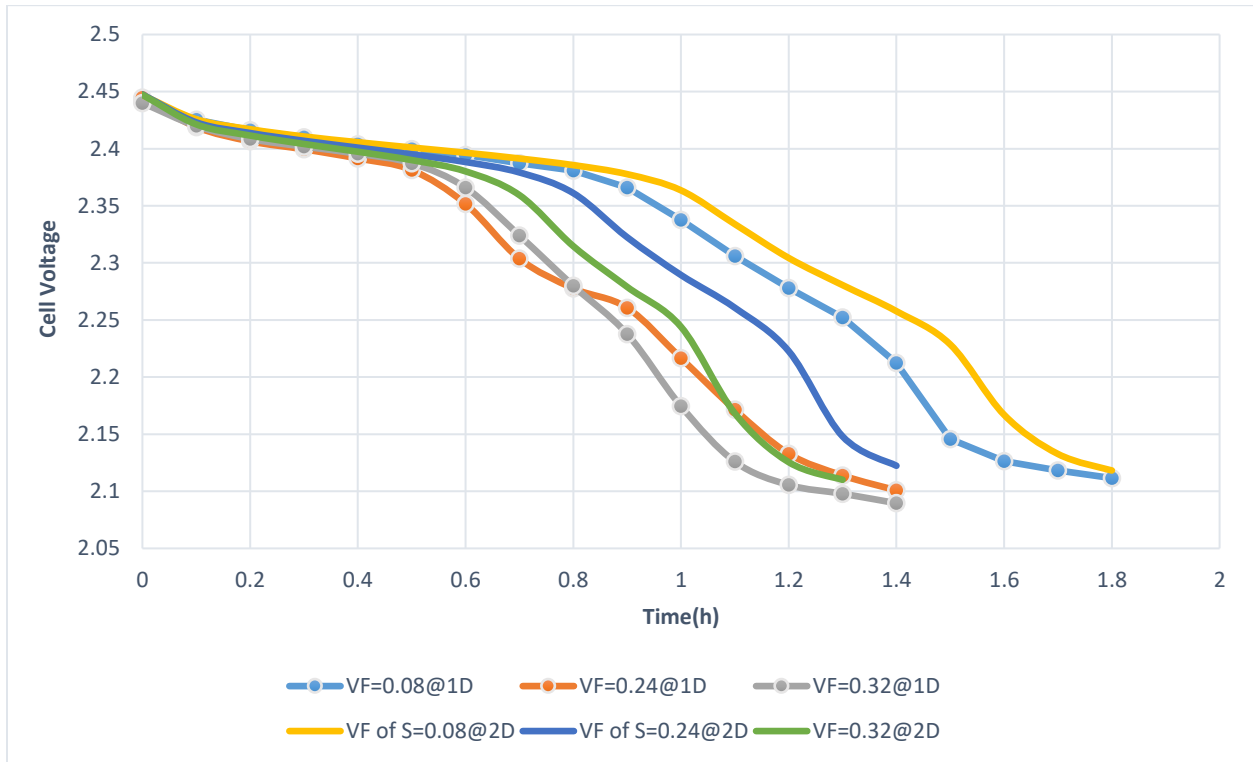


Figure 20:- Cell voltage vs time (h) for 1D and 2D for Different Volume fraction of Sulfur

It is important for us to understand the microstructure of Lithium-Sulfur cell, previous macro-scale continuum model is a volume average model consider some of the parameters to be homogeneous medium, so it is important for us to develop a pore-scale model, one of the major drawbacks of the continuum scale model of Lithium-sulfur cell is it doesn't account for the active surface area loss by including the insulating nature of Sulfur and Li_2S precipitate.

As the first step of it, we developed a 2D model considering transport equation, current conservation equation in electrolyte and electrode, electrochemical reaction. But we did not consider the chemical reaction like precipitation and dissolution and also the pore volume change due to this precipitation and dissolution reaction. In this model we also omitted the tortuosity

Here we modelled for both 1D and 2D for different Volume fraction of Sulfur including the insulating properties of sulfur in 2D where the Volume fraction of carbon is 0.15, and it is constant, there is slight difference in the voltage profile which is mainly due to the active surface area, here in this 2D model, the active surface area was much larger than the active surface area in the 1D model, We need to continue further the precipitation and dissolution of the Li_2S and Sulfur respectively, where we are planning to model thickness-dependent electrical conductivity of Li_2S , this work was inspired by Charles et al. [14] in pore-scale modelling of the Lithium oxygen cell.

Chapter 5 - CONCLUSIONS AND FUTURE WORK

In this research work, the effect of active surface area in the cathode of Lithium-Sulfur cell have been studied where the increase in active surface area increases the operating voltage of the cell and decreases in voltage with decrease in the active surface area, too much less active surface area also causes the decrease in the discharge capacity with the unutilized active sulfur and the effect of initial porosity in continuum scale is studied which has an direct influence in the active surface area but it did not account for conductivity of sulfur in the sulfur carbon matrix cathode and also conductivity of the lithium sulfide at the end of discharge. So the pore-scale model needs to be developed with the precipitation and dissolution reaction considering Conductive carbon phase, electrolyte phase, Lithium Sulfide phase and Sulfur phase. Morphological changes due to this need to be studied, the concentration is not varying spatially, which makes the need for developing a pore-scale model.

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