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Metal Oxides as Lithium Polysulfide Adsorbents in Lithium Sulfur Batteries

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Materials Science and Engineering

by

Setareh Jahansouz

June 2019

Dissertation Committee:
Dr. Juchen Guo, Chairperson
Dr. Bryan Wong
Dr. Ruoxue Yan

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The Dissertation of Setareh Jahansouz is approved:

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Committee Chairperson

University of California, Riverside

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I would like to express my appreciation for my committee members, Dr. Bryan Wong and Dr. Ruoxue Yan for their input and assistance answering my questions. I would like to thank you my fellow lab mates on the energy storage team; Jiayan Shi, Weilu Liang, Xiaoyu Wen, Jian Zhang, Yifan Zhao, Chengyin Fu, Linxiao Geng, Haiping Su, Noam Hart, Zheng Yan, Rahul Jay; for their help and contributions. Finally, I would like to thank my loving family for their unwavering trust and support.

Dedication

This dissertation is dedicated to:

my dearest parents, Gohar and Jahanbakhsh Jahansouz

my loving husband, Mehdi

my adorable children, Massih and Samih

the best advisor, Professor. Juchen Guo

ABSTRACT OF THE DISSERTATION

Metal Oxides as Lithium Polysulfide adsorbents in Lithium Sulfur Batteries

by

Setareh Jahansouz

Doctor of Philosophy, Graduate Program in Materials Science and Engineering
University of California, Riverside, June 2019
Dr. Juchen Guo, Chairperson

Recently, higher energy density storage devices are highly requested by a growing market. Researchers' choices for the next-generation of electrochemical energy storage devices are limited between few options [16]. Lithium–Sulfur batteries have been counted as the best option for energy storage devices, such as rechargeable batteries. These types of cells attracted tremendous attention because of their higher capacity and reasonable cost compared to the other types of available batteries. Although the lithium-sulfur battery has tremendous advantages over lithium ions batteries, the performance and capacity of Lithium–Sulfur batteries suffers from high cathode volume, insulation of sulfur species, lithium dendrites formation and soluble polysulfide [25]. Li-S batteries have limited cycle life and rate capability due to the low electronic conductivity of sulfur. To solve these issues, Hollow Carbon Nanospheres (HCNs) have been used for improving the conductivity problem [50].

To achieve better bonding between mechanistic penetration and high performance Li-S battery's performance, the weak interchange between carbon and polysulfide's source should be minimized through stronger interactions [1,16]. Also, using alternative options to recapture the active sulfur species diffused in the electrolyte can improve the final performance. To overcome these obstacles and achieve better electrochemical properties, the introduction of transitional metal can improve the common interlinkage to strong bond [25]. Hence, understanding of the interaction between lithium polysulfides and transitional groups is important. The transitional metal oxide with lithium polysulfides adsorbents as a cathode material is a promising option for Lithium Sulfur batteries to obtain the relationship between product properties and capacity [25,16].

This important material is a stepping stone to achieve higher capacity, conductivity and strong binding between Li- S species [1,16,17]. Metal oxide, such as MgO and $Mn\ O_2$, can absorb sulfur particles. These materials, due to their intrinsic hydrophilic surfaces, will sort sulfur in electrolyte stronger with higher conductivity, less sulfur solubility, and stronger chemical bonding [1]. Subsequently, hollow sulfur sphere nanocomposites with metal oxide nanoparticles can effectively change the electrochemical stability of Li- S batteries. As a result, $Mn\ O_2$ shows even more efficient corresponding electrochemical performances including cycling stability, higher gravimetric, capacity and coulombic efficiency.

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1.0 Introduction

1.1 background of renewable energy storage devices

The world's environmental CO_2 pollution is increasing. Scientists are trying to decrease fossil fuels usage and develop more renewable energy systems. Thus, the increasing request for using renewable energy storage systems, such as electric vehicles, mobile devices, smart houses and solar power plants, were introduced to consumer's market [1,25,58].

Earlier, the culture of rechargeable cells transformed by lithium-ion batteries. This concept developed lighter weight, open circuit voltage and brought a more portable application to the market [1-8]. Later, the electrical vehicle market (including EV: Electrical vehicle, BEV: Battery Electric Vehicle, and PEV: Plug-in Electric Vehicle) developed because of these new types of alternative achievement like battery technology [1,2,4]. Now, Lithium-sulfur batteries are the most promising option for future high-energy applications, such as aerospace and heavy industries, since sulfur is incompatible. However, Li-S batteries can be used at the highest altitude and longest flight for hybrid electrical aircrafts covering higher mileages. [50].

However, these types of batteries exhibit a few limitation factors such as low quantities of theoretical capacity around 300 $m\ Ahg^{-1}$[1,8,31]. On the other hand, Li-S cells are limited by their capacity to decompose because of polysulfide phenomenal. The intuitive understanding of this concept developed fundamental surface application's

knowledge which is related to electrochemical cell's stability and performance [1,15,16]. This type of knowledge provides a mutual connection between mechanistic information and Li-S batteries [16]. Therefore, the urgency of developing materials for cathode and anode with higher electrochemical performance and energy density was considered as the top priority [25]. As the result, Sulfur is one of the best candidates because of its unique specification. This element is one of the basic segments of the earth, and it is nontoxic, environmentally friendly with a higher potential capacity [25,32,33]. Furthermore, the supplementation of Lithium cathode is accessible and provide a high energy density as well.

Thus, the lithium–sulfur cell is considered for the new generation of energy storage applications [1,9,10]. In this respect, Li-S cells with higher specific capacity constitute more attractive cathode materials with safer lithium metal-free anode capability [11,12].

The image below shows the prediction of electrochemical energy storage devices, including rechargeable Lithium-Sulfur batteries. As shown below, the revolutionary changes for energy storage technology will take place after 2020. On the other hand, the market's demand is shifting to choose batteries for the next generation of heavier applications, such as electrical hybrid aircrafts or ships. However, future revolutionary products will need to achieve new types of batteries with lower cost, safer, higher capacity, and environmentally friendly aspects [59].

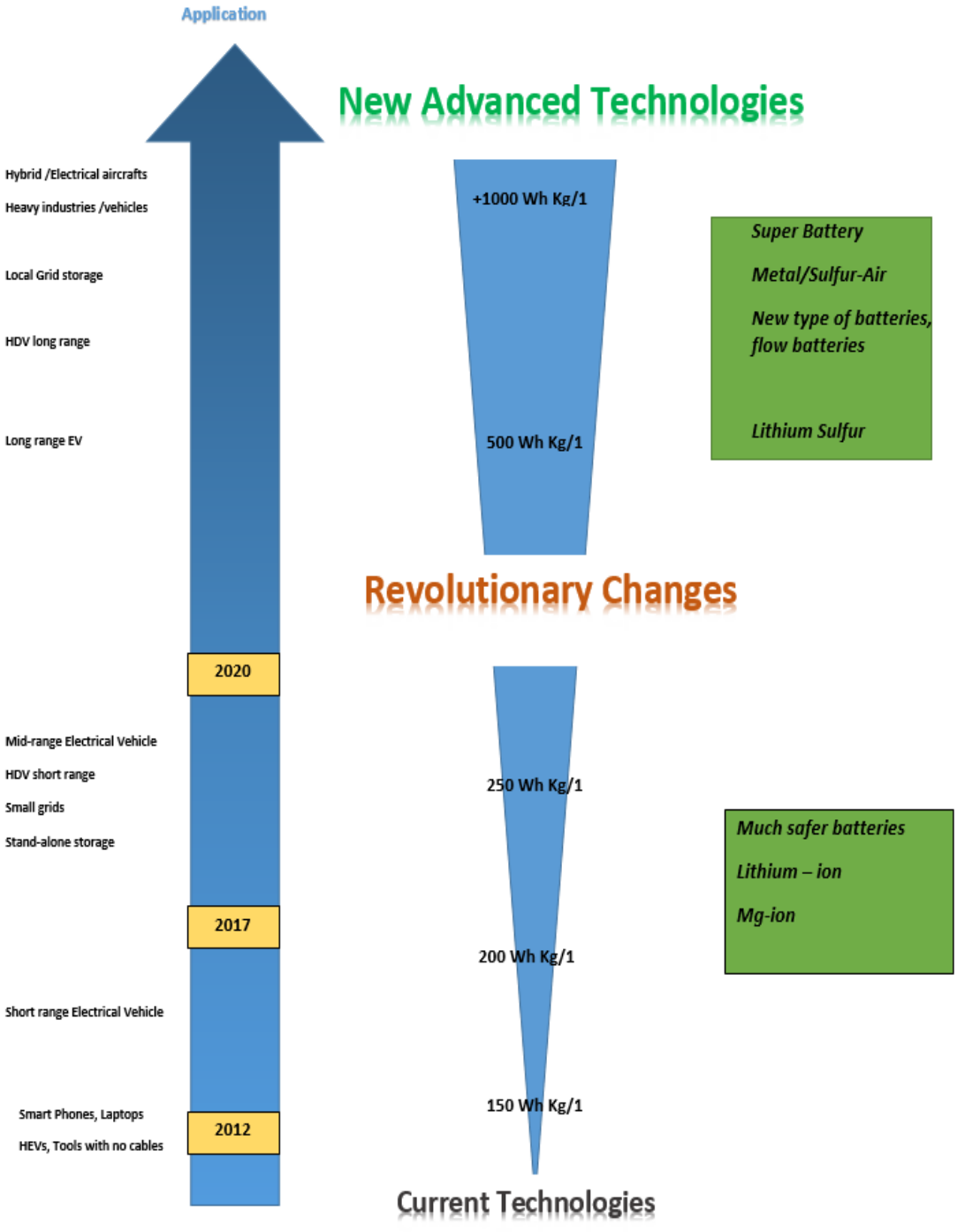


Figure 1- Prediction of our future. "evolution scenario of electrochemical energy storage devices for various range of electrical, hybrid and heavy-duty vehicles" [58]

However, achievement in the evolution of lithium–sulfur batteries cannot progress unless critical issues such as cell failure from the Li metal and the polysulfide shuttle effect can be adequately addressed" [17].

The Lithium-Sulfur (Li-S) battery is considered an enthralling energy storage system. It is a fantastic candidate for the next-generation of electrochemical energy storage devices, and has received much attention because of its low cost, higher energy density, and environmentally friendly aspects.

Material	**Available Capacity ($m\,Ahg^{-1}$)**	**Theoretical Capacity ($m\,Ahg^{-1}$)**
Sulfur	**+500**	**+1200**
Graphite	**372**	**372**
$LiCoO_2$	**140**	**274**

Table 1- Theatrical capacity of sulfur material comparison [60]

Indeed, the lithium-sulfur battery is an enthralling energy storage system because its tremendous advantages surpass Li-ion batteries. However, there are still a few problems hindering Li-S cells from achieving commercial expectations. Adding nanostructured composites to prevent polysulfide from dissolving in the electrolyte is one solution. Developing nanostructured sulfur cathode to increase the volumetric energy density, cycling and capability concurrence is another. The capability of the Lithium Sulfur battery can improve by identifying different types of frameworks, such as changing porous carbon's structure and adding metal oxides to the process [1,2,3,25].

1.2 The fundamentals of an Electrochemical Cell and motivation for Li – S composite Cathode materials

Typically, an electrochemical cell includes three major components: solid cathode with positive electrode, anode negative electrode, and liquid electrolyte. The electrolyte uses as an ion conducting for chemical reaction between anode and cathode. During electrochemical reactions, electrons transfer from electrode to the other side of the battery. This mechanism depends on charge or discharge situations and the external circuit causes the transportation of the ion through the electrolyte.

The same principal has been occupied by the Li-S batteries charge and discharge process. In principle, Lithium ions are stripped from the anode during discharge and form Li-polysulfide in the cathode. This means the sulfur molecules (S_8) are reduced to Li_2S. During the charging process the lithium ions return onto the anode as Li2 S and move toward S_8. High order Li-polysulfides ($Li_2S_3$to Li_2S_8) are soluble in the electrolyte and migrate to the anode side. The Li_2S in the cathode is the result of a complete discharge and shown in figure 2. The whole reaction within a Lithium Sulfur cell is represented by: S8 + 16 Li = 8 Li_2S [25,34,35,36]. Indeed, the dissolved polysulfides diffuse to the anode side and react with metallic part (lithium), creating a composed layer of insulating Li_2S /Li_2S_2 . The dissolution of polysulfide particles form during the discharge process and are largely suppressed by electrode's surface.

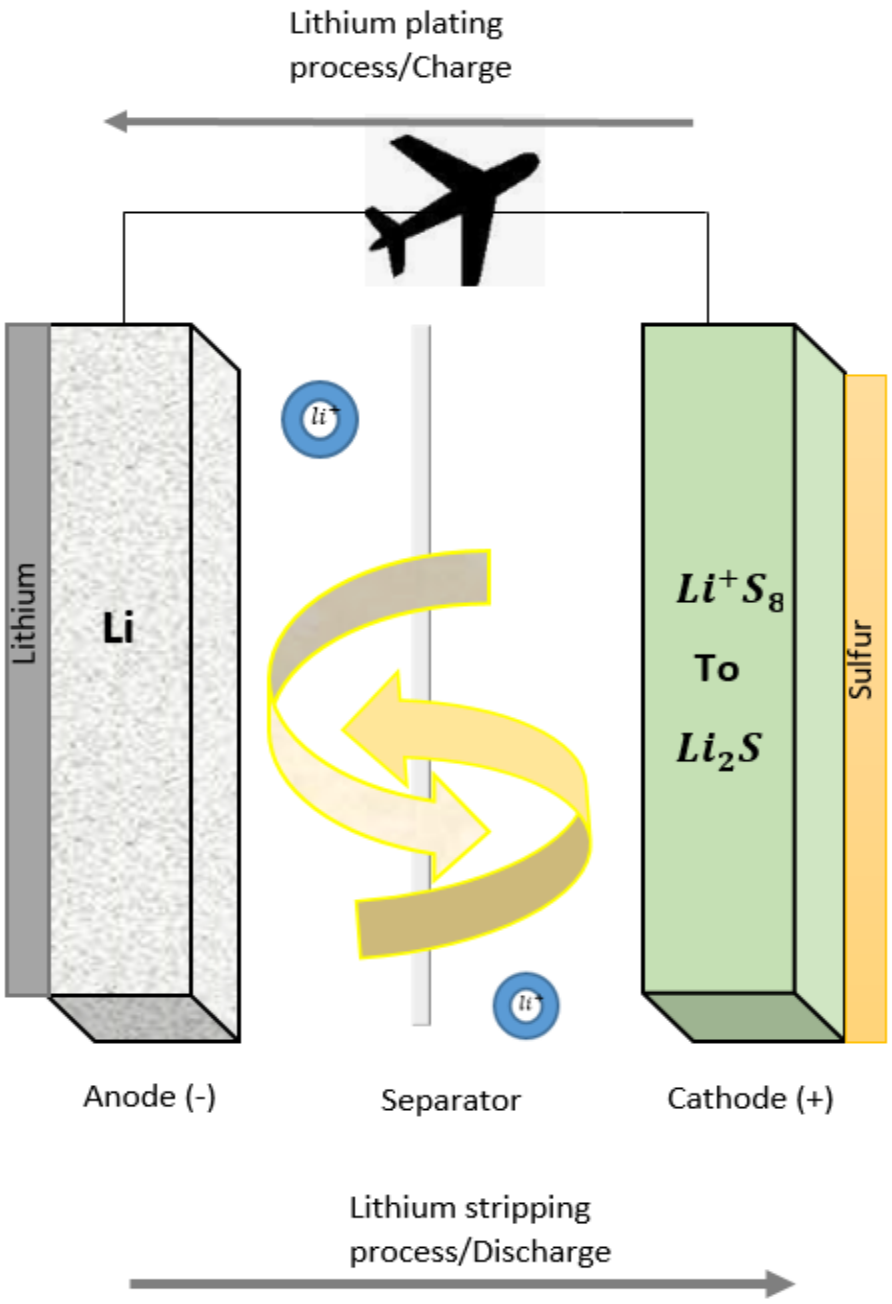


Figure 2 - A schematic illustration of the redox reactions in Li-S batteries [25]

The diffusion of lithium polysulfide has remarkable side effects on the electrochemical performance of Lithium Sulfur battery [36,37]. As the result of dissolution, the active materials will reduce during cycling process. On the other hand, intemperate dissolution and loss of lithium polysulfide's species (Li_2S_n, n = 4–8) into electrolytes is the other challenge. As the result of diffusion, the specific capacity and coulombic efficiency will be reduced [11,12].

Therefore, the dissolved lithium polysulfide ions move to the lithium metal anode and react with it. Then, the polysulfide species diffuse from anode toward cathode. As a result, active materials will be lost during discharge and charge transitions which is called "Shuttle Effects" [25]. Li_2S is the final result of the discharge process that remains on the surface of lithium metal anode.

Since the Li_2S isn't soluble, the impedance of lithium Sulfur batteries increase significantly. Consequently, the harmful polysulfide particles initiate along the discharge process and reduce the Li-S batteries' capacity [25,35,36,37,38,39].
All issues related to the dissolution of lithium polysulfide (Li-PS) species can improve by adding different additives to the whole system [16,18,19].

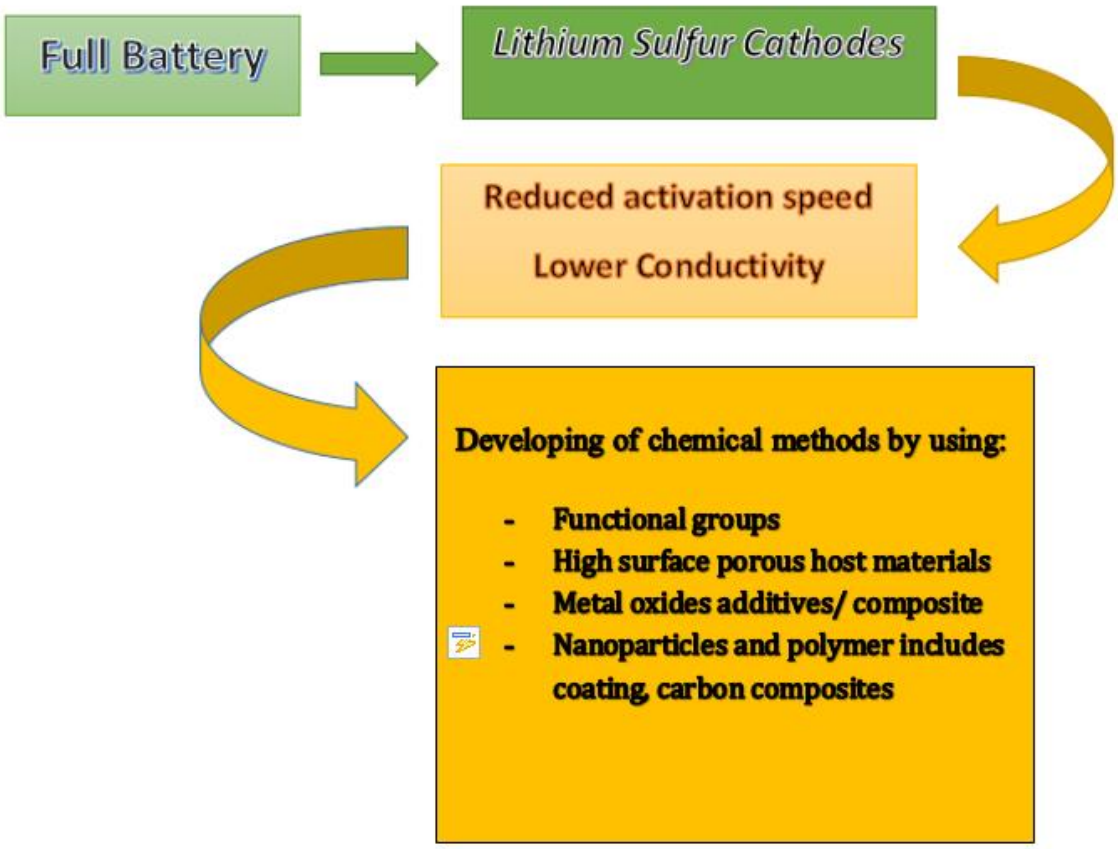


Figure 3 - The systematic study trends for improving Li-S cathode materials [17, 20, 25,22,23].

The migration of the soluble polysulfide species through electrolyte drives lithium batteries towards more sufficient and longer-cycle life. Intensive investigation has been performed to incarcerate the soluble polysulfide phase by occupying more efficient methods such as using large surface area pore composition (Hollow Carbon Spheres) or metal oxides [16, 20,21,22,23].

In point of fact, the electrochemical cells that are made with higher carbonaceous surface area reveal substantial specific capacity intensification for the first few hundred cycles. These types of batteries show a massive decay of stability during longer cycling due to unstable interaction between sulfur polysulfide and carbon particles [24].

Based on the description above, adding hollow carbon nanoparticle species to the cathode materials provides an ideal candidate to address low conductivity and additional obstacles.

1.3 Striking new approaches to harvest Lithium Sulfur batteries with a longer life

Extensive research on chemical methods have been performed to address dissolution of polysulfide species through electrochemical procedures [25,40,41]. In this research, the disperse poly-sulfides reduction happens by introducing metal oxide additives and hollow carbon particles to the cathode side. These techniques effectively improve the specific capacity and cycling stability of Lithium sulfur batteries [1].

1.3.1 High surface area carbon to absorb lithium polysulfides

A facile method to prevent diffusing polysulfide into liquid electrolyte is using nanostructure hollow carbon. “However, utilizing chemical bonding is more effective to arrest lithium polysulfides than simply physical restriction" [42,43,25]. However, functional groups such as B, N and O can contribute through carbon base substrates. Hence, dissolved polysulfide species can be obtained by doped heteroatoms hollow carbon sphere particles. These types of carbon have larger surface area and unique characterization which can improve the performance of Li-S cells [42,43,25].

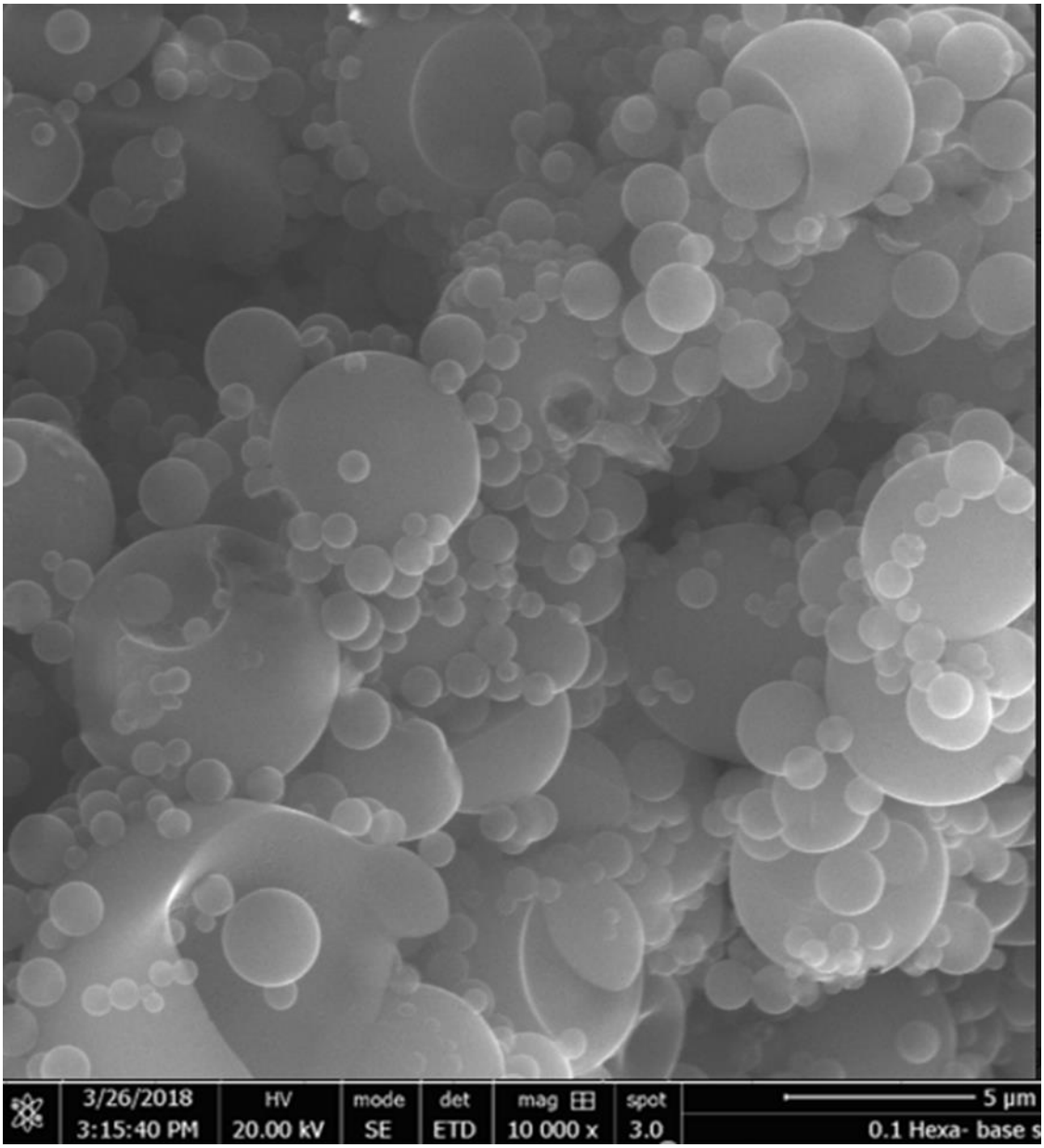


Figure 4 - Hollow Carbon Nanoparticles with 0.1ml hexacadane - SEM image

1.3.2 Metal oxide additives confine Li polysulfides and improve electrochemical performance

The other approach to immobilizing dissolved polysulfide is deploying metal particles in the cathode side of Li-S batteries. The affinity of metal species can introduce to the system metal oxides such as $Mn\ O_2$ and MgO.

The bonding between metal particles and polysulfide species helps to prevent lithium polysulfide dissolution through electrolyte [44,25,45]. To magnify the utilization of sulfur, the metal oxide with nanoparticle hollow carbons make inviolable chemical bonding with polysulfide species. In reality, the single dopant atoms intensify the electrochemical performance of lithium sulfur batteries, but heteroatoms co-doped like Sulfur in carbon matrixes has even more influence on the electrochemical systems. Consequently, the carbons with multi-heteroatom co-doped has a higher volume of lithium polysulfies compared to single doped types [25,46,47, 48].

The results show that the additive polar materials create stronger bonding connections and attract more sulfur pieces. For this reason, the polar metal oxides(S_n^{-2}) have hydrophilic specification [44].

The interspace of hollow carbon nanoparticle enhances the exchange of sulfur material within the cell. Hence, the diffusion of Lithium polysulfide is eliminated during the charge and discharge process. The results demonstrate that the dissolution of Polysulfide in $Mn\ O_2$ is less than MgO. Consequently, the S - $Mn\ O_2$ composite has a unique configuration of high level electron's absorption with minimal chemical bonding [25].

During the discharge step, the molecules of Sulfur (S_8) anchor with MnO_2 ions. As a result of the discharge step, the Li_2S_8 will form and strong chemical bonding energy will happen between Li-O and S-O molecules. Hence, the nanocomposites initiated by MnO_2 provide excellent Coulombic efficiency with stability cycles and improve the electrochemical performance of lithium sulfur cells significantly [25,44].

Another important factor is introducing the metal oxide composites to generate strong chemical surface bonding with polysulfide intermediates. As the result of this bonding, Li-S performance and cycle's stability will improve significantly. However, the slow redox reaction rate can cause minor changes during the diffusion process. Thus, metal sulfides enhance kinetics towards slow redox reactions and improve high efficiency in immobilizing sulfur particles [49,25].

1.4 Research objectives

Of all the additive species discussed in earlier chapters, there is strong support to achieve higher capacity, efficiency and chemical stability for rechargeable Lithium Sulfur electrochemical systems. The first phase shows the development of sulfur cathodes with higher capacity and stability to generate high energy lithium-sulfur batteries with longer cycle life. The carbon source used throughout this research has unique textures and structures. This type of carbon is synthesized separately to achieve hollow carbon spheres with larger surface area through vulcanization and hydrothermal method. Furthermore, the poly-sulfides dispersed are reduced by immobilizing sulfur penetration and introduce metal additives in the cathode side of lithium sulfur cell. Therefore, the systematic mechanism of Li-S cell's production is introduced based on the steps below:

1. Synthesize hollow carbon spheres through hydrothermal and vulcanization method. In reality, sulfur-carbon composite based on the carbon substrate shows higher electrochemical activity and more favorable capability rate.

2. Complete experimental investigation of carbonized hollow carbon with different amounts of hexacadane (0.1,0.2,0.3 ml) to obtain higher capacity results due to experimental parameters including particle shape, carbonization temperature, and hydrothermal reaction time on the formation of hollow prose carbon composite.

3. The best result from step two will be used to fabricate Li – S carbon composite cathode

4. The metal oxide can be used as lithium Polysulfide adsorbents in Li-S battery and can retrieve electrochemical and performance of the final product.

2. Experiment

2.1 Synthesis and characterization of Hollow Carbon Nanoparticles(HCN)

An additional method to increase conductivity of sulfur carbon base composite cells is introducing hollow carbon nanospheres (HCNs) to the whole production procedure.
The hollow carbon nanospheres (HCNs) are achieved during vulcanization process. Indeed, the vulcanization is a chemical process to transform a polymer compound, such as rubber, to an elastic and final shape of carbon. The final result of HCNs has wide prose volume with larger surface area and manifold morphologies. These unique specifications will qualify HCNs to create covalent bonds with sulfur species and reduce the dissolution of lithium polysulfides [50].

On the other hand, hollow carbon nanosphere particles play a key role within carbon-sulfur composites, such as increasing electron conductivity and exertion surfaces during charge-discharge steps. Also, they are key to preventing the growth of large grain products during the discharge and charge process into electrochemical reaction [51].

Hence, carbon-sulfur composites improve the total performance of Li-S cells while the dissolution of polysulfides immobilize battery's capacity because of weak physical bonding between carbon molecules and lithium polysulfides [51,52].

Hollow Carbon Nanoparticles (HCNs) are prepared by dissolving 8.8g of Polyvinylpyrrolidone (MW 40,000)- PVP into 100 mL of DI water, 0.1 g of Polybutadiene (PBD) and 0.3g amount of sulfur in 5 ml carbon disulfide (CS_2). To achieve hollow carbon shape, the result was mixed with different amounts of hexacadane (e.g., 0.1,0.2 and 0.3 ml). The hollow carbon particles formed by adding hexacadane to the vulcanization stage. The mixture should remain 10 min under magnetic stirring and sonication at room temperature. As a result, the well-dispersed mixture was hydrothermally treated under 200^0C for 15 hours. The autoclave samples should be cooled down and the final results will have turned into a pale white solution. This result is needed for centrifuge and must be rinsed out with water 4 times and 3 times with Acetone [59].



Figure 5 - Lightweight hollow nanoparticles carbon particles (after 7 times centrifuging)

The final product contained wet dark nanoparticles that needed to dry for an additional 24 hours in the oven under 70^0C temperature. The obtained dark brown carbon powder carbonized under argon atmosphere at 900 °C and maintained at that temperature for 3 h. The obtained hollow carbon powder was used as 20% of the weight for the carbon source, while the sulfur source contained 80% of the total weigh of cathode.

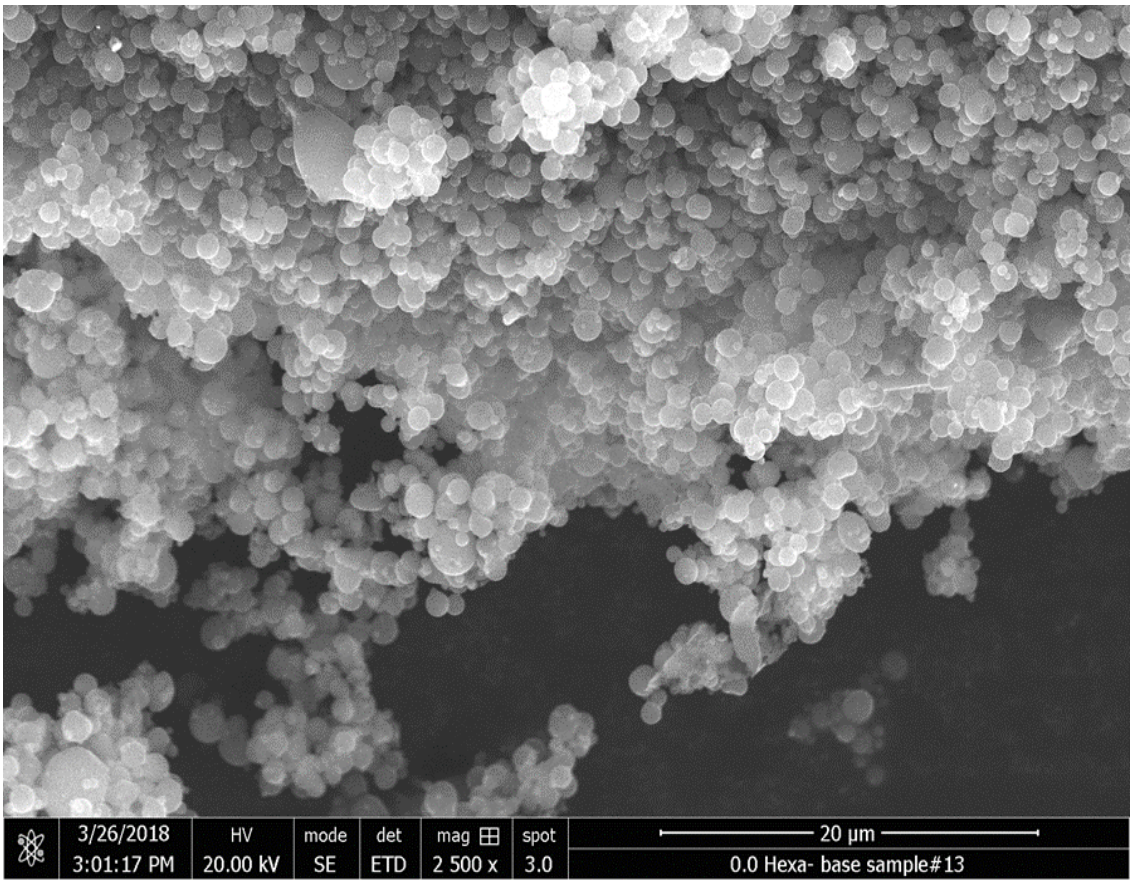


Figure 6 - SEM carbon nanoparticles, carbonization sample with 0.0 ml hexadecane under 900^0C temperature –The result doesn't contain any hollow shape yet.

The schematic of Hollow Carbon Nanoparticles(HCN) synthesis is shown below:

8.8 g of Polyvinylpyrrolidone (MW 40,000)- PVP was dissolved in 100 mL of DI water and mixed with 0.1 g of Polybutadiene (PBD) and 0.3g amount of sulfur in 5 ml CS2.

different amount of Hexacadane (e.g., 0.1,0.2 and 0.3 ml) in separate experiment. After 10 min under magnetic stirring and sonication at room temperature, the well-dispersed mixture was hydrothermally treated under 200C for 15 hours. The final results turned pale white solution

The result was centrifuged 4 times with water and 3 times with Acetone. After 24 hours @70C, The obtained dark brown carbonize under Ar @ 900 °C and maintained at that temperature for 3 h.

The obtained hollow carbon powder use as 20% wt.% of sample carbon source

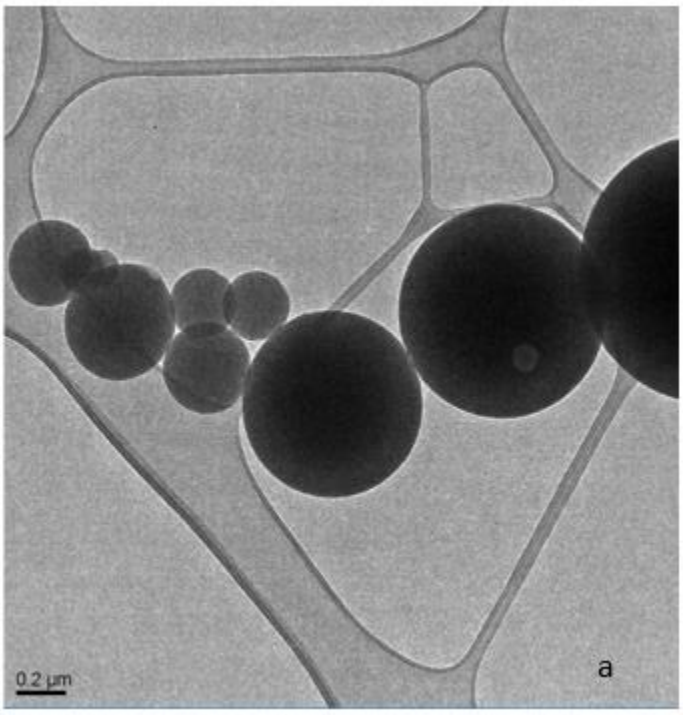


Figure 7 - a) TEM (transmission electron microscopy) image of carbonized carbon nanoparticles with 0.0ml hexacadane

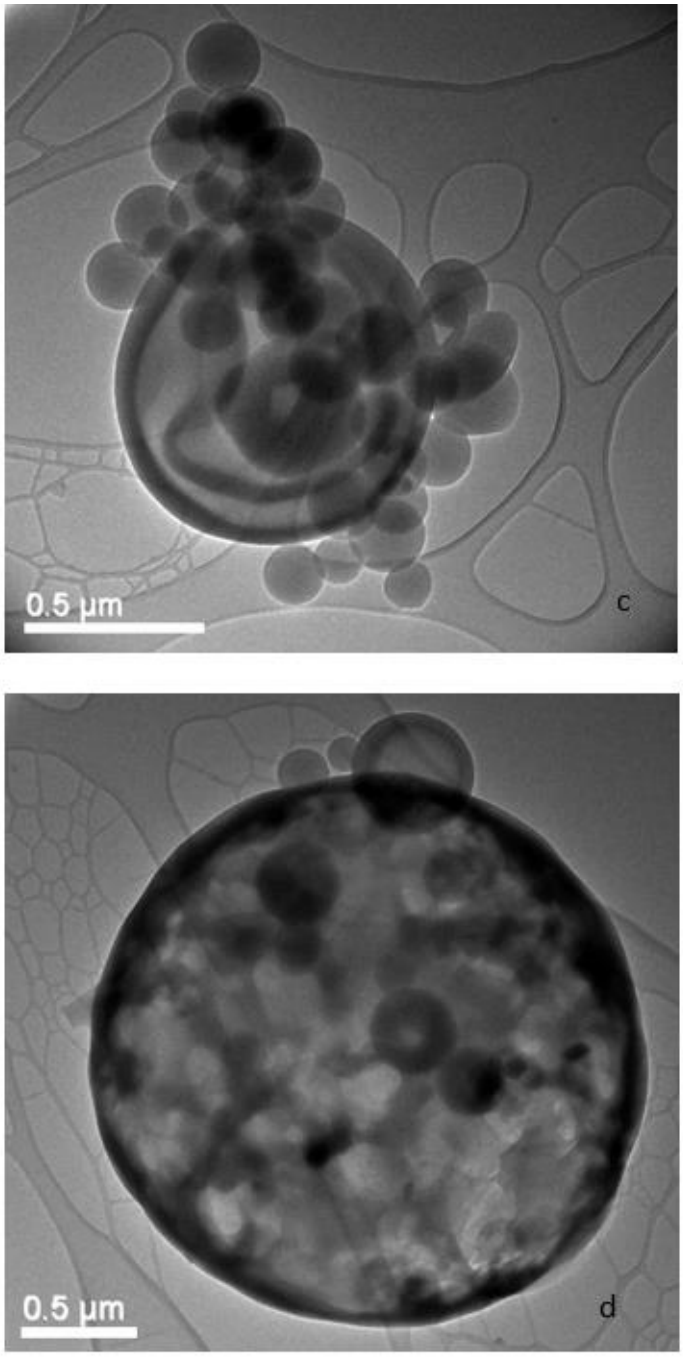
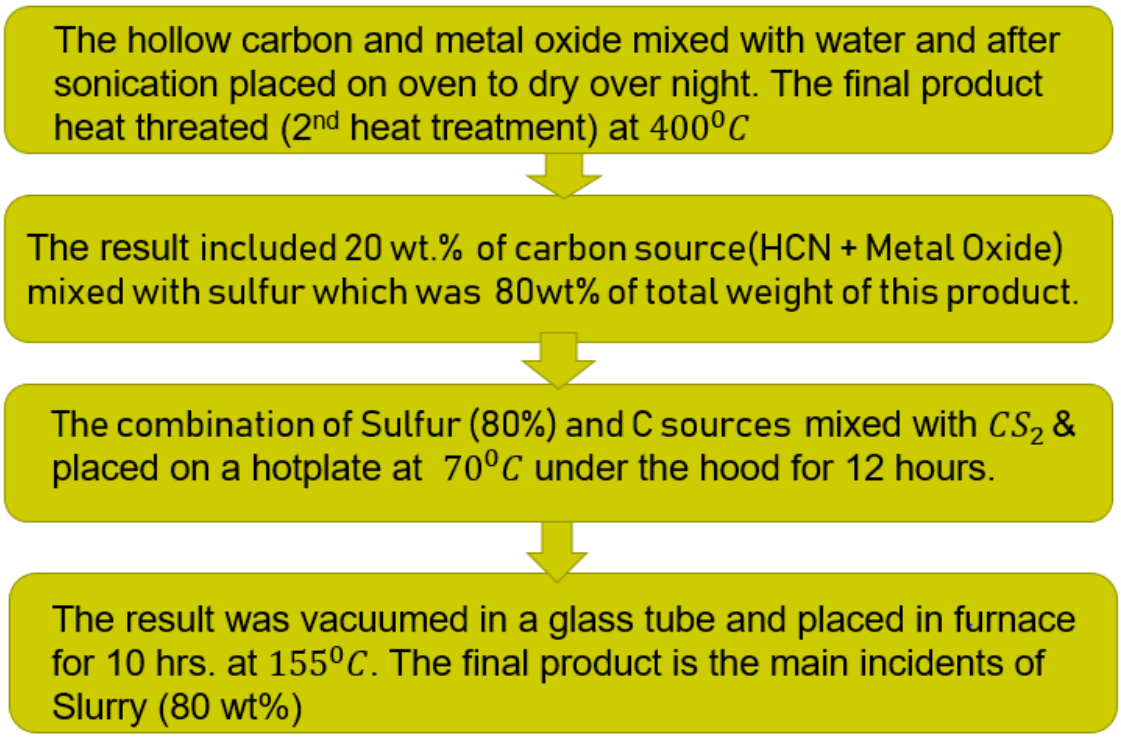


Figure 8 - TEM (transmission electron microscopy) images of different amounts of hexacadane. c) 0.1ml hexacadane hollow carbon; d) 0.3ml hexacadane hollow carbon after 900^0C carbonization step

This final composite product containg 80wt% Sulfur and 20 wt% Carbon is mixed together. As mentioned earlier, CS_2 is added to the composite product and placed on a hotplate at 70^0C . Then, the final result needs to complete the heat treatment process and be left under the hood for 12 hours. The second heat treatment is completed under Argon gas and under 155^0C temprature for 10hrs.The result is dark gray/black powder carbon.

The below is showing the other steps of cathod prepration. [25]



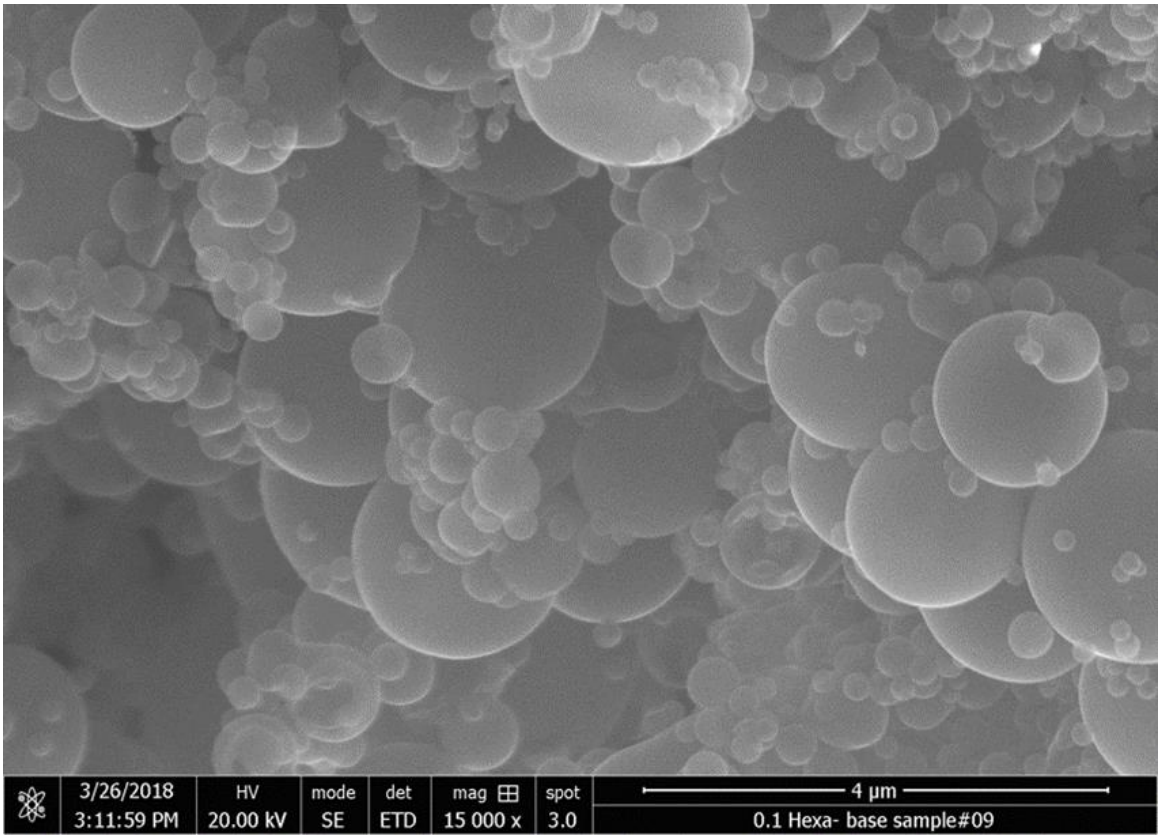


Figure 9- Scanning Electron Microscopy (SEM) carbonization sample with 0.1 ml hexadecane under a tempreture of 900^0C – carbon hollow shape

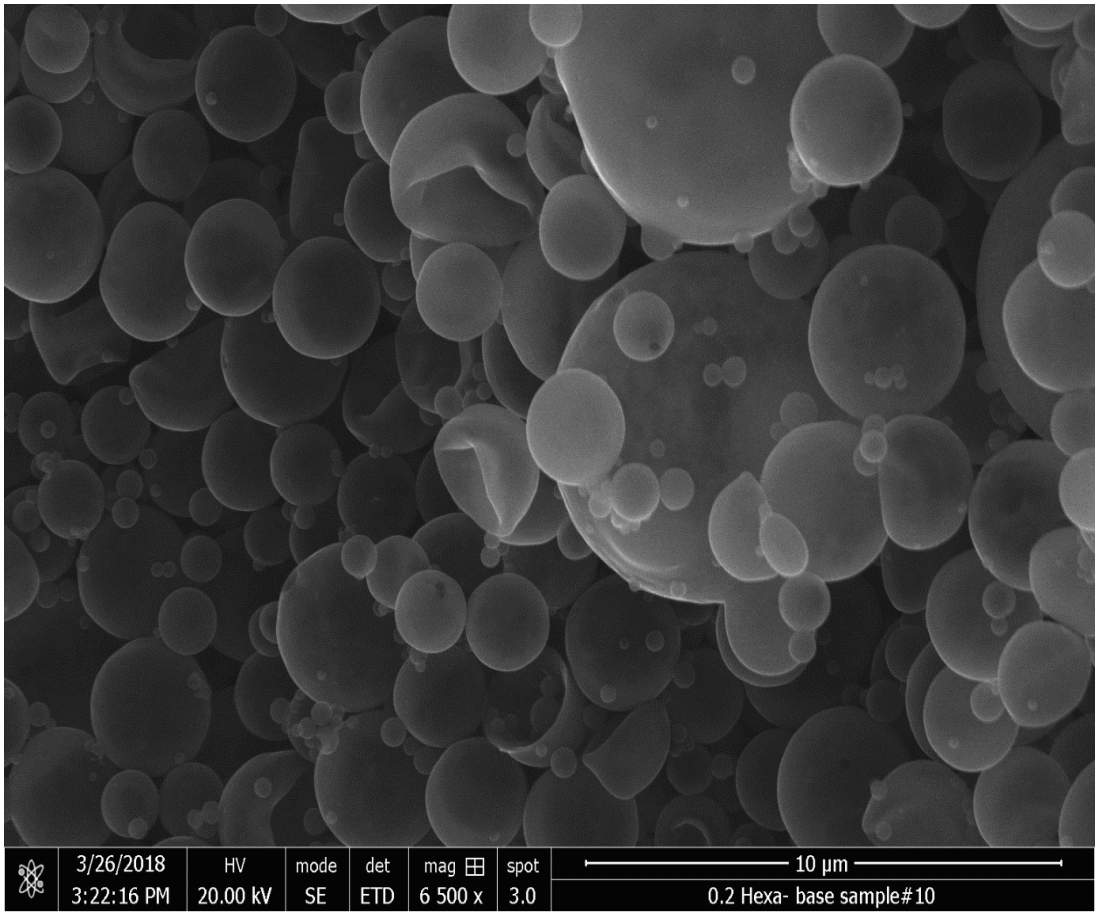


Figure 10 - Scanning Electron Microscopy (SEM) carbonization sample with 0.2 ml hexadecane under a tempreture of 900^0C – carbon hollow shape

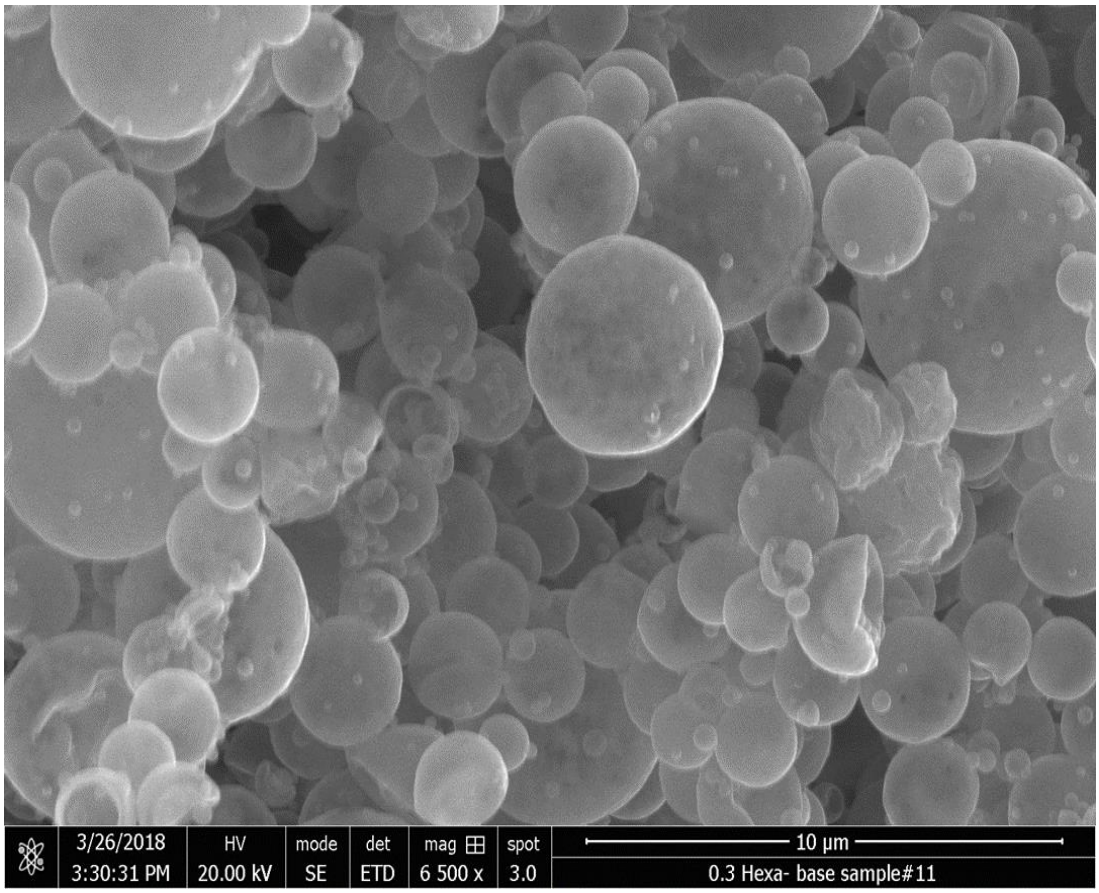


Figure 11- Scanning Electron Microscopy (SEM) carbonization sample with 0.3 ml hexadecane under a tempreture of 900^0C – carbon hollow shape

The sphere shape of carbon nanospheres change after adding hexadecane. The new structure contains a hollow shape (HCNs). In the images below, the sphere's structure changes to a hollow shape.

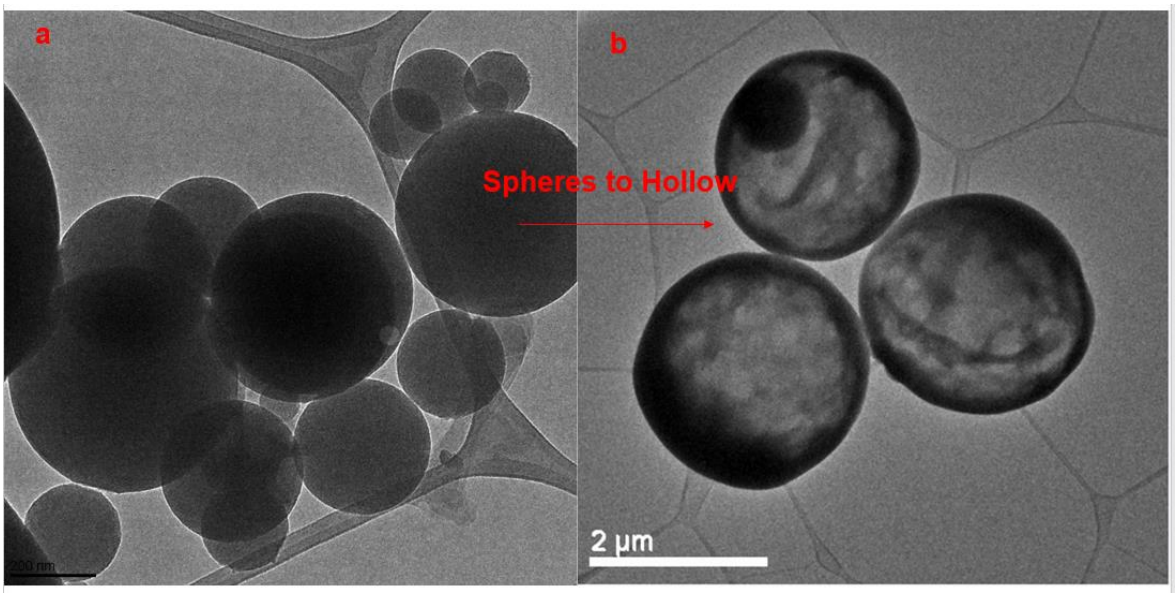


Figure 12- Transmission Electron Microscopy(TEM) images; a) carbonized carbon nanoparticles with 0.0ml hexadecane; b) 0.2ml hexadecane

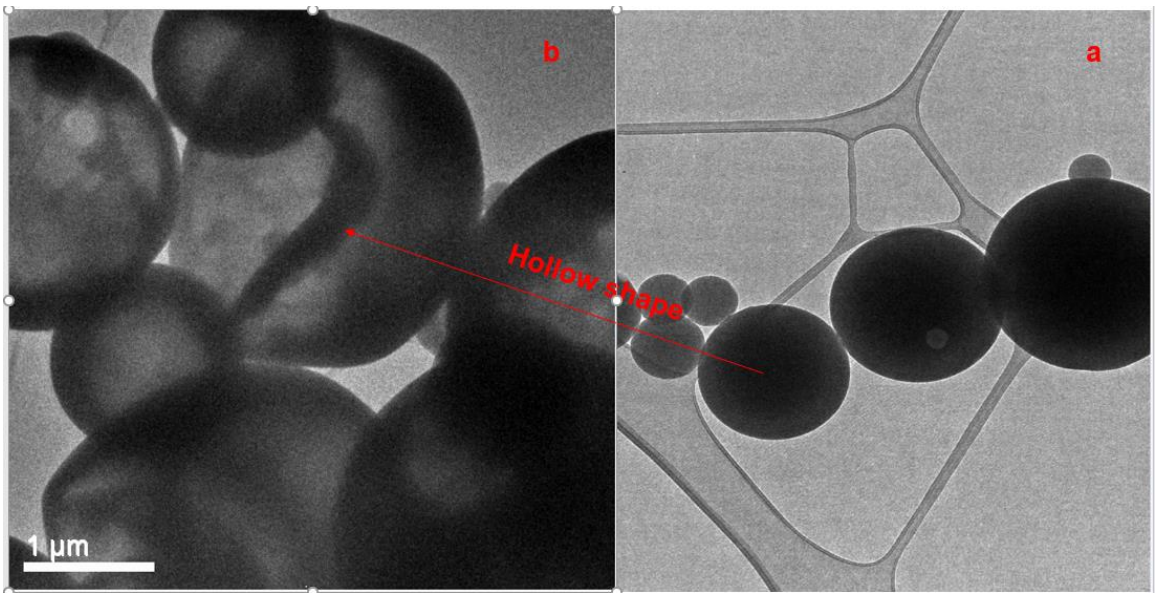


Figure 13- TEM carbonized carbon nanoparticles with 0.0ml hexadecane ;b) 0.1ml hexadecane added

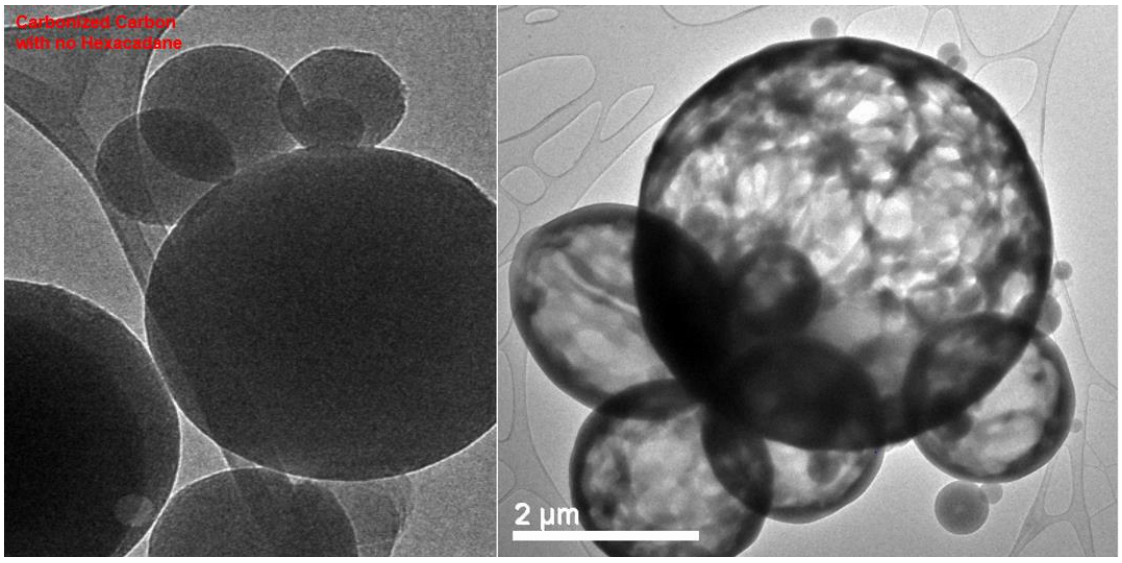


Figure 14 - Transmission electron microscopy images of Li-S with 0.3ml hexadecane

The image below shows the carbonized hollow carbon with 0.2 ml hexadecane. The experimental parameters including particle shape, carbonization temperature, and hydrothermal reaction time can have an affect on the formation of hollow prose carbon composite.

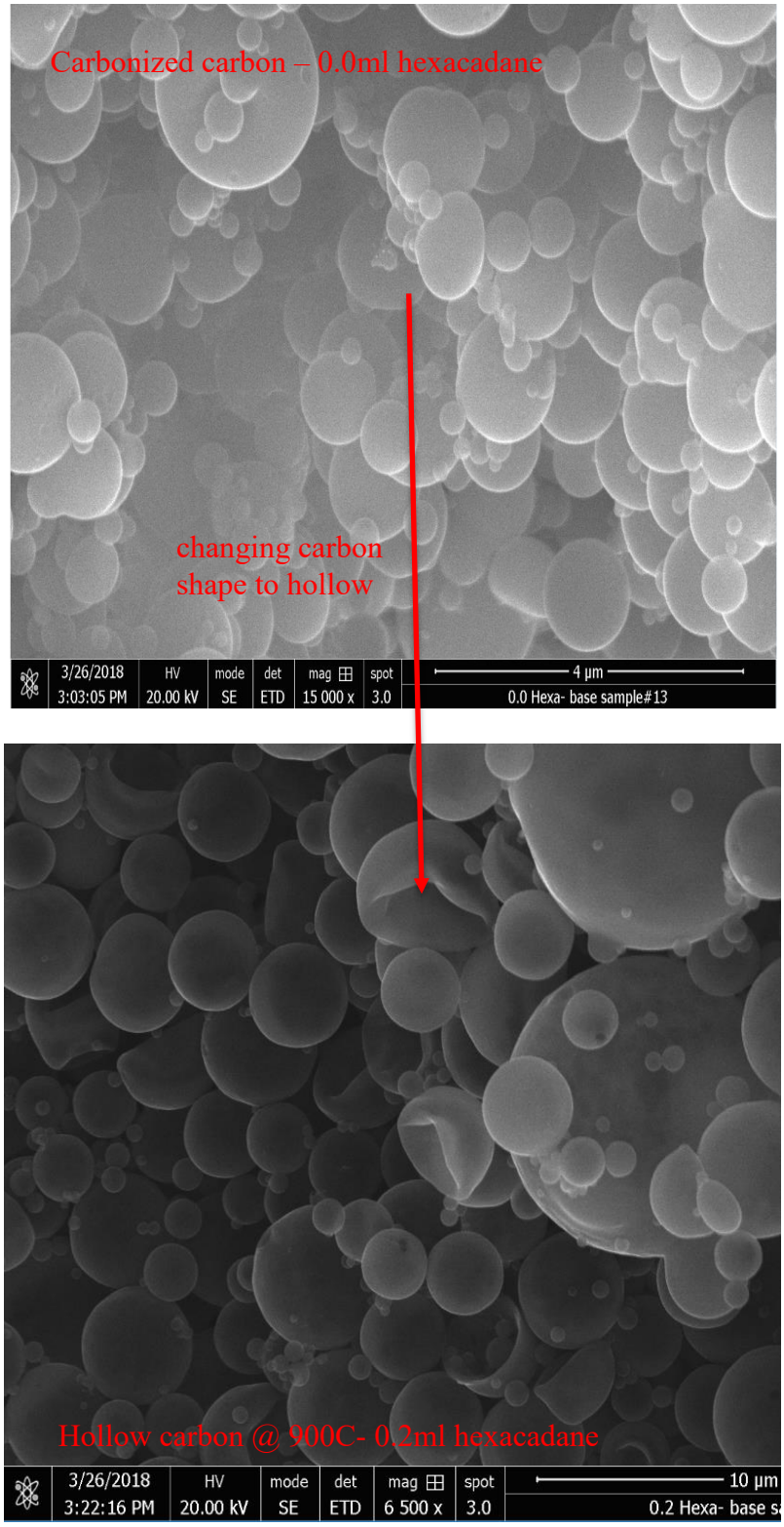


Figure 15 - Carbonized hollow carbon with 0.2 ml hexadecane.

2.2 Sulfur Cathode Preparation

The sulfur cathode slurry requires being mixed inside the ball-mill mixer. The mixing material include 80 wt% of slurry' s weight and the rest contain 10 wt% carbon black (Super P) with 10 wt% polyvinylidene (PVP) and N -Methyl-2-pyrrolidinone (NMP, 5wt %).

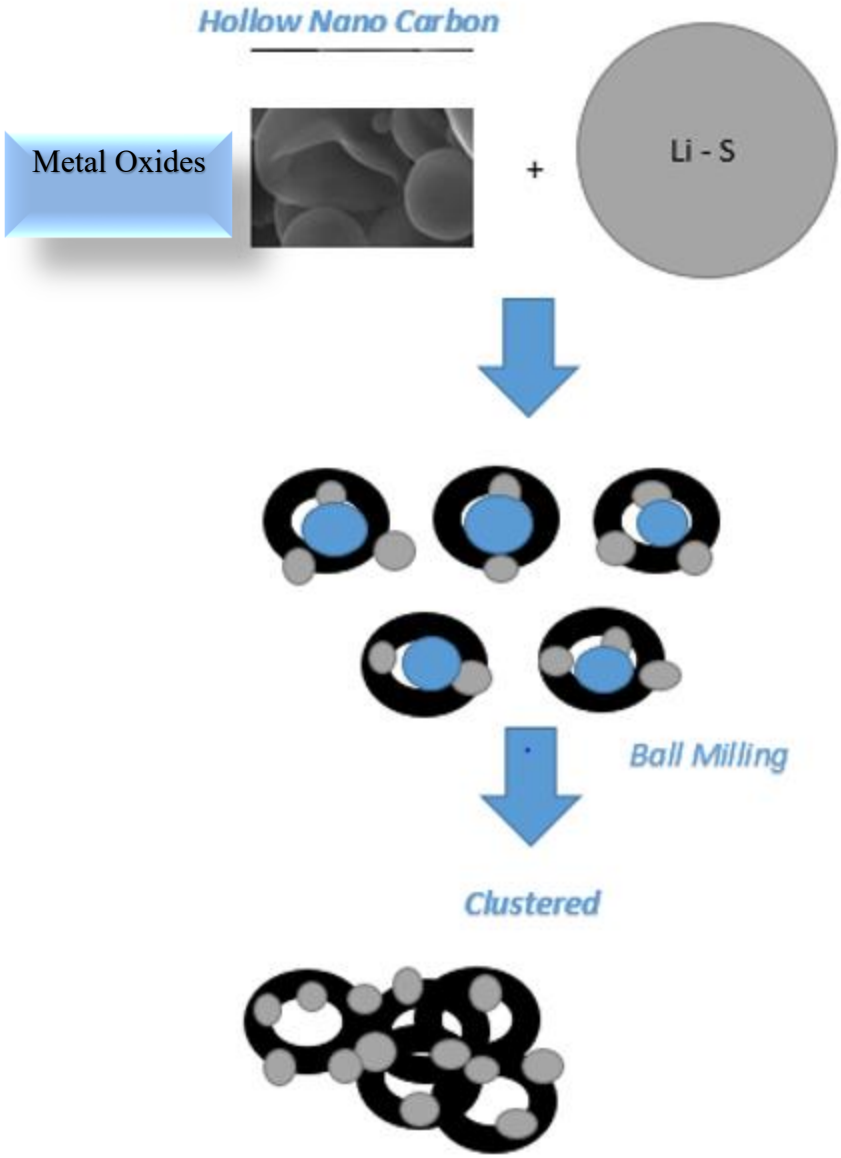


Figure 16 - Schematic of Li-S particles mixture with Hollow Carbon Nanoparticle and metal oxides [17]

The result is a homogeneous viscous paste which represents composite cathode material of Lithium Sulfur cells [25,26]. Then, the slurry blade is cast onto carbon-coated

aluminum foil and dried at 50 °C for 12h under a vacuum oven. The sulfur cathode is then cut into circular 0.5inches pieces.

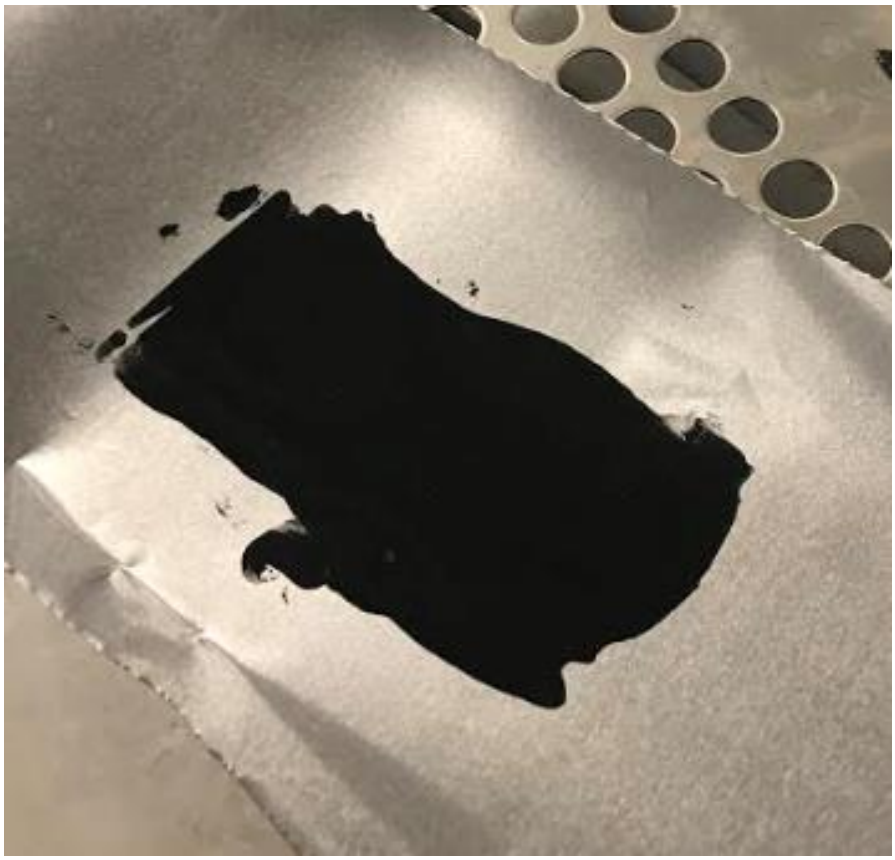


Figure 17- Cut out slurry on the aluminum foil

2.3 Cell fabrication and measurements

The electrochemical performance of Sulfur composites is evaluated by fabricating circular coin type electrodes in an Argon filled glove box [1,27,50]. The electrolyte was composed of “1 M bis (trifluoromethane) sulphonamide lithium salt with a 1:1 by volume

(v/v) in a mixture of 1,2- dimethoxyethane and 1,3-dioxolane with LiNO3 additive (1 wt%)" [28,61]. The charge-discharge processes were conducted on battery checker instruments with voltage of 1.5–3.0 V versus Li+/Li, and cycled at 0.1 C while 1 C is above 800 $m\ Ahg^{-1}$. The assembled cells were first charged to a high cutoff voltage of 3.0 V [1]. Then, each cell was also disassembled in the discharged state of 1.5V at the end of 200 cycles to examine the morphology of the cathode surface after the cycling stage [1]. The image below shows the assembly of a Lithium sulfur battery [1,2,3].

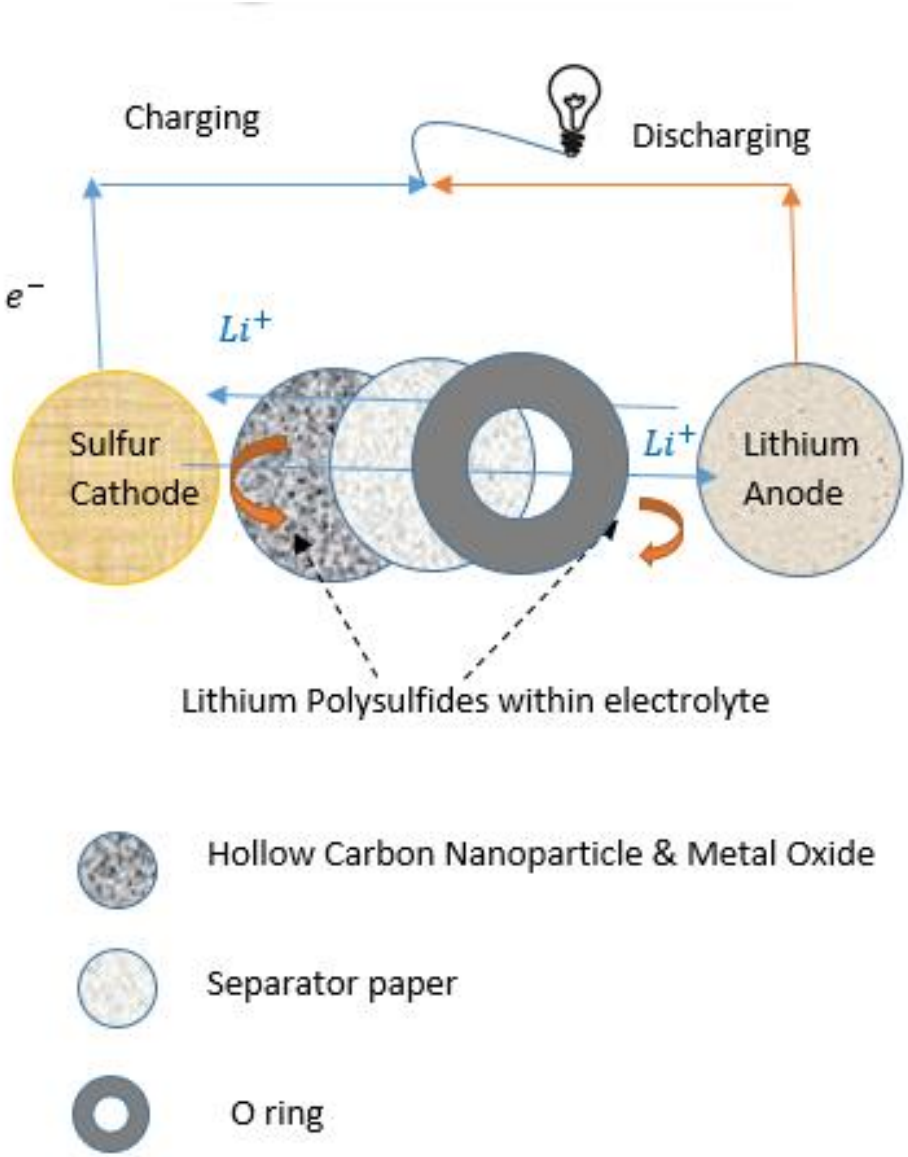


Figure 18 - Schematics of battery assembly [1,2,3]

The schematic steps of sulfur cathode preparation are shown in the graph below:

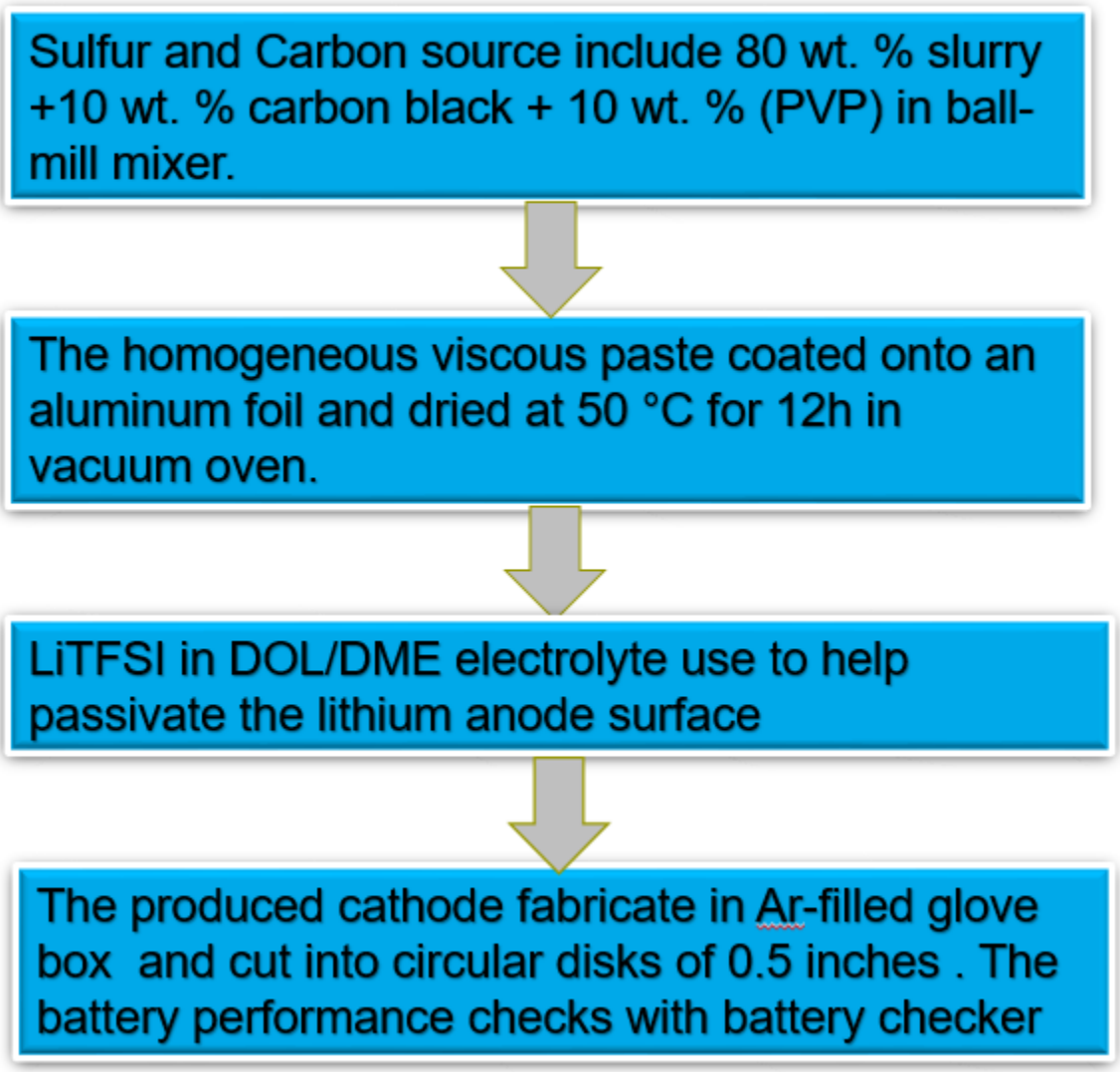


Figure 19- Schematic of sulfur cathode preparation

3.0 Results and discussion

3.1 Electrochemical Impedance Spectroscopy(EIS) performance

Electrochemical Impedance Spectroscopy (EIS) is a measurement of domain frequencies created by the interaction of an electrochemical cell with applied voltage. Electrochemical Impedance Spectroscopy is the best electroanalytical tool to study the kinetics of different electrochemical cells. However, the EIS process requires a circuit model to examine chemical procedures and evaluate kinetic factors. In this research, Electrochemical Impedance Spectroscopy is utilized to review Lithium sulfur batteries behaviors [54,55].The EIS spectrum is usually composed between two controversial high frequent semicircles and one inclined line [54,56].

The electrochemical performance kinetics of lithium sulfur batteries including hollow carbon nanospheres (HCNs)is examined with various quantities of hexacadane (0.1,0.2,0.3ml). For each sample, the coulombic efficiency and specific capacity of the batteries are considered for specific cycles ($m\ Ahg^{-1}$). As mentioned earlier, the HCN can effectively inhibit the dissolution of polysulfides species and eventually enhance the conductivity of sulfur cathode. However, different amounts of hexacadane play key roles to emphasize the best result of electrochemical performance of each sample.

Consequently, various amounts of hexacadane were considered to achieve higher capacity value.

The results show that the capacity of Li-S cells can improve significantly when using 0.1ml of hexacadane. Figure 20 demonstrates the specific capacity versus voltage of Lithium Sulfur cell with a quantity of 0.1 ml hexacadane. The specific capacity is considered for both discharge and charge at the first and fifth cycles with the rate of 0.1 C (Figure 20) [53].

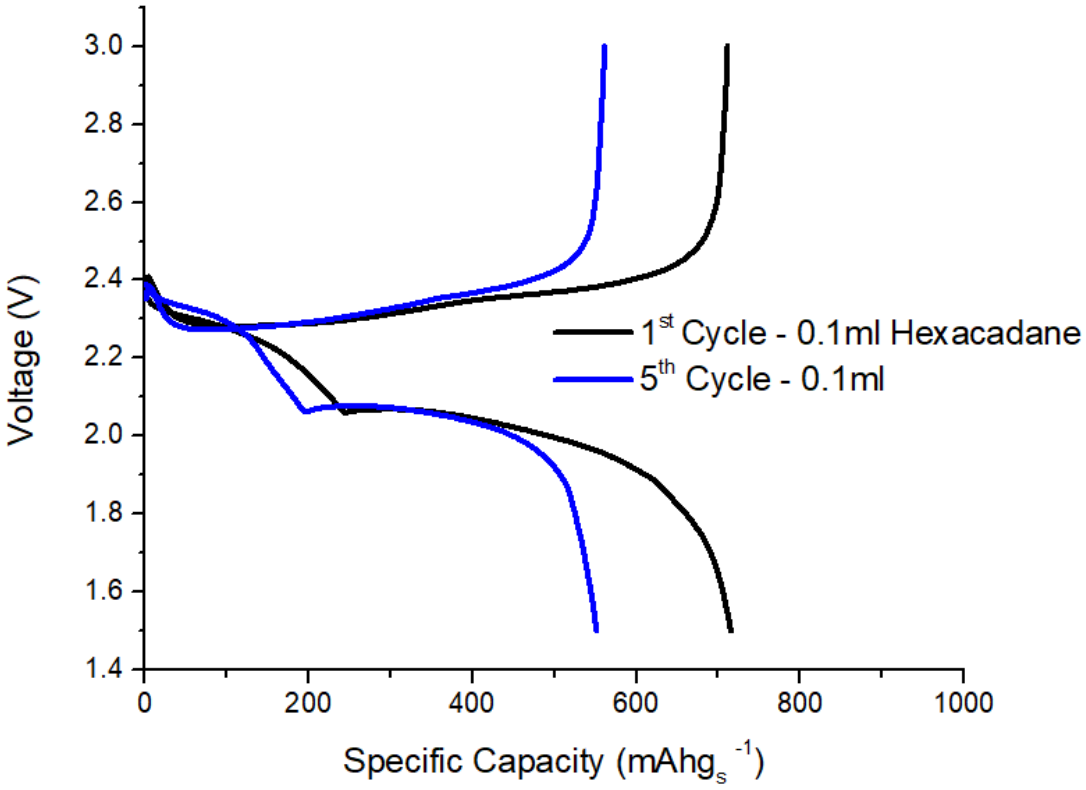


Figure 20- Electrochemical performance of Li - S cathodes for 0.1 ml hexacadane. This sample tested for Specific Capacity Vs. Voltage at the 1st and 5th cycles. The data compared is considered for both charge and discharge process.

The next sample contains 0.2 ml of hexacadane. The sample is tested for the specific capacity versus voltage for a Lithium Sulfur cell. The specific capacity is considered for both discharge and charge at the first and fifth cycles with the rate of 0.1 C (Figure 21) [53].

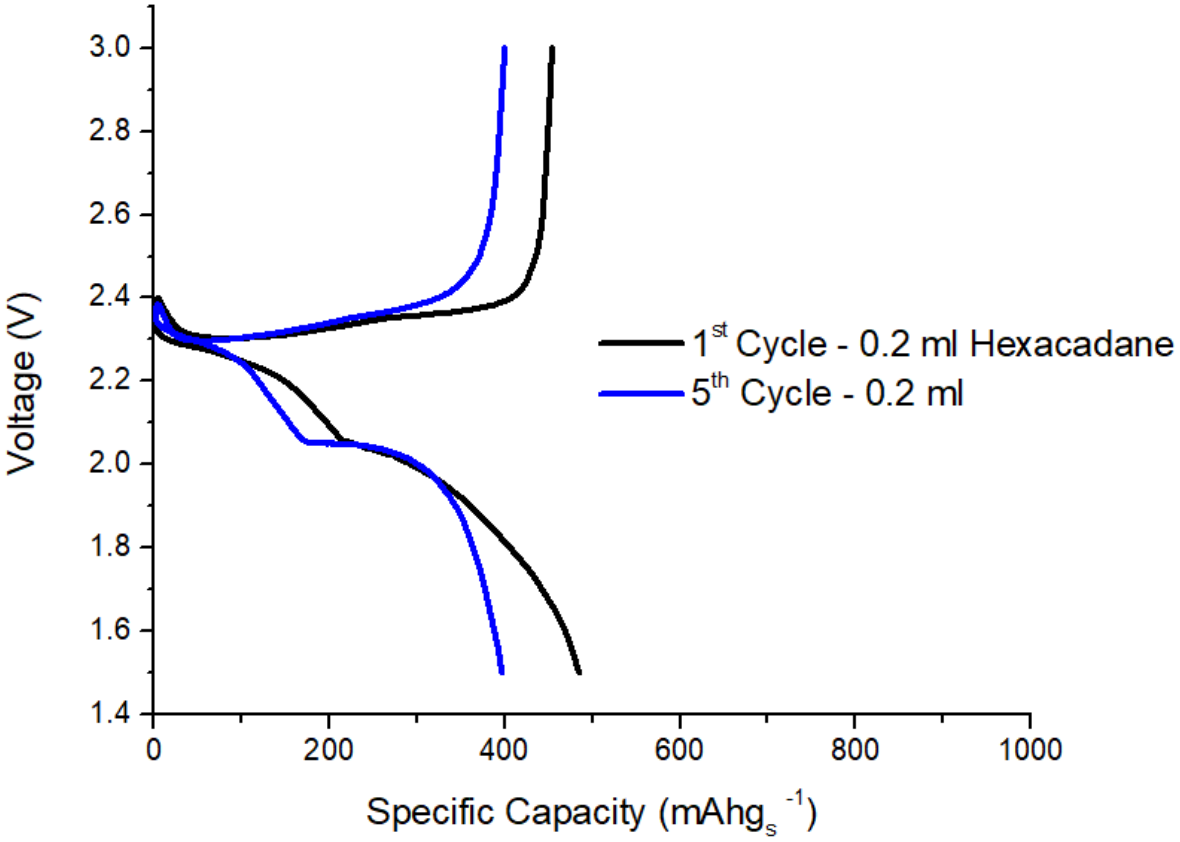


Figure 21 – Electrochemical performance of Li - S cathodes for 0.2 ml hexacadane. This sample tested for Specific Capacity Vs. Voltage at the 1st and 5th cycles. The data compared is considered for both charge and discharge process.

Finally, the last sample contains 0.3 ml of hexacadane. This sample is tested for the specific capacity versus voltage. The specific capacity is considered for both discharge and charge steps at the first and fifth cycles with the rate of 0.1 C (Figure 22) [53].

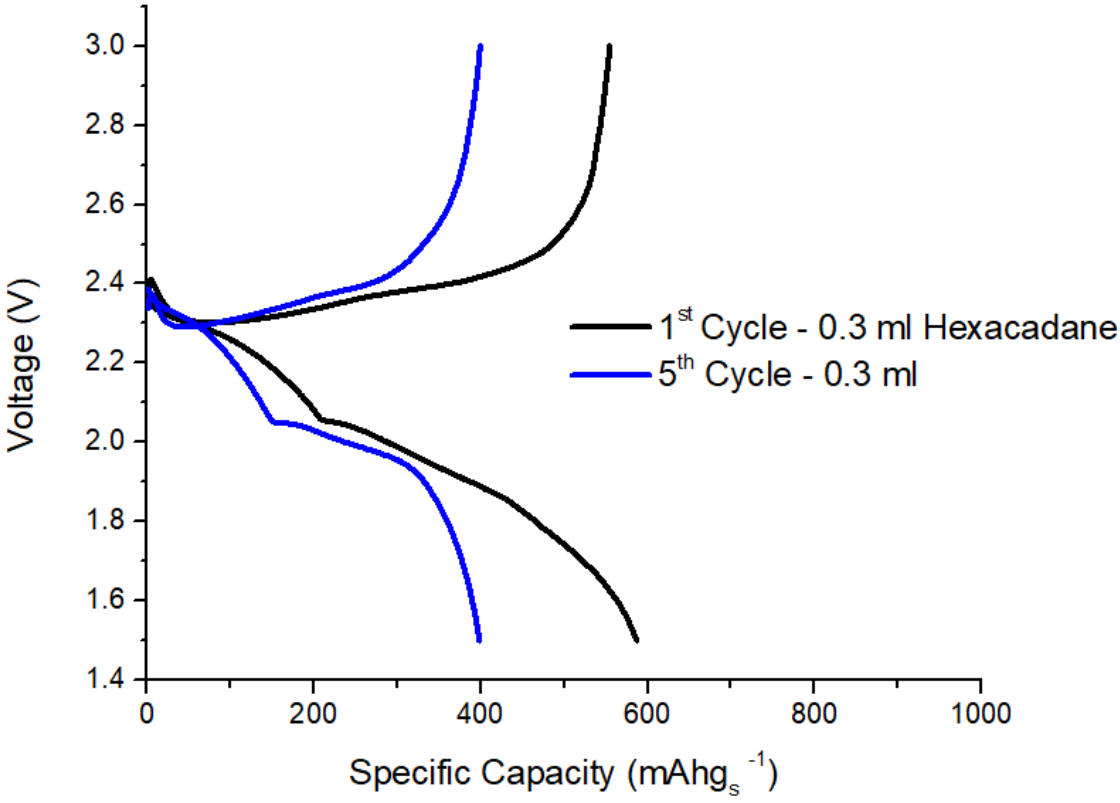


Figure 22- Electrochemical performance of Li - S cathodes for 0.3 ml hexacadane. This sample tested for Specific Capacity Vs. Voltage at the 1st and 5th cycles. The data compared is considered for both charge and discharge process.

Moreover, the same cells were examined against specific capacity and coulombic efficiency along with various cycle numbers. The results show that the specific capacity and coulombic efficiency were at a rate of 0.1 C with 0.1ml of hexacadane.

Among of tested samples, the lithium sulfur composite with 0.1ml hexacadane (figure 23) shows composites exhibited a capacity of 715 $m\ Ahg^{-1}$ at the initial discharge process at 0.1 C. In the second discharge step, the capacity reaches 633 $m\ Ahg^{-1}$.

$$\text{Coulombic efficiency} = \frac{\text{Lithiation capacity}}{\text{Delithiation capacity}} \times 100\%$$

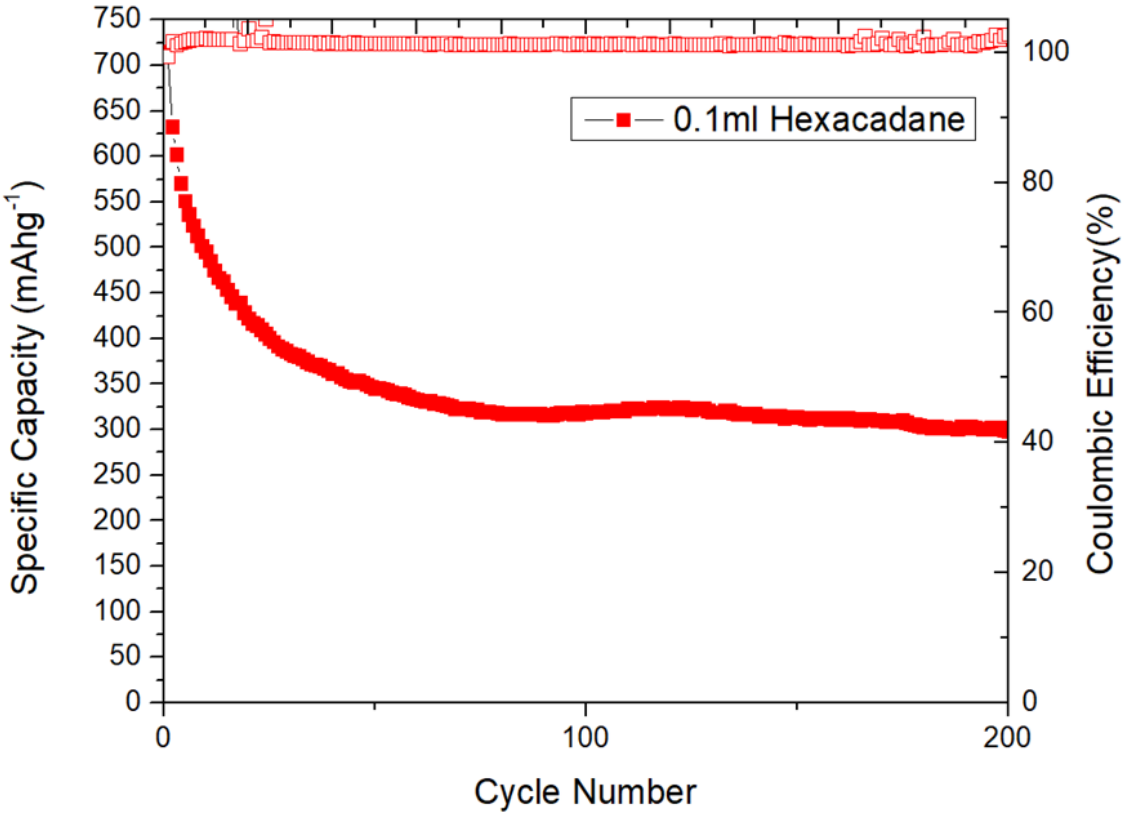


Figure 23 - Specific capacity and coulombic efficiency of Li-S cell with 0.1ml hexacadane at 0.1 C rate

However, the current results demonstrate significant capacity fading within prolonged cycling steps. The capacity of a Lithium Sulfur cell is reduced because of the solubility of

polysulfides within the electrolyte phase. “The capacity fading leads to decrease the active materials exertion during discharge phenomena. Other important factors for fading sulfur cathode capacity and coulombic efficiency is[are] the irreversible precipitates species because of Li_2S and Li_2S_2 Indeed, the insoluble particles are the main cause to obscure the [of obscuring in] electrochemical performance” [1,54].

The second sample contains 0.2ml of hexacadane. Figure 24 shows the specific capacity and coulombic efficiency with 0.2ml of hexacadane at 0.1 C rate. Among tested samples, the lithium sulfur composite with 0.2ml hexacadane (figure 24) shows composites exhibited a capacity of 485 $m\ Ahg^{-1}$ in the initial discharge process at 0.1 C. During the second discharge step, the capacity reaches 430 $m\ Ahg^{-1}$.

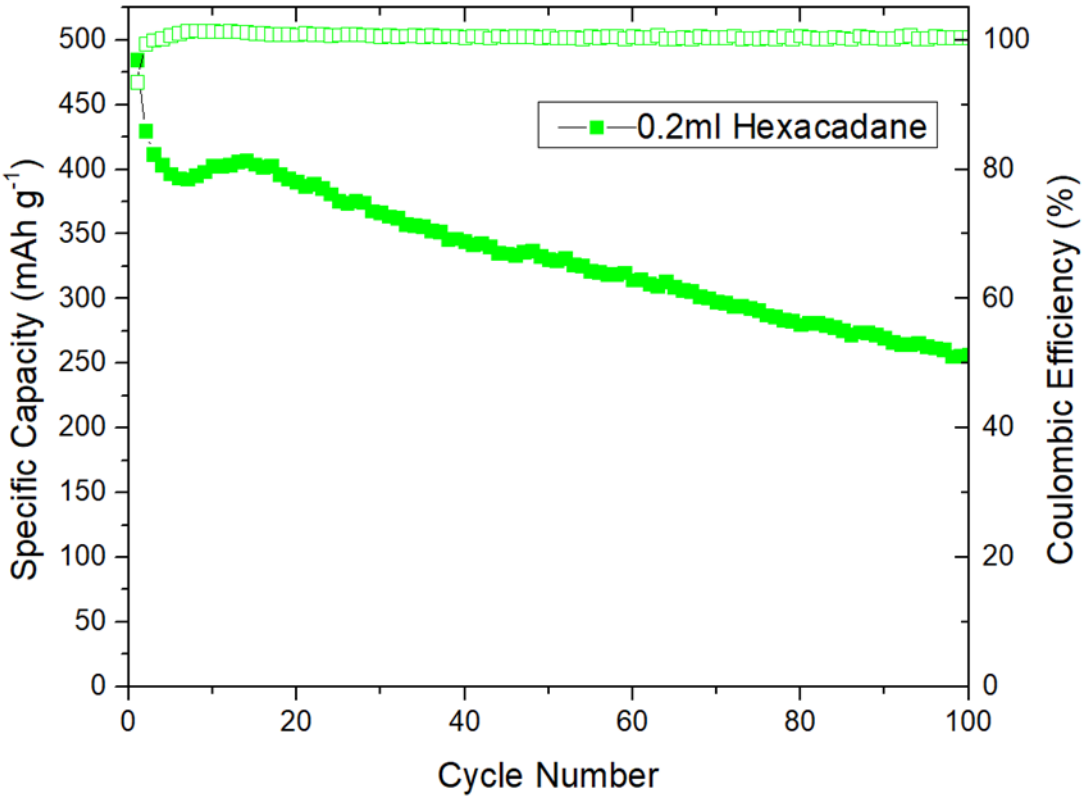


Figure 24: Specific capacity and Coulombic efficiency of Li-S cell with 0.2ml hexacadane at 0.1 C rate.

The third sample contains 0.3ml of hexacadane. Figure 25 shows the specific capacity and coulombic efficiency with 0.3ml of hexacadane at 0.1 C rate. Among tested samples, the lithium sulfur composite with 0.3ml hexacadane (figure 25) shows composites exhibited a capacity of 473 m $m\ Ahg^{-1}$ in the initial discharge process at 0.1 C. During the second discharge step, the capacity reaches 439 $m\ Ahg^{-1}$.

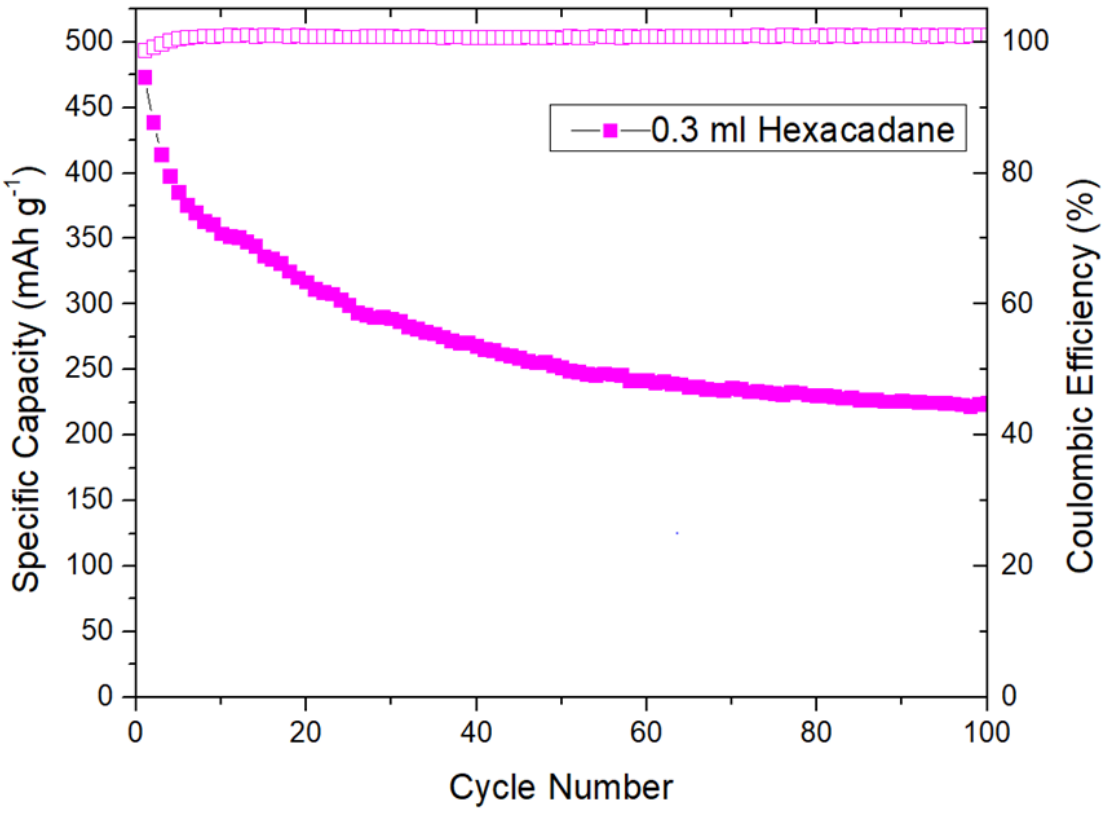


Figure 25 - Specific capacity and Coulombic efficiency of Li-S cell with 0.3 ml hexacadane at 0.1 C rate.

As a result, the Lithium cathode composite results show that higher discharge capacities contain lower amounts of hexacadane (0.1 ml). Furthermore, the sample with 0.1ml hexacadane shows higher specific capacity and coulombic efficiency. The specific capacity ($m\,Ahg^{-1}$)of each individual Li-S is examined for 100 cycles.

Indeed, the impedance spectrum of the assembled Li_2S with 0.1ml hexacadane shows a higher capacity compared to a larger quantity of hexacadane such as 0.2ml or 0.3ml [1,29,54]. Accordingly, the 0.1ml of hexacadane was used to fabricate the lithium Sulfur batteries while introducing metal oxide to the whole system.

3.2 Adding metal oxide within Li – S carbon composite cathode

Metal oxides such as Mn O_2 and MgO have an anion of oxygen (O_2) with a strong polar surface. The oxygen molecule and metal ion create a strong bind. Hence, the metal oxides species are insoluble in most electrolytes. For instance, the cathode contains hollow carbon nanoparticles along with $Si\ O_2$ and metal oxide additives for Li–S cells. Hence, the Mn O_2 and MgO are added to the construction of cathode structures to prevent polysulfide' diffusion through liquid electrolytes [57,58]. This type of sulfur cathode may enhance the cycling performance and capacity of lithium sulfur batteries. Accordingly, nonconductive/conductive metal oxide nanostructure additives such as Mn O_2 and MgO can absorb polysulfide particles and provide higher energy density and capacity.

3.2.1 $Mn\ O_2$ as a conductive host for Lithium Sulfur batteries

The MnO2 is achieved from Manganese(ll) nitrate, 50% w/w aq. soln. liquid Mn $(NO3)_2$. The metal oxide additive contains 10 wt% of total weight of carbon source and hollow carbon nanoparticles include 90 wt%. During the experimental process the MnO2 achieved during below heat treatment at 400^oC:

$$\text{Mn (NO3)}_2 \longrightarrow \text{Mn O}_2 + N\text{O}_x$$

Indeed, the total weight of cathode material includes 20wt% of carbon base material and 80 wt% sulfur. The rest of the process to fabricate the cathode material remains the

same as explained in section 2-2. During the discharge and charge processes, the $Mn\ O_2$ reduces the solution of polysulfides species during conversion electrolyte. Indeed, this step will help to reduce species of Li_2S and improve the capacity of Li-S cell [58]. On the other hand, the hollow carbon nanoparticles contacted with $Mn\ O_2$ and produced a larger surface area. The cathode includes the composite nanomaterial having sulfur loading of 80 wt%.

As shown in Figure 26, The results show that the capacity of Li-S cells can improve significantly by using metal oxide such as $Mn\ O_2$ within 0.1ml hexacadane. Figure 26 demonstrates the specific capacity versus voltage of a Lithium Sulfur cell with 10 wt% of $Mn\ O_2$. The specific capacity is considered for both discharge and charge at the first and fifth cycles with the rate of 0.1 C [53].

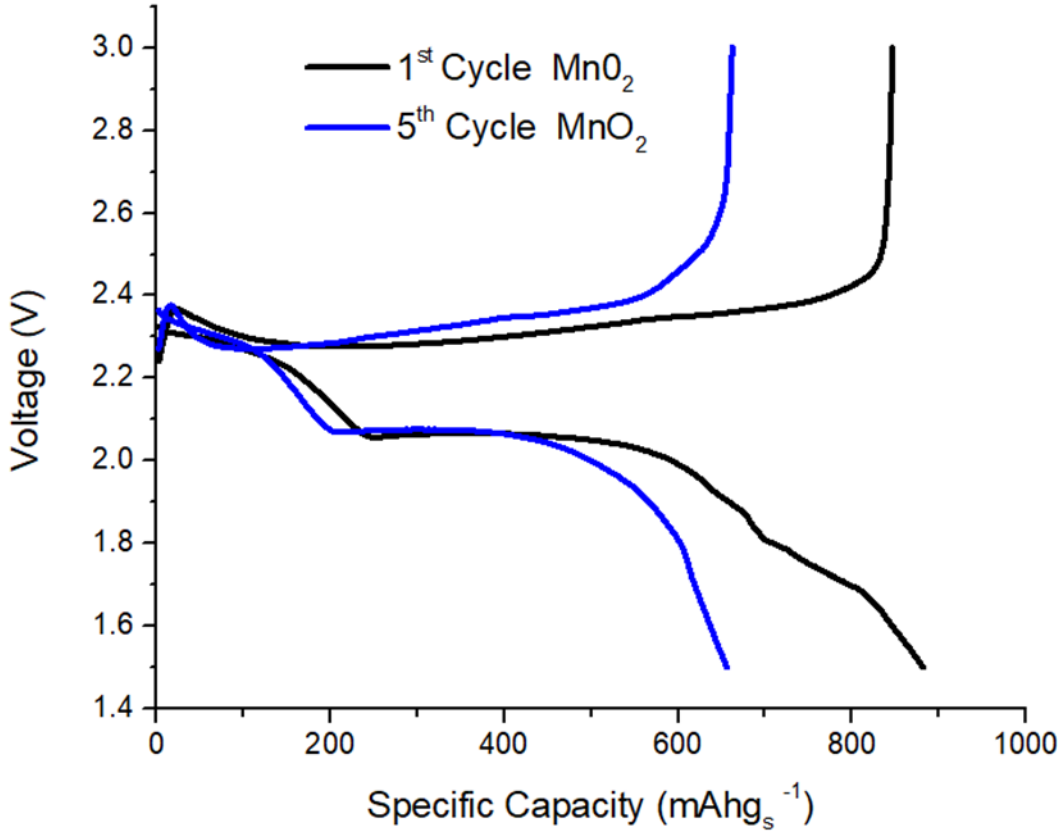


Figure 26 – Electrochemical performance of Li - S cathodes containing Mn O_2. This sample tested for specific Capacity Vs. Voltage at the 1st and 5th cycles. The data compared is considered for both charge and discharge processes.

3.2.2 MgO as an additive for Lithium Sulfur cells

In this research, MgO is the other type of metal oxide used as a host material for lithium sulfur batteries. During the experimental process, the MgO achieved from Magnesium nitrate was hydrated by a heat treatment under $400^{o}C$:

$Mg(NO_3)2.6H_20 \longrightarrow MgO$

The result was added to the CS_2 and placed on a hotplate under a temperature of 70^0C. Then, the output was placed on a hotplate under the hood for 12 hours.

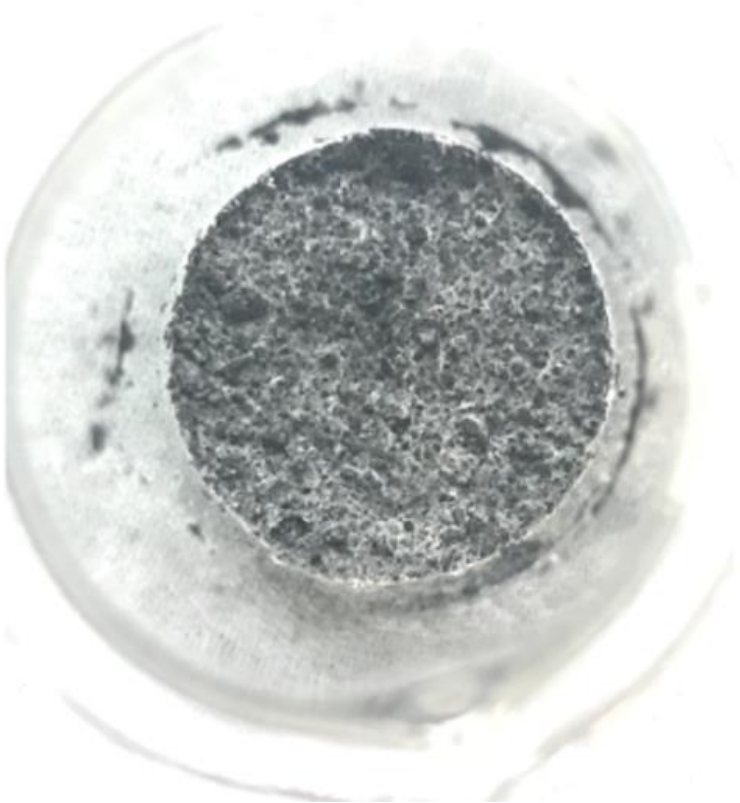


Figure 27 - The cathode composite material includes MgO after mixing with CS_2

The mixture was left under the hood for 12 hours on a 70^0C hotplate The second heat treatment was completed under Argon gas with a $155\ ^0C$ temperature for 10hrs.The result is dark gray/black powder carbon base material. The final step uses the outcome of this step toward making the slurry [58].

The metal oxides such as MgO count as polar material. MgO can host sulfur and are able to anchor with polysulfides species in a Li–S battery. In general, metal oxides can absorb sulfur species due to intrinsic hydrophilic surfaces with respect to the control species. Indeed, the absorptivity of this type of metal oxide plays a key role. Subsequently, hollow sulfur sphere nanocomposites with metal oxide nanoparticles eventually can change the electrochemical stability of Li- S batteries [30, 25].

The corresponding electrochemical performances of MgO composite cathodes are evaluated for cycling stability with coulombic efficiency and respective characterization. The cells containing MgO demonstrate enhanced reversibility. This means the specific capacity of cathodes with MgO ($m\ Ahg^{-1}$) is lower than $\mathrm{Mn\ O_2}$. This performance's result is attributed to the addition of $\mathrm{Mn\ O_2}$ additives to transform the capacity of Lithium Sulfur Batteries (figures 28, 29).

Electrochemical performance of Li - S cathodes containing Mn O_2. This sample tested for specific Capacity Vs. Voltage at the 1st and 5th cycles.

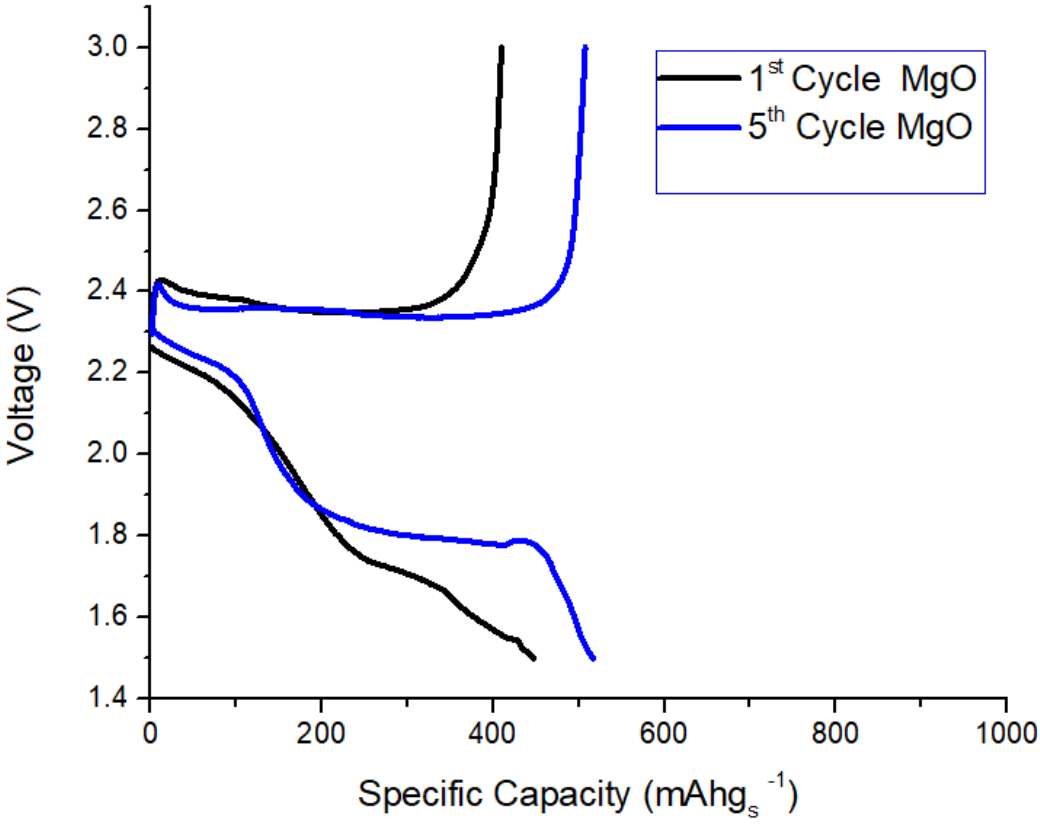


Figure 28 - Electrochemical performance of Li - S cathodes contain MgO . This sample was tested for specific Capacity Vs. Voltage at the 1st and 5th cycles. The data compared is considered for both charge and discharge processes.

In fact, MgO nanostructures were coupled with carbon materials to improve the conductivity of the cathode side and eventually enhance the performances of the Li–S cells. However, the absorption of the intermediate polysulfides species by MgO particles do not significantly change the initial discharge capacity of the cell. [58].

The Mn O_2 composite cathode improves the initial discharge capacity of a lithium sulfur cell up to 882 $m\ Ahg^{-1}$, and more importantly, this capacity is increased compared to the same cell's performance with MgO. The cycling performance shows stable progress for 70-100 discharge cycles at 0.1C. The voltage range of 1.5 to 3.0 is considered to check the Li-S battery's capacity.

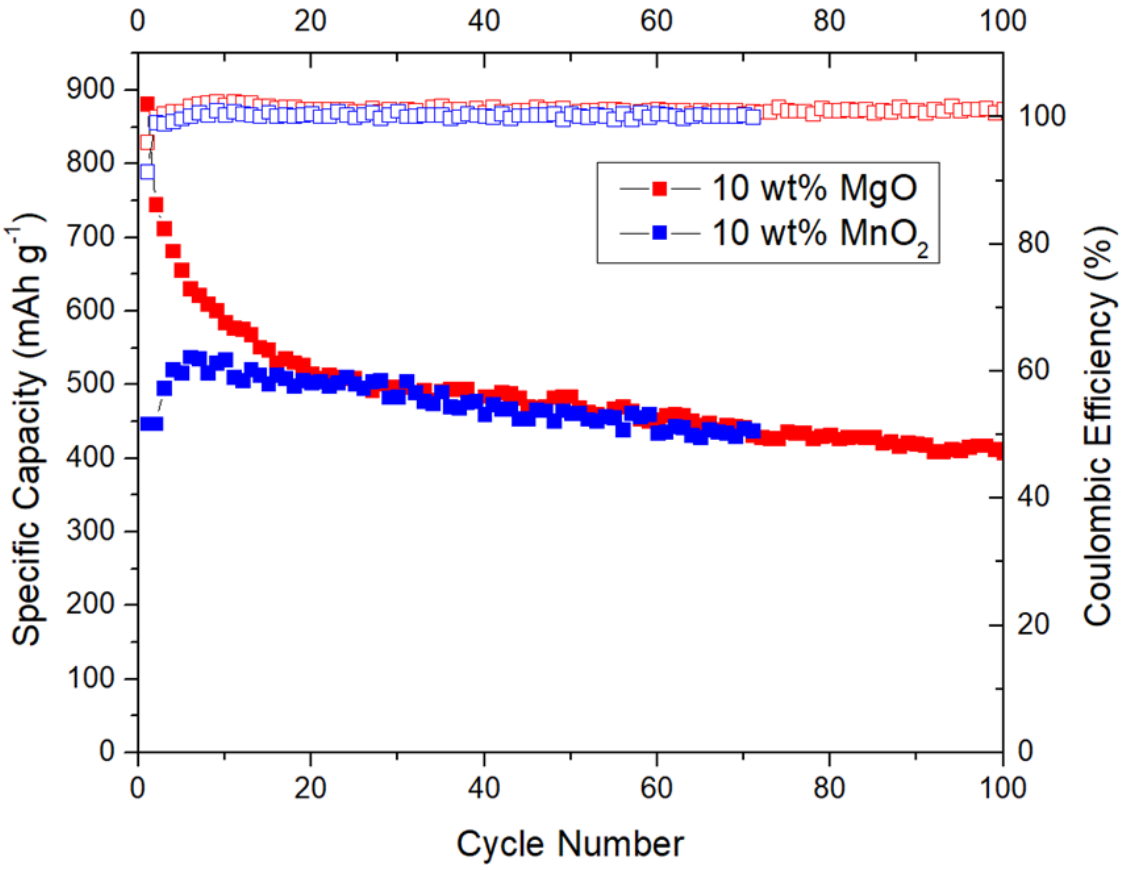


Figure 29 - Specific capacity and Coulombic efficiency of Li-S cell with Mn O_2 Vs. MgO and 0.1ml of hexacadane

The result demonstrates improved performance because of adding MnO_2 to the cathode. The efficient combination of insulating MnO_2 composite with conductive scaffolds can be used to fabricate Li-S batteries more efficiently [58].

4.0 Conclusion

In this research, the strongest advantage of using metal oxides and lithium polysulfide adsorbents is investigated within Lithium Sulfur cells. There are various factors that influence the specific capacity, coulombic efficiency and performance of Lithium Sulfur batteries:

1- The harmful dissolution of lithium polysulfides (Li-PS)
2- The protective characteristic of Lithium Sulfur materials because of sulfur utilization's deficiency
3- Lack of conductivity of sulfur carbon base composite materials
4- Improper diffusion and loss of lithium polysulphides (Li_2S_n, n = 4–8) particles in liquid electrolyte [11,12].

The usage of nanostructured metal oxides and higher surface area particles can improve the life of Li-S batteries. Indeed, the relationships between the intrinsic specification of metal oxide and chemical bonding of electrolytes play an important role within solid sulfur cathode's life. As a result, the metal oxides species have strong absorption characteristics toward polysulfides particles and enhance the utilization of sulfur [1].

However, selecting the best type of metal oxide among many probable metal oxides is a challenging process for Lithium Sulfur cells. New characterization techniques are trying to improve the fabrication steps and reduce loss of cost and time.

Moreover, increasing the conductivity of sulfur carbon base composite cells is another important factor. To achieve this goal, hollow carbon nanospheres (HCNs) were introduced to the system. The results show that HCNs have wide prose volume with larger surface area and manifold morphologies. These unique specifications will qualify HCNs to create covalent bonds with sulfur species and reduce the dissolution of lithium polysulfides [50]. On the other hand, choosing the correct amount of hexacadane is another challenge of working with carbon-sulfur composites. In this research, the cathode with 0.1mh of hexacadane showed better electron conductivity and performance' improvement during charge-discharge process [51,52].

Toward the empirical barriers of Lithium Sulfur batteries, acquiring correct metal oxide material requires close attention and is considered a holistic solution. Besides all known obstacles including large electrolyte volume, lack of energy density, and large sulfur ratio, shortage of coulombic capacity is the key element which needs to be addressed gradually.

Hence, the conversion mechanism of soluble polysulfides is addressed by using two types of metal oxides such as MnO_2 and MgO. In fact, these metal oxides nanostructures were

coupled with carbon materials (including high surface area hollow nanoparticles) to improve the conductivity of the cathode material and eventually enhance the performances of the Li-S cells. The $Mn\ O_2$ composite cathode improved the initial discharge capacity of lithium sulfur cell more than MgO cathodes. The final result demonstrates performance and capacity enhancement adding $Mn\ O_2$to fabricate Lithium Sulfur batteries [58].

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