Nano-Structured Electrocatalysts For High Performance Lithium Sulfur Batteries

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NANO-STRUCTURED ELECTROCATALYSTS FOR HIGH PERFORMANCE LITHIUM SULFUR BATTERIES

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To my parents and their unconditional love and support
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CHAPTER 1 INTRODUCTION

1.1 Battery technology

Batteries are devices, which convert stored chemical energy to electrical energy through chemical reactions. Battery cells usually consist of a negative electrode, a positive electrode, and a porous membrane (separator), which are all connected by electrolyte (an ionically conductive material). The overall chemical reactions are divided into two processes: an oxidation process at the battery negative electrode, and a reduction process at the positive electrode. The ion passes through the electrolyte while the electrons move through the external circuit, where they provide power for portable devices such as cellular phone or electronic devices.

Based on the redox reactions, battery cells are categorized under two main categories: primary and secondary cells. Primary cells have irreversible electrochemical reactions, which allow the active materials to only have a single discharge. The discharge process occurs when the battery provides spontaneous electrical current from the cell through the reduction of the positive electrode, and the oxidation of the negative electrode. Secondary or rechargeable batteries benefit from being able to recharge. The reversible reduction/oxidation (redox) reactions of the battery cell with a flow of ions moving through the electrolyte, and the electrons passing through the external circuit assist the recharging process. The most common rechargeable batteries are: Lead Acid (PbA) batteries, Nickel cadmium (NiCd), Nickel Metal Hydride (NiMH), and Lithium ion (Li-ion) batteries.

1.1.1 Lead acid (PbA)

PbA is a mature and well-established rechargeable battery. Although PbA batteries have high specific power and are not expensive, they have very low specific energy and cyclability. Lead is also toxic and can damage the environment if not disposed of properly. Lead acid battery
the large format is used for as backup supplies of cell phone towers and stand-alone power systems.

1.1.2 Nickel cadmium

The NiCd battery offers good performance and cyclability at low temperature. In addition, it delivers its full capacity at high discharge rates. Thus, it is used where extreme temperatures, long service life, or high discharge current are required. NiCd materials are rather expensive and have a high self-discharge rate. NiCd battery main applications are in medical devices, power tools, and aviation. In addition, Cadmium is a toxic element and requires recycling.

1.1.3 Nickel metal hydride

NiMH has only mildly toxic metals and provides higher specific energy. This battery has high volumetric energy density. Its gravimetric energy density in large format cell may approach 100 Wh/kg. NiMH has a high self-discharge rate, particularly at high temperatures above 50°C. Although, modification of the hydride materials decreases the self-discharge rate and corrosion of the alloy, it decreases the specific energy of the battery. NiMH is available in various size formats for consumer use. It is used for medical and industrial applications, and hybrid vehicles.

1.1.4 Lithium ion

Lithium ion is the most promising and commonly used type of secondary battery with a high open circuit voltage. It has a high energy density and a very low self-discharge rate. However, it struggles with some issues, such as: poor cycle life in high current application, internal resistance increase during cycling, safety concerns related to being over charged or over heated. Li-ion batteries are used widely in military, electric vehicle and aerospace applications.
1.1.5 Lithium sulfur batteries

Much research has been done on developing a next generation of batteries. Li-S batteries are one of the most promising systems for beyond lithium ion battery technologies due to their high theoretical specific capacity of 1,675 mAh g\(^{-1}\) sulfur, and high theoretical energy density, nontoxicity and low-cost. However, it suffers from some issues, such as low cycling stability and high self discharge rate.

1.2 Scope of the thesis

Unfortunately, Li-ion battery technology is approaching its ceiling, and the lack of its ability to keep up with rapid growth of mobile technology is evidenced. Although advanced Li-ion batteries have been introduced, researchers have recently moved their interest to energy storage systems beyond the current state of the art Li-ion batteries, such as Li-S batteries. Despite the apparent remarkable superiority of Li-S battery technology, there are some intrinsic limitations plaguing Li-S battery market penetration, such as: poor cycling stability, low efficiency, and high self-discharge rate. In this work, high capacity carbon-free materials were investigated as electrocatalyst for high capacity cathode materials for the Li-S battery to overcome these hurdles and enhance Li-S batteries performance for practical application.

First, Ni nanoparticles have been investigated as a carbon-free electrocatalyst to enhance lithium polysulfide conversion reactions and improve Li/S battery performance. Ni showed a promising behavior due to its high conductivity and electrocatalytic activity toward the polysulfide reduction reaction. In addition, the effect of Ni in graphene supported Ni nanoparticles, and Ni particle size on Li-S battery performance has been studied by preparing electrodes with a series of Ni nanoparticles with nominal particle size of 20, 40, and 100 nm.

Based on the understanding of the electrocatalytic effect of Ni and capacity fading
mechanism, transition metal nitrides have been investigated as a new class of electrocatalyst for Li-S batteries. Titanium nitride (TiN) nanoparticle was studied as a novel electrode material for Li/dissolved polysulfide batteries. It exhibited a superior performance in a Li/dissolved polysulfide battery configuration. In addition, X-ray photoelectron spectroscopy (XPS) analysis was used to obtain a deeper understanding of the mechanism underlying polysulfide conversion reactions during charge and discharge processes.

Knowing the superior performance of TiN, we expand our studies to different transition metal nitrides to investigate the role of surface composition and morphology in enhancing the electrochemical performance of Li-S batteries. WN, Mo$_2$N, and VN were synthesized and the electrochemical performance, surface composition, and oxidation/reduction mechanism of these cathodes electrodes were studied for lithium sulfur batteries.

Last but not the least, the effect of TiN nanotube size and length on cycling stability of Li-S battery has been studied. A series of TiN nanotube with the average nanotube size of 20, 50, and 80 nm were grown and synthesized on Ti foil using an anodization method. The electrochemical performance and capacity retention of these nanotubes with different length were studied.

**1.3 Significant of research**

The current research provides efficient methods of enhancing Li-S battery performance. The realization of this study can potentially solve the cost, cycling stability and safety of traditional batteries. The following areas are affected by the result of this study:

Lithium ion battery is the major type of battery that is used in cell phones, laptop computers and also today’s electric vehicles (EVs). However, most lithium ion batteries used in EVs cost more than half of the total cost of vehicle. In order to compete with the gasoline-based
vehicle market an EV requires a battery with a lower cost of today's Li-Ion batteries. Engineering and integration of Li-S battery technology decrease the high cost of traditional battery technologies. Thus, Li-S battery benefits from the low cost of sulfur as its active material.

The growth of large-scale energy storage application and green transportation increase the demand of new energy storage technologies with high energy densities. Thus Li-S battery has a high theoretical energy density, it can potentially meet the requirement for those systems. One of the objectives of this project is to employ high capacity cathode material that optimizes Li-S battery performance for practical application.

Furthermore, by increasing the Li-S batteries in EVs, the dependence on oil will be reduced. This affects the economy of countries such as United States that utilize more than 25% of the world total oil consumption. Therefore, battery technologies can potentially replace fossil fuel as a source of energy and enhance the world economics. In addition, relieving oil and gas dependence would reduce greenhouse gas emissions, which 28% of it comes from the transportation sector.
CHAPTER 2 BACKGROUND AND LITERATURE REVIEW

2.1 Lithium sulfur battery

Lithium–sulfur (Li-S) batteries could potentially revolutionize the rechargeable battery market due to their high theoretical capacity and energy density, which is 3-5 times higher than those of Li-ion batteries. In addition, sulfur has a low cost and is environmentally friendly, compared to the toxic transitional metal compounds, which are used in other type of batteries.

2.2 Chemistry of Li-S battery

Elemental sulfur undergoes a series of reactions during the charge/discharge process. In general, reduction of Li$_2$S$_8$ to Li$_2$S occurs through a series of intermediate Li$_2$S$_x$ species (2<x<8) at different potentials [1]. Hence the Gibbs free energy ($\Delta G^\circ$) of different polysulfide anions are close, they can co-exist in the electrolyte solution through a serious of reactions. A typical galvanostatic discharge-charge (GDC) profile of Li-S battery is shown in (Fig 2.1). It demonstrates two plateaus in the voltage range of 2.45 and 2.0 V (vs. Li/Li$^+$) which correspond to 25% and 75 % of the practical capacity. The higher voltage cathodic peak corresponds to the reduction of dissolved Li$_2$S$_8$ in the catholyte on the surface of the cathode to soluble higher order lithium polysulfide Li$_2$S$_x$ (4<x<6), and the lower voltage cathodic peak represents the further reduction of polysulfides to insoluble lithium sulfides (Li$_2$S$_2$ and Li$_2$S) [1]. In general, the discharge process has been divided into 4 regions based on phase change of sulfur. The main products of these regions are, Li$_2$S$_6$, Li$_2$S$_4$, Li$_2$S$_2$, and Li$_2$S. Insoluble solid polysulfides (Li$_2$S and Li$_2$S$_2$) start to form at the end of the third region and during the forth region.

During the charge process, lower order polysulfides oxidize back to elemental sulfur. It contains two plateaus. A longer lower plateau, which represents the oxidation of insoluble polysulfides and a higher charge plateau (which is almost difficult to distinguish sometimes), representing the
oxidation reactions in soluble polysulfide regions.[2]. Crystalline sulfur were reported to form at the end of charge process.[3]

![Discharge profile of Li-S battery.](image)

**Fig 2.1.** Discharge profile of Li-S battery.

### 2.3 Li-S battery configuration

Based on existence of active material in the liquid electrolyte or within the composite cathode matrix, the Li-S battery can have two configurations; conventional Li-S cells (solid configuration) and dissolved polysulfide Li-S cells (liquid configuration). Conventional cells consist of a sulfur composite cathode, lithium metal anode, and an organic liquid electrolyte (Fig.1). In order to make a strong contact between sulfur and the carbon structure, cathode composites have been synthesized by various methods such as: ball milling, sulfur melting or vaporization by thermal treatment, and synthesizing sulfur on carbon matrices.

Liquid cells consist of a conductive structure, which is mainly carbon, a separator, lithium metal anode, and a lithium polysulfide compound, which is dissolved in electrolyte solution (catholyte). This liquid configuration of a Li-S battery with an organic electrolyte has been demonstrated by Rauh et al. in 1979 [4]. Although solid systems have higher cycle life than
dissolved liquid systems, dissolved polysulfide format can enhance the reaction kinetics in electrodes. Thus, the conversion of higher order dissolved polysulfides to insoluble Li$_2$S and Li$_2$S$_2$ is difficult due to the energy required for nucleation of insoluble polysulfides in the solid-state phase. In addition, the complete conversion of insoluble polysulfides may not occur due to the very slow solid-state diffusion into the bulk.

**Fig 2.2.** Schematic representation of conventional Li-S cells (solid system).

**Fig 2.3.** Schematic representation of conventional Li-S cells (dissolved polysulfide).
2.4 Challenges of Li-S batteries

Although Li-S batteries present excellent performance and the potential to be the next generation of batteries, it is still has several drawbacks that result in a low utilization of active material, poor cycle life, and low system efficiency. These obstacles are reviewed in detail in this section.

2.4.1 Insulating active materials

The capacity of the Li-S battery strongly depends on the cathode. However, sulfur active material and some intermediates formed during redox reactions have a very poor electronic conductivity. As a result, Li-S cathode electrode must be composed of electronically conductive additives (such as carbon). These additives need to have a good electronic conductivity, good ionic conductivity to enhance lithium ion transportation within the cathode matrix and also between cathode and the anode electrodes. They need to posses pores that accommodate polysulfides and provide the liquid electrolyte with accessibility to active material. Moreover, they must retain a stable framework to suppress the stress generated by the volume expansion/compression of the active material during cycling. They should not react with the electrolyte and active material as well.

2.4.2 Volume expansion

Because Sulfur (α-S₈) and Li₂S have densities of 2.07, and 1.66 g cm⁻³ respectively, the Li-S battery experiences a distinguishable expansion of about 79% during cycling [3, 5]. Volume expansion of the cathode electrodes can fracture the conductive structure and increase the polarization within the cell, which cause lower performance stability and rapid capacity deactivation. One of the important factors to buffer the volume expansion is the cathode pore size. The large internal pores within the cathode structure can accommodate sulfur volume
expansion. Flexible carbon materials with conductive polymer coating can also be used to buffer the volume expansion of the cathode. [6, 7]

2.4.3 Shuttle reactions

During the charging step, short-chain PS (Li$_2$S, and Li$_2$S$_2$) oxidizes to long-chain PS. The dissolved higher chain PS can diffuse to the Li anode and be electrochemically or chemically reduced on the lithium anode surface by the following reactions [1]:

\[
(n - 1) \text{Li}_2\text{S}_n + 2\text{Li}^+ + 2e^- \rightarrow n\text{Li}_2\text{S}_{n-1} \quad \text{Electrochemical Reduction}
\]
\[
(n - 1) \text{Li}_2\text{S}_n + 2\text{Li} \rightarrow n\text{Li}_2\text{S}_{n-1} \quad \text{Chemical Reduction}
\]

The produced short-chain PS on Li surface can diffuse back to the cathode surface and oxidize to long-chain PS again. This parasitic reactions can cause different problems such as (1) depletion of active material due to sulfur consumption, (2) corroding Li anode, and (3) polarizing

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**Fig 2.4.** Schematic illustration of the polysulfide shuttle mechanism[8].
Li anode due to \( \text{Li}_2\text{S} \) and \( \text{Li}_2\text{S}_2 \) formation on Li anode surface [1]. Thus, reducing redox shuttles can enhance the Li-S battery cycle life time.

2.4.4 Non soluble lithium sulfide and sulfur plating

The insoluble polysulfides (\( \text{Li}_2\text{S} \), and \( \text{Li}_2\text{S}_2 \)) accumulate on the cathode surface at the end of discharge process. These two discharge products have a very poor electrical conductivity. They form a passivation layer on the cathode electrode, which reduces Li-S battery performance in several ways [9]. It decreases the sulfur active material utilization due to reducing the active surface area of the cathode. In addition, it increases the charge transfer polarization on the cathode electrode surface. Furthermore, it increases the sulfur active material loss due to the quasi-reversible nature of polysulfide redox reactions.

2.4.5 Lithium anode

Li anode can be corroded by parasitic reactions of Lithium surface dissolved PS. It also can react with organic electrolyte solvents. These reactions consume lithium. They also form a passivation layer on the Li anode surface with a lower ionic and electronic conductivity, which increases the charge transfer resistance at the anode electrode/electrolyte interface. [10]

2.4.6 Self discharge

Active sulfur material in the cathode electrode (solid configuration) or higher order polysulfides in the catholyte solution (Liquid configuration) can react with Li ions. As a result, soluble polysulfides are produced and diffuse out toward the lithium anode in which it can reduce further by reacting with Li on the anode surface. When self discharge happens, the oxidation state of the active material declines. Therefore, the open circuit voltage of the Li-S cell recedes and the higher discharge plateau, which occurs around 2.3-2.4 V, disappears [11, 12].
2.4.7 Electrolyte

A good electrolyte for Li-S batteries should have specific properties such as: high ionic conductivity for Li ions, low viscosity which allows Li ion diffusion through cathode electrode, good electrochemical stability with Li anode, moderate PS solubility and wide voltage range and electrochemical window. Practically, there is no organic solvent that could meet all these requirements. Therefore, different type of additive and mixture of solvents with various ratios are used to optimize the electrolyte properties. Conventional salts are used as an additive to the electrolyte to provide good ionic conductivity. However, conventional salts such as LiPF$_6$, LiBF$_4$, and LiBOB that were used in lithium ion batteries can not be used for Li-S due to their side reactions with dissolved PS. Different salts such as LiTFSI, LiSO$_3$CF$_3$, and LiN(SO$_2$CF$_3$)$_2$ are reported to show a good performance for Li-S batteries [13, 14].

2.5 Research focus

As stated above, the majority of Li-S problems are associated with the dissolution of PS in the electrolyte and their parasitic reactions with Li anode. However, dissolution of polysulfide is crucial for Li-S battery performance. Therefore, much of research has been done on developing new materials for the cathode electrode. These materials enhance Li-S battery performance by improving active material utilization and reducing parasitic reactions by various means such as trapping PS, bonding with sulfur species, chemical or physical adsorption. Some of these methods are reviewed in detail in this section.

2.5.1 Carbon composite

Several types of carbon composites have been developed to provide the Li-S cathode electrode with good electrical conductivity and also to reduce the dissolution of polysulfide out of the cathode structure. Shim et al. used more than 10% carbon black to obtain the required
conductivity. They reported that using a higher content of carbon provides a higher initial capacity but faster capacity deactivation as well [15].

Multi-wall carbon nanotube (MWCNT) structure of sulfur-carbon composite have been reported to trap polysulfides and reduce redox shuttle reactions [16]. This cathode showed a capacity of almost 900 mAh g\(^{-1}\) after 30 cycles at 100 mAh g\(^{-1}\) rate of discharge.

**Fig 2.5.** SEM images of (a) raw sulfur, (b) nano-sulfur (sample B), (c) MWCNTs and (d) nano-sulfur/MWCNTs composite (sample A)[16].

Wang et al. reported a good capacity retention for a polyphenylene wrapped multi wall carbon nanotubes cathode. Thus it suppresses PS dissolution to the electrolyte [17]. They reported a capacity of 1015 mAh g\(^{-1}\) Sulfur after 75 cycles.
Fig 2.6. Cyclic and rate performance of Li/S cell with the two cathodes at various discharge rates of (a) 100 mAg\(^{-1}\) (b) 200 mAg\(^{-1}\) (c) 300 mAg\(^{-1}\)\cite{16}.

2.5.2 Graphene composite

Graphene is a two-dimensional honey-comb lattice allotrope of carbon. It attracted considerable attention in the field of energy storage due to its excellent properties such as: high electrical conductivity, superior chemical stability, and high surface area (over 2600 m\(^2\) g\(^{-1}\)). Cao, et, al. reported a capacity of almost 700 mAh g\(^{-1}\) for a functionalized Nafion coated graphene sheet sulfur nanocomposite, at 0.1 C rate and after 100 cycles \cite{18}. In addition, poly(ethylene glycol) coated graphene-sulfur composite was reported to exhibit a capacity of 500 mAh g\(^{-1}\), at 0.2 C rate, after 100 cycles \cite{19}. Li. et al, measured a capacity of 928 mAh g\(^{-1}\) at 0.2 A g\(^{-1}\) rate, after 100 cycles for a carbon–sulfur nanocomposite coated with reduced graphene oxide (RGO) \cite{20}.
2.5.3 Polymer composite

The attachment of conductive polymer onto sulfur-carbon composites suppresses the diffusion of polysulfides out of the cathode electrode. As a result, it enhances the Li-S electrochemical performance such as cycle stability, efficiency, and rate capability. Fig 2.9 presents the SEM images of two sulfur-polypyrrole composite cathodes: a sulfur particles coated with polypyrrole, and a orthorhombic bipyramidal sulfur particles coated with a polypyrrole nanolayer. These cathodes exhibited a capacity of almost 600 mAh g\(^{-1}\) sulfur after 50 cycles at 0.2 C rate [21, 22].
Fig 2.8. (a) Typical voltage capacity profiles and (b) cycle life of the TG–S and RGO–TG–S nanocomposites at a rate of 0.2 A g⁻¹.

2.5.4 Mixed ionic electronic conductor (MIEC)

Conductive polymers provide a matrix for electron transport, however they have much lower electronic conductivity compared to carbon material. In order to overcome this issue, MIEC have been investigated. Fig 2.10 shows good electrochemical stability of a MIEC of
polypyrrole. Thus MIEC retain polysulfide species while it facilitates ion and electron transfer within the electrodes. This cathode presents a capacity of over 600 mA h g$^{-1}$ at 0.1 C rate and 500 mA h g$^{-1}$ at 1.0 C rate after 50 cycles [24].

**Fig 2.10.** (a) Cyclability of the MIEC composite at various C rates; the capacity values are in terms of the percentage of the sulfur active mass. (b) SEM image of the synthesized Sulfur-MIEC composite [24].

2.5.5 Oxide additives

Oxide additives have been shown to enhanced Li-S battery performance due to both physical trapping and surface chemical adsorption of polysulfide species. A hydrogen reduced TiO$_2$ with an inverse opal structure revealed a discharge capacity of 890 mAh g$^{-1}$ after 200 cycles at a 0.2 C rate [25]. Also a sulfur/carbon composite with coupled mesoporous titania additive was shown to maintain a discharge capacity of above 750 mA h g$^{-1}$ after 200 cycles. It was shown that a cell containing TiO$_2$ with 5nm pore size exhibited a 37% higher capacity retention after 100 cycles compared to a cell without the titania additive [26]. Thus, it absorbs lithium polysulfides within the pores of the nanoporous titania. Al$_2$O$_3$ also was shown to reduce lithium polysulfide dissolution in liquid electrolyte. A sulfur electrode with nano Al$_2$O$_3$ particle additive was shown to display a capacity of 660 mAh g$^{-1}$ sulfur. It was also presented a higher capacity retention compared to an electrode without Al$_2$O$_3$ [27]. Porous silica is another material that
presents absorption behavior toward lithium polysulfide species. It allows reversible desorption and release of lithium polysulfides, as a result of the weak binding that it makes with them. A porous silica embedded within the carbon–sulfur composite exhibited an enhanced cycling stability and capacity performance of 350 mAh g\(^{-1}\) sulfur, at 1.0 C rate after 100 cycles [28].

2.5.6 Metal sulfide

 Transitional metal disulfides have been also reported to improve Li-S battery performance with their high conductivity and strong binding with polysulfide species. Two dimensional layered titanium disulfide has been used to encapsulate Li\(_2\)S cathode materials and exhibited a high capacity of 503 mAh g\(^{-1}\) Li\(_2\)S at 1.0 C rate (Fig. 2.11) [29].

![Diagram](a) Schematic of the synthesis process, (b) specific capacities at 0.2 C (1.0 C = 1,166 mA g\(^{-1}\) Li\(_2\)S) for Li\(_2\)S@TiS\(_2\) and bare Li\(_2\)S cathodes, (c) specific capacity of Li\(_2\)S@TiS\(_2\) cathodes cycled from 0.2 to 4.0 C [29].

2.5.7 Catalyst

 Different electrocatalyst such as Pt, Au and Ni were found to be catalytically active toward PS redox reactions. Thus Pt, Au and Ni coated current collectors exhibited a reduction in
polarization and increase in discharge capacity over the conventional Al substrate [30]. Engineering these current collectors instead of carbon additives could potentially eliminate some of the Li-S batteries challenges, such as volume expansion and redox shuttle reactions. The two-dimensional Ni current collectors as a cathode delivered a discharge capacity of 700 mAh g⁻¹. This capacity was enhanced further to 900 using engineered three-dimensional current collectors.

These studies clearly show that Li-S batteries could potentially succeed Li-ion battery technology as a result of its higher energy density and lower price. However, they suffer from several obstacles such as higher capacity deactivation rate and self discharge rate. In order to commercialize this batteries, this issues need to be overcome. The main focus of this research is developing new electrocatalysts and carbon free cathode materials, which enhance Li-S battery electrochemical performance.
CHAPTER 3 EFFECTS OF NICKEL PARTICLE SIZE AND GRAPHENE SUPPORT ON THE ELECTROCHEMICAL PERFORMANCE OF LITHIUM/DISSOLVED POLYSULFIDE BATTERIES

3.1 Introduction

Advances in portable electronic devices and electric vehicles require advanced electrical energy storage systems, such as rechargeable batteries with high energy density and long lasting cycle performance. Among the most promising energy storage systems, lithium sulfur (Li-S) batteries have received increasing attention due to their high energy density of 2600 Wh kg\(^{-1}\) and theoretical capacity of 1675 mAh g\(^{-1}\).\(^1\) In addition, sulfur is environmentally friendly and has a low cost.\(^1, 8, 31\) However, the development of lithium sulfur batteries presents some obstacles such as poor cyclability, lower practical capacity and high self-discharge rate.\(^1, 8, 31\) The poor conductivity of sulfur and its final discharge products, Li\(_2\)S\(_2\) and Li\(_2\)S, limits the specific capacity of Li-S batteries. Furthermore, the dissolution of lithium polysulfide intermediates in the liquid electrolyte during the charge-discharge process causes the polysulfide shuttle process and lithium corrosion, which results in low cyclability, charging inefficiency and high self-discharging rate of batteries.\(^32, 33\).

In recent years, efforts have been made to improve the performance of Li-S batteries and overcome the above challenges. Much of the research has focused on the development of new cathode materials to enhance the electrical conductivity, to accommodate and absorb polysulfide and active materials within the pores or layers of the cathode structure. In order to improve cathode material performance, conductive carbon additives such as: mesoporous and nano-structured carbon \(^{34-36}\), porous hollow carbon spheres \(^{37, 38}\), carbon multi-walled nanotubes \(^{39, 40}\), graphene \(^{19, 41}\), conductive polymers \(^{42-44}\), and carbon interlayers have been used. Several studies have been conducted on the design of alternative current collectors such as...
Ni foam as an interlayer, cathode conductive structure [45], and a protective layer [46], which improves the active material utilization, cycle life, and battery performance due to its metallicity and 3-D network structure.

It has been reported that the reaction kinetics of aqueous polysulfide can be enhanced by using electrocatalytic electrodes in photoelectrochemical solar cells [47] and redox flow battery cells [48]. Metal oxides such as CeO$_2$ [49, 50], MnO$_2$ [51-53], have been demonstrated to be promising cathode catalysts for rechargeable batteries electrochemical reactions. In addition, some metal oxides such as TiO$_2$ [26], Al$_2$O$_3$ [54], SiO$_2$ [28] and MnO$_2$ [55] have been shown to enhance Li-S discharge capacities and cycling stability. This can be attributed to their strong ability to adsorb sulfur species, thus effectively suppressing the diffusion of polysulfide species into the electrolyte. Ti$_4$O$_7$ has also been reported to enhance the Li-S batteries redox chemistry due to its sulphilic surface and good electron conductivity [33]. In our recent study, carbon-free electrocatalysts such as Pt, Au and Ni have been found to enhance lithium polysulfide conversion reactions and improve Li-S battery performance [56]. Among these electrocatalysts, Ni showed a promising behavior due to its high conductivity along with electrocatalytic activity toward polysulfide reduction reaction [56].

Very few studies have been conducted on lithium polysulfide dissolved configuration with electrocatalytic electrodes. Babu et al. [56] found that with a 200 nm thick Ni electrode and 10 $\mu$l of 0.2 M Li$_2$S$_8$ catholyte, a capacity of 420 mAh g$^{-1}$ sulfur was observed after 40 cycles; while Zhang et al. [57] measured a capacity of 490 mAh g$^{-1}$ sulfur with a super-p carbon electrode and 20 $\mu$l of 0.25 m Li$_2$S$_8$ catholyte, also after 40 cycles.

In the present study, the electrocatalytic effect of nickel (Ni) nanoparticle sizes on the lithium polysulfide conversion reactions in dissolved lithium sulfur battery configuration is
investigated. The Ni particles of 20 nm with the higher geometric surface area show a superior capacity of 1066 mAh g$^{-1}$ sulfur compared to Ni particles of 40 and 100 nm for the first cycle. In addition, to further improve the capacity retention and discharge capacity of the cell, the effect of the graphene support on Ni nanoparticle dispersion and cycling performance is investigated. The results show a significant improvement in the discharge capacity compared to the other electrodes, and Ni/graphene electrode exhibits a capacity of 753 mAh g$^{-1}$ sulfur after 40 cycles which is significantly higher than similar studies. This could be explained by the homogeneous distribution of Ni nanoparticle within the carbon matrix, which suppress the agglomeration and surface area loss of the Ni nanoparticle after cycling; as well as a synergetic effect of graphene structure and Ni nanoparticle.

3.2 Experimental

3.2.1 Preparation of electrocatalysts

Nickel nanoparticles (Ni, 99.9% with sizes of 20 nm, 40 nm and 100 nm, US Research Nanomaterial Inc.) were activated under hydrogen for 3 h at 150 °C. To prepare Ni/graphene hybrids, 5 grams of graphene (Angstrom Materials) were refluxed with 250 mL of 70% HNO$_3$ at 110 °C for 3 h to functionalize and also remove metallic impurities. The material was then washed with water and dried at 70 °C for 12 h. 0.8 g of the functionalized graphene was then stirred with 300 mL of ethylene glycol, and nickel chloride hexahydrate (NiCl$_2$.6H$_2$O, Sigma Aldrich) was added to the resulting suspension. Ni metal loading on graphene support can be controlled by changing the amount of Ni precursor (nickel chloride hexahydrate NiCl$_2$.6H$_2$O) during the preparation. In the present work, we have used 0.81 g of nickel chloride hexahydrate (NiCl$_2$.6H$_2$O) to achieve Ni metal loading of 20 wt.% on graphene. The resulting suspension was then heated to 140 °C and held for 10 min. Thereafter, 0.65 g sodium borohydride (NaBH$_4$,
Sigma Aldrich) dissolved in 20 mL of ethylene glycol was slowly added and refluxed for 2 h. Finally, the solution was filtered, washed with water/ethanol, and dried overnight.

3.2.2 Fabrication of electrodes and electrochemical measurements

The electrode slurry was prepared by adding 10 wt% of poly(acrylonitrile-methyl methacrylate) (Polysciences Inc) AN/MMA=94:6 , as binder and N-methyl pyrrolidinone (NMP) as solvent to the electrocatalyst materials (Ni nanoparticles, Ni/graphene, or graphene). The slurry was coated on Al foil and dried at 80 °C under vacuum for 10 h.

Elemental sulfur $S_8$, lithium sulfide $Li_2S$, Bis(trifluoromethane)sulfonimide lithium salt $LiN(SO_2CF_3)_2$, LiTFSI, Triethylene glycol dimethyl ether (TG$_3$), were purchased from Aldrich and used as received. A catholyte solution with 0.2 M $Li_2S_8$, 0.1 M LiTFSI, and 1 M LiNO$_3$ was prepared by stirring appropriate amounts of $S_8$ and $Li_2S$ into TG$_3$ at 80 °C for 6 h. 10 μL of 0.2 M $Li_2S_8$ catholyte solution containing 0.54 mg sulfur was added onto positive electrodes with 8 mg Ni cm$^{-2}$ loading. In addition, a Polypropylene separator (Celgard 2400), and lithium foil anode were used to assemble coin cells (CR2032) inside an argon filled glove box. The effect of catholyte concentration on Ni catalyst has been investigated in our recent study on a 200 nm Ni film, with 100, 200 and 600 mM of $Li_2S_8$ catholyte concentration at 0.1 C rate [56]. The results show a decrease in specific capacity with increase in the concentration of polysulfide due to increase in the electrolyte viscosity. Therefore, 0.2 M electrolyte was used in the present study.

3.2.3. Characterization and electrochemical measurements

Phase purity of the positive electrode materials was characterized using a Rigaku Miniflex 600 X-Ray Diffractometer. Morphological features of the Ni electrode before and after cycling were observed with field emission scanning electron microscopy (JEOL 7600F, FESEM). The specific surface area analyses were measured by Braugauer-Emmet-Teller (BET)
multimolecular adsorption method (Micromeritics Tristar II surface area/porosimeter). Galvanostatic discharge-charge tests were conducted using a Maccor Model 4200 Automated Test System between the voltage range of 1.5 to 3 V (vs. Li/Li$^+$) at room temperature. Cyclic voltammetry experiments were performed using a Gamry potentiostat reference 3000 at different scan rates ranging from 0.05 to 1 mV s$^{-1}$ in the voltage range of 3 to 1.5 V (vs. Li/Li$^+$).

3.3 Results and discussion

3.3.1. Structure and morphology

SEM images of the Ni nanoparticles, graphene and graphene supported Ni nanoparticles were recorded at high magnification and show the uniform distribution of the spherical shaped Ni nanoparticles (Fig. 3.1a-c). The average particle size was calculated from the measurement of about 250 particles found in an arbitrarily chosen area of the enlarged images. It was found to be about 17, 38, and 92 nm for the nominal 20, 40, and 100 nm Ni nanoparticles, respectively. In the case of Ni/graphene, average size of about 11 nm Ni nanoparticles are homogeneously distributed within the graphene matrix (Figure 1d). It was also confirmed from the corresponding EDS mapping images shown in Fig. 3.2.

The surface area of Ni nanoparticles was measured by BET sorptometry and results are provided in (Figure 1e). As expected, the surface area of 20 nm size Ni nanoparticles is 28.9 m$^2$ g$^{-1}$ which is higher than 3.6 and 2.7 m$^2$ g$^{-1}$ for the 40 and 100 nm Ni nanoparticles, respectively.
Fig 3.1. SEM images of Ni nanoparticles: (a) 20 nm, (b) 40 nm, (c) 100 nm, (d) Ni/Graphene, (e) BET surface area of Ni nanoparticles, and (f) XRD patterns of all of the nanoparticles.

Crystal structure of the nanostructured electrocatalysts is analyzed by XRD. Figure 1f shows the XRD pattern of Ni nanoparticles and the graphene supported Ni nanoparticles. A face-centered cubic phase Ni diffraction pattern without any other peaks was observed for all of the samples, which indicates that the Ni nanoparticles are single-phase fcc. Ni crystallite size is determined using Scherrer’s equation and considering the full width at half maximum (FWHM)
of all the Ni diffraction peaks, the average Ni crystallite sizes are calculated to be 10, 20, 39, and 58 nm for the Ni/graphene, 20, 40, and 100 nm Ni nanoparticles, respectively.

![SEM and EDS mapping images](image)

**Fig 3.2.** SEM and the corresponding EDS mapping images recorded for Ni/graphene.

### 3.3.2. Electrochemical performances

In order to have a better understanding of Ni electrocatalyst activity towards polysulfides conversion reaction, cyclic voltammograms were performed at different scan rates from 0.05 to 1 mV s\(^{-1}\). All cycles present one anodic oxidation peak at 2.54 V (vs. Li/Li\(^+\)) and two cathodic reduction peaks at 2.0 and 2.4 V (vs. Li/Li\(^+\)). The higher voltage cathodic peak corresponds to the conversion of sulfur to higher order lithium polysulfide (Li\(_2\)S\(_n\) n>4) and the lower voltage cathodic peak represents the transformation of dissolved higher order lithium polysulfide to insoluble lower order lithium polysulfide (Li\(_2\)S\(_n\) n<4) [1]. (Fig.3.3). The 20 nm Ni nanoparticle
electrode shows a more stable behavior for polysulfide conversion reaction during the first 4 cycles (Figure 3.3.a).

**Fig 3.3.** Voltammograms for first 4 cycles: (a) Ni 20 nm, (b) Ni 40 nm, (c) Ni 100 nm, and (d) Ni/Graphene.

In addition, Graphene electrode without Ni also exhibited similar redox behavior (Fig. 3.4). Fig. 3.5 shows the cyclic voltammograms at different scan rates. Anodic and cathodic peak positions shift toward higher and lower voltage, respectively, as scan rate increases, which indicates the quasi-reversible nature of polysulfide reactions [58]. Furthermore, the Randlese-Sevcik are shown a linear relationship of the cathodic peak height as a function of the square root of the scanning rate, which clearly indicates that polysulfide conversion reaction are diffusion controlled [59].
Fig 3.4. Cyclic voltammograms recorded for graphene electrode.

Fig. 3.6a-c presents the charge and discharge voltage profile of Ni electrodes at a 0.1 C rate. All of the discharge curves present two plateaus in the voltage range of 2.0 to 2.4 V (vs. Li/Li$^+$), which are in good accordance with the two cathodic peaks in the charge voltage curves (Fig. 3.3). It is known that one of the factors determining electrocatalytic activity is the surface area [60]. Therefore, the 20 nm Ni particles electrode with higher geometric surface area displays a high initial discharge capacity of 1,067 mAh g$^{-1}$ sulfur, contrasting with the 580 and 496 mAh g$^{-1}$ sulfur discharge capacity of the 40 nm and 100 nm electrodes, respectively. In addition, after 40 cycles, the electrode with 20 nm shows the highest discharge capacity of 583 mAh g$^{-1}$ sulfur, compared to the 493 and 298 mAh g$^{-1}$ sulfur capacity of the 40 nm and 100 nm electrodes, respectively. In order to further improve the capacity retention and discharge capacity of the cell, the effect of the graphene support to anchor the Ni nanoparticle has been investigated.
Fig 3.5. Cyclic voltammograms at different scan rates (0.05 to 1 mV s$^{-1}$): (a) Ni 20 nm, (b) Ni 40 nm, (c) Ni 100 nm, and (d) Ni/Graphene.

The capacity performance of the cell with Ni/graphene electrode is significantly improved to a high initial capacity of 1216 mAh g$^{-1}$ sulfur compared to 766 mAh g$^{-1}$ sulfur capacity of graphene electrode. Ni/graphene electrode and graphene electrode capacities decreased to 753, and 408 mAh g$^{-1}$ sulfur after 40 cycles (Figure 4d). In addition, capacity retention of the Ni/graphene electrode is around 10 percent higher than graphene electrode during 40 cycles. Moreover, we have demonstrated Ni electrochemical activity by investigating the effect of polysulfide concentration and temperature on Li-S battery performance in our recent study [56].
Fig 3.6. Voltage vs specific capacity profiles at different cycles: (a) Ni 20 nm, (b) Ni 40 nm, (c) Ni 100 nm, (d) Ni/Graphene, and (e) Graphene.

Therefore, the superior Ni/graphene cell performance can be attributed to the synergetic effect of both Ni nanoparticle catalyst and graphene structure. Moreover, the homogeneous distribution of Ni nanoparticle within the carbon matrix can minimize the agglomeration of the Ni nanoparticle which decreases the geometric surface area loss after cycling. Regarding the quasi-reversible nature of polysulfide reactions and the formation of passivation layer on positive electrode and lithium surface, the original mass of active sulfur on the positive electrode can become lower during cycling which is one of the main reasons of capacity fade after cycling.
Although the capacity of all electrodes decreases with cycling, the Ni/graphene electrode has the highest capacity 40 cycles compared to all of the other electrodes (Fig. 3.7a). The rate capability of the Ni electrodes is presented in Fig. 3.7b. The C rate is based on the theoretical capacity of sulfur (C=1675 mAh g$^{-1}$ sulfur). All of the electrodes were first subjected to a low 0.1 C rate to obtain stable nominal capacity. Subsequent cycling was performed at higher current rates of 0.2, 0.5, and 1.0 C, each for 5 cycles. Finally, it was operated at 0.1 C for more 6 cycles. The capacity of all of the Ni electrodes decreases with increasing cycle numbers. The Ni/graphene cell shows a higher capacity performance of 1170, 827, 629, and 489 mAh g$^{-1}$ sulfur, compared to the other electrodes at 0.1, 0.2, 0.5, and 1.0 C rates, respectively. All of the cells recovered most of their capacity when the current rate was returned back to 0.1 C.

Fig 3.7. Effect of particle size and graphene support on cycling performance: (a) capacity performance, and (b) rate capability at different current rates.
3.3. Morphological changes of the Ni electrode

The Ni electrodes were completely washed with TG3 prior to SEM measurements to remove the soluble polysulfides. Fig.3.8 shows the SEM images of the Ni nanoparticle, graphene, and graphene supported Ni nanoparticle electrodes before and after cycling. After the 40\textsuperscript{th} full charge process, a passivation layer is observed on the particle surface, which appears to be thinner in the 40 and 100 nm nanoparticle electrodes. The formation of this layer, which is reported to be mostly lithium sulfide Li\textsubscript{2}S \cite{5, 61-65}, may reduce the cell performance in several ways. It diminishes the interfacial property between the electrodes and electrolyte \cite{65}. In addition, while the polysulfide reactions occur at the surface of the electrode, the insulating nature of the passivation layer may cause a capacity fade \cite{63}. Furthermore, this passivation layer decreases the electrochemical active surface area of the electrode. More importantly, the precipitated Li\textsubscript{2}S in the conductive electrode matrix at fully charged state does not contribute to discharge capacity and can be regarded as irreversible loss of active material \cite{5}. There may be a possibility for the formation of NiS\textsubscript{x} during the charge-discharge process. However, the formation of NiSx was not reported in Nickel foam and Ni film that have been used in Li/S batteries \cite{45, 56}. Therefore, the capacity fade in the cases of the Ni 20 nm and Ni/graphene electrodes are more significant compared to the other electrodes. These results are in a very good agreement with the electrochemical measurement.
Fig 3.8. SEM images of electrodes before cycling (left column), and after 40 cycles (right column): (a) Ni 20 nm, (b) Ni 40 nm, (c) Ni 100 nm, and (d) Ni/Graphene.

4. Summary

The effects of Ni particle size and graphene support on the lithium polysulfide conversion reactions and Li-S battery performance have been studied. The results indicate the 20 nm Ni electrode with higher surface area has good electrochemical performance. Moreover, the 40 nm
Ni electrode shows more superior stability, which is possibly because of thinner passivation layer formation and less morphological changes of the positive electrode. Ni/graphene electrode exhibited higher initial capacity and capacity retention compared to the graphene electrode. This is probably due to the better dispersion of Ni nanoparticles on graphene support, large surface-volume ratio and synergetic effect of graphene and Ni.
CHAPTER 4 NANOSTRUCTUED TITANIUM NITRIDE AS A NOVEL ELECTROCATALYST FOR HIGH PERFORMANCE LITHIUM/DISSOLVED POLYSULFIDE BATTERIES

4.1 Introduction

Despite Li-S battery remarkable superiority, there are some intrinsic limitations facing its performance, which was discussed in detail in pervious chapters. In order to overcome these obstacles, many studies have attempted to develop various cathode materials such as functionalized carbon materials, graphene oxides, and conducting polymers with high surface area and porosity [20, 23, 35, 40, 42]. These materials were designed to enhance Li−S cell capacity retention due to their ability to maintain polysulfides by physisorption, or to chemisorb lithium polysulfides because of their hydrophilic nature [23, 66]. Metal oxides, such as TiO₂, Al₂O₃ and SiO₂ as well as metal sulfides, such as TiS₂ and ZrS₂ were also reported to adsorb lithium polysulfides and reduce redox shuttle reactions in Li-S batteries [26, 28, 29, 54, 67]. In addition, Ti₄O₇ has been demonstrated to enhance the redox chemistry and cyclability due to its sulfiphilic surface and good electron conductivity [68].

On the other hand, a dissolved polysulfides configuration has been reported to have high reaction activity and sulfur utilization compared to conventional Li-S batteries [1, 57, 69]. Barchasz et al. demonstrated that the discharge capacity could be increased to up to 1,400 mAh g⁻¹ at a low rate of C/100, using carbon foam and dissolved 0.5 mol L⁻¹ Li₂S₆−Li₂S₈ catholyte. However, its capacity decreases to 1,200 mAh g⁻¹ within 10 cycles [70]. Demir−Cakan et al. showed the capacity performance of Li₂S₅ with a Ketjen Black carbon electrode at C/10 rate. Their results show an almost 1,200 to 500 mAh g⁻¹ capacity, and 500 to 300 mAh g⁻¹ capacity deactivation for 0.3 and 0.1 M Li₂S₅ catholyte concentrations, respectively, within 70 cycles [71]. The low performance of carbon materials is mainly due to their poor adsorption properties.
toward lithium polysulfides. Therefore, in order to take full advantage of dissolved polysulfide Li–S battery, it is important to enhance its capacity retention and cycle lifetime using efficient electrocatalysts. The studies that emerged from the reported works indicate that the battery performances focused mainly on the development of cathode materials. Based on our experiences in improving the battery performances using nanostructured electrodes [30, 69, 72], we investigated transition metal nitrides as a new class of electrocatalysts for Li-S batteries and demonstrated the superior performance in a Li/dissolved polysulfide battery configuration for the first time. Transition metal nitrides are well known materials for supercapacitors and lithium-ion batteries due to their high reversible insertion and extraction of ionic species and the capability of storing lithium by the intercalation mechanism [73-78]. Different types of metal nitride such as TiN [79], VN [80], Mo₂N [81, 82], Zn₃N₂[83], Ni₃N [84], NbN [85], have been demonstrated as efficient electrode materials for lithium-ion batteries and supercapacitors. Among the metal materials, titanium nitride (TiN) has unique properties such as high electrical conductivity (4,000–55,500 S cm⁻¹) [85] and thermodynamic stability and corrosion resistance due to the presence of a triple covalent bond between titanium and nitrogen.

In this work, titanium nitride (TiN) is investigated as a novel electrocatalysts for Li/dissolved polysulfide batteries since it can adsorb lithium polysulfides effectively and transfers electrons in a facile manner. As revealed by X-ray photoelectron spectroscopy (XPS) analysis, sulfur interacts with TiN nanoparticles during the discharge process, and resulted in S-Ti-N, which retains the sulfur species on the electrode surface. The adsorbed higher order polysulfide species undergo reduction to lower order polysulfides by transfer of electrons from the TiN electrode. As a result, the active material and surface area loss were reduced and the capacity and capacity retention of the cell were enhanced. The resultant cells demonstrated a
high initial capacity of 1,524 mAh g\(^{-1}\) and a good capacity retention for 100 cycles at a C/10 current rate.

4.2. Experimental details

4.2.1 Preparation of Titanium nitride

Titanium oxide powder (TiO\(_2\), 10-25 nm size, US Research Nanomaterials) was used as precursor. The powder was first loaded into a zirconia boat and placed in a tubular reactor, which was connected to the gas feed system. Initially, the reactor was purged using 150 mL/min Argon (Ar) gas for 1h; followed by 200 mL min\(^{-1}\) pure NH\(_3\) gas for 30 min to stabilize the gas flow. The reactor was then heated to 250 °C, in 8 h, held for 40 min, then raised to 1000 °C over 3h and maintained for 1h. The furnace cooled down to room temperature followed by flowing 150 mL min\(^{-1}\) Ar gas overnight.

4.2.2 Fabrication of electrodes and cell assembly

The TiN electrode slurry was prepared by adding 10 wt% of Poly (vinylidene fluoride) PVDF, as binder and N-methyl pyrrolidinone (NMP) as solvent to the electrocatalysts (TiN). The slurry was then coated on aluminum (Al) foil (0.1 mm thick) and dried at 80 °C under vacuum for 12h. Elemental sulfur S\(_8\), lithium sulfide Li\(_2\)S, Bis(trifluoromethane)sulfonimide lithium salt LiN(SO\(_2\)CF\(_3\))\(_2\), LiTFSI, triethylene glycol dimethyl ether (TG\(_3\)), were purchased from Aldrich and used as received. Catholyte solutions with 0.2, 0.6, 0.8 M Li\(_2\)S\(_8\), 0.1 M LiTFSI, and 1 M LiNO\(_3\) were prepared by stirring appropriate amounts of S\(_8\) and Li\(_2\)S into TG\(_3\) at 70 °C for 8 h. 10 μL of catholyte solution was added on the positive electrodes with 7 mg cm\(^{-2}\) electrode loading. Coin cells (CR2032) were assembled using polypropylene separator (Celgard 2400) and lithium foil anode inside the Ar-filled glove box.
4.2.3 Characterization and electrochemical measurements

The phase purity of the TiN was characterized using a Rigaku Miniflex 600 X-Ray Diffractometer. TiN electrode morphology was characterized with field emission scanning electron microscopy (JEOL 7600F, FESEM). The specific surface areas of the electrode materials were measured by Braunauer-Emmet-Teller (BET) multimolecular adsorption method (Micromeritics Tristar II surface area/porosimeter). Galvanostatic discharge-charge tests were conducted using a Maccor Model 4200 Automated Test System between the voltage range of 1.5 to 3 V and 1.8 to 3 V (vs. Li/Li⁺) at room temperature. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) measurements were applied using a Gamry potentiostat reference 3000. The voltammetry was performed at a scan rate of 0.05 mV s⁻¹, and a voltage range of 3 to 1.5 V (vs. Li/Li⁺). EIS were recorded between 1 MHz and 0.1 Hz, and AC amplitude of 10 mV at room temperature.

4.3. Results and discussion

4.3.1 Structure and morphology

Nanostructured TiN was prepared by heating titanium oxide (TiO₂) under an ammonia atmosphere. Crystal structure of the prepared TiN analyzed by X-ray diffraction (XRD) (Fig. 4.1a) presents five diffraction peaks of TiN (111), (200), (220), (311) and (222). The positions and intensities of TiN diffraction peaks can be indexed to the face-centered cubic phase structure of TiN (JCPDS file no. 38-1420) with lattice constant a = 0.424 nm (Fig. 4.1b). Crystallite size was calculated to be 16 nm from broadening of the diffraction peak using Scherrer’s equation [86].
Fig 4.1. (a) Powder XRD pattern of TiN, (b) face-centered cubic structure of TiN (blue and red spheres represent Ti and N atoms respectively, (c) SEM image of TiN powder, (d) TEM image of TiN powder, (e) SAED pattern of TiN.

Scanning electron microscopic (SEM) image depicted agglomeration of TiN nanoparticles (Fig. 4.1c). Transmission electron microscopic (TEM) image showed the connectivity between irregular shaped grains, imparting electronic conductivity (Fig. 4.1d). Average particle size was found to be 30 nm from the measurement of about 100 particles found in an arbitrarily chosen area of the enlarged microscopic images. Selected area electron diffraction (SAED) pattern further confirmed the polycrystalline nature of the sample (Fig. 4.1e). The d-spacing from inner to outer can be indexed to the (111), (200), (220), (311) and (222) planes of a cubic phase, which is in a good agreement with the XRD results. The BET surface area of TiN was measured to be 22.1 m² g⁻¹ using BET sorptometry.

4.3.2. Electrochemical performance

The electrochemical performance of the TiN electrode at a 0.1 C rate was examined with an Al foil without TiN coating, and TiN coated Al foil with loadings of (3, 6 and 7 mg cm⁻¹) and
with a 0.2 M Li$_2$S$_8$ catholyte concentration. The results are presented in (Fig. 4.2). It was observed that the aluminum foil without TiN loading revealed almost zero capacity performance. Moreover, the electrode with 3 mg cm$^{-2}$ loading shows lower capacity performance and higher capacity retention compared to the cells with 6 and 7 mg cm$^{-2}$ loadings. Therefore, the cell with 7 mg cm$^{-2}$ TiN loading and with the higher initial capacity was chosen for further capacity retention studies.

In addition, the effect of Li$_2$S$_8$ catholyte concentrations on Li-S battery performance with TiN electrode has been investigated. It is observed that the capacity and cycle performance of the Li-S battery can be influenced by the catholyte concentration. The capacity fade of 52%, 47%, and 33% after 100 cycles was calculated for 0.2, 0.6, and 0.8 M Li$_2$S$_8$ concentrations.
respectively. Although cells with 0.6 and 0.8 M concentrations of Li$_2$S$_8$ revealed more stable performance, their capacities stay lower than the cell with 0.2 M Li$_2$S$_8$ during 100 cycles. This could be due to the high Li$_2$S$_8$ catholyte concentration, which reduces the Li ion diffusion into the TiN electrode and wettability of the electrode surface by the electrolyte. It was also reported that increasing viscosity might lead to higher active material loss as a result of the insoluble lithium polysulfides (Li$_2$S$_2$, and Li$_2$S) formation, which were detected on the surface of TiN electrode [87, 88]. Insoluble lithium polysulfide deposition during cycling can cause capacity fading and lower cyclability, thus, irrespective of different catholyte concentration, similar capacities (around 700 mAh g$^{-1}$) were observed after 100 cycles.

In order to have a better understanding of TiN electrode activity towards the polysulfide conversion reactions, cyclic voltammetry was performed for a cell with a 0.2 M Li$_2$S$_8$ catholyte concentration at a scan rate of 0.05 mV s$^{-1}$ (Fig. 4.3b). The typical sulfur redox reactions with one oxidation and two reduction peaks were observed for all cycles. In general, reduction of Li$_2$S$_8$ to Li$_2$S occurs through a series of intermediate Li$_2$S$_x$ species (2<x<8) at different potentials [1]. The higher voltage cathodic peak corresponds to the reduction of dissolved Li$_2$S$_8$ in the catholyte on the surface of the TiN electrode to soluble higher order lithium polysulfide Li$_2$S$_x$ (4<x<6), and the lower voltage cathodic peak represents the further reduction of polysulfides to insoluble lithium sulfides (Li$_2$S$_2$ and Li$_2$S) [1]. The final region that occurs lower than 1.8 V potential is associated with the deeper reduction of Li$_2$S$_2$ to Li$_2$S, both of which are insoluble in most electrolyte media [1, 23, 69]. Therefore, by limiting the lower voltage to 1.8 V, with less Li$_2$S formation, active material and active surface area loss should be suppressed.
4.3.2.2 Effect of voltage limit

Fig. 4.4a and 4b show the galvanostatic discharge-charge (GDC) profiles of the TiN electrode at 0.1 C rate, with 0.2 M Li$_2$S$_8$ catholyte concentration and voltage limits of 1.5-3.0 V and 1.8-3.0 V, respectively. They both demonstrated two plateaus in the voltage range of 2.45 and 2.0 V (vs. Li/Li$^+$). The higher and lower voltage plateaus correspond to the conversion of...
Li$_2$S$_8$ to higher order (Li$_2$S$_n$ n>4) and lower order lithium polysulfide (Li$_2$S$_n$ n<4), respectively. These two plateaus correspond to 25% and 75% of the practical capacity. By limiting the lower voltage limit to 1.8, a small percent of capacity was confined. However, the overall capacity was enhanced. Fig. 4.4c shows the performance of the cell with a narrow voltage limit of 1.8 to 3.0 V, which exhibits almost 30% higher capacity retention compared to the cell with voltage limit of 1.5 to 3.0 V. The capacity of 726 mAh g$^{-1}$ sulfur after 100 cycles at 0.1 C rate (1.5 to 3.0 V) is comparable to reported capacities for lithium/dissolved polysulfide systems with the same voltage limit, such as capacity of 789 mAh g$^{-1}$ and 600 mAh g$^{-1}$ after 100 cycles for Pt/graphene electrode with 0.2 M Li$_2$S$_8$ catholyte concentration [72], and vertically-aligned carbon nanotubes with 0.3 M Li$_2$S$_6$ concentration [89] respectively. However, with a narrower voltage limit (1.8 to 3.0 V), a higher capacity, 1,040 mAh g$^{-1}$ sulfur after 100 cycles at 0.1 C rate, was observed.
Fig 4.4. Effect of voltage limit on the Li/dissolved polysulfide battery performances at 0.1 C rate: (a) GDC profiles in the voltage limit 1.5-3.0 V, (b) GDC profiles in the voltage limit 1.8-3.0 V, (c) Cycling performances.

AC impedance measurements between the 10th and 100th cycles (Fig. 4.5) also suggest that the charge transfer resistance at the TiN/electrolyte interface increased almost 37 Ω for the voltage limit of 1.5 V; while only a 5 Ω increase was observed for the voltage limit of 1.8 V (Table. 4.1). The increase in resistance can be attributed to the passivation layer formation on the TiN electrode surface, which decreases the conductive surface area of the electrode.
Fig 4.5. Electrochemical impedance spectra (EIS) of the cycled TiN electrodes with cut-off voltages, 1.5 and 1.8 V.

Table 4.2. Charge transfer resistance with cut-off voltages, 1.5 and 1.8 V.

<table>
<thead>
<tr>
<th>Cycle Number and Voltage Limit</th>
<th>Charge Transfer Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>10th Cycle 1.8-0.3 V</td>
<td>4 Ω</td>
</tr>
<tr>
<td>10th Cycle 1.5-0.3 V</td>
<td>12 Ω</td>
</tr>
<tr>
<td>100th Cycle 1.8-0.3 V</td>
<td>9 Ω</td>
</tr>
<tr>
<td>100th Cycle 1.5-0.3 V</td>
<td>49 Ω</td>
</tr>
</tbody>
</table>
Fig 4.6. Effect of voltage limit on the Li/dissolved polysulfide battery performances at 1.0 C rate: (a) GDC profiles in the voltage limit 1.5-3.0 V (b) GDC profiles in the voltage limit 1.8-3.0 V, (c) Cycling performances.

Cycling performance of the cells was also measured at 1.0 C and the results are plotted in Fig. 4.6. Capacity retention of the cells with 1.5-3.0 V and 1.8-3.0 V limits at 1.0 C rate per 100 cycles were measured to be 55% and 83%, respectively. GDC profiles at a 1.0 C rate presented in Fig. 4.6a indicate that insoluble polysulfides (Li$_2$S$_2$ and Li$_2$S) started to form almost at the voltage of 1.5. In contrast, at 0.1 C rate (Fig. 4.4a), significant amount of insoluble polysulfides were formed. Therefore, restricting the lower voltage limit to 1.8 V at the 1.0 C rate did not significantly reduce solid polysulfide formation, however, it reduced the overall capacity.
Fig 4.7. Rate capability at different current rates in the voltage limit 1.8-3.0 V.

In addition, the rate capability of the TiN electrodes was studied at different C rates for two cells with the same configuration (Fig. 4.7). The C rate is based on the theoretical capacity of sulfur (C = 1675 mAh g⁻¹ sulfur). The cells were first subjected to a low 0.1 C rate to obtain stable nominal capacity. Subsequent cycling was performed at higher current rates of 0.2, 0.5, 1.0, and 2.0 C each for 10 cycles. Finally, it was reverted to 0.1 C for 10 additional cycles. Interestingly, TiN electrode capacity retention increases as the C rate increases. The results show a very low rate of capacity fade (~ 1%) at the 2.0 C rate, compared to 6 percent at the 0.1 C rate. Although the specific capacity decreases with increasing cycle numbers, the TiN electrode recovered most of its capacity when the current rate was returned back to 0.1 C.

4.3.3 Morphological changes of the TiN electrocatalysts

Microstructural changes of the TiN electrodes during cycling were ascertained by SEM (4.8a-c). After the first discharge process to 1.8 V, some precipitation was detected on the electrode surface, which formed a thin passivation layer on the TiN surface (Fig. 4.8a and 4.9a). This precipitation appeared to be reduced after the first charging process to 3.0 V (Fig. 4.8b and 4.9b). However, after the 100th charge, besides having more passivation layer formed on the electrode
In order to identify the surface chemical environment of the TiN composites after cycling, X-ray photoelectron spectroscopy (XPS) analysis was conducted on TiN electrodes extracted from cells at the end of the first charged and discharged states. The deconvoluted spectra in the S2p region are presented in Fig. 4.8d-e. When the cell was discharged to 1.8 V, peak binding energies of 160 and 161.2 eV suggested Li$_2$S and Li$_2$S$_2$ were formed, respectively [90-92]. The intensity of the Li$_2$S$_2$ peak is stronger because the voltage limit of 1.8 V prevents further Li$_2$S formation. After the first charge, no Li$_2$S peak was observed, which indicates that Li$_2$S was completely oxidized back to higher order lithium polysulfides. However, there is still some Li$_2$S$_2$ precipitation detected on the TiN electrode surface. Moreover, long chain polysulfides Li$_2$S$_n$ (n\(\geq4\)) were detected at 162.6±0.1 eV [90-92] for both first discharge and charge status, consistent with incomplete redox reactions before the formation of solid electrolyte interlayer (SEI). SEI layer, which has been reported to form mostly during the first cycle on the Li anode, prevents the continuous electron transfer from the Li anode to dissolved polysulfides and suppresses redox shuttle reactions [93].

A strong peak of Li$_2$S in addition to Li$_2$S$_2$ peak was detected on the XPS spectra of the electrode after the 100$^{th}$ charge, which explains the capacity fading of the TiN electrode after 100 cycles. The peaks with the binding energy of 167±0.2 eV, which can be attributed to the -S-O bonding in -SO$_3$ and -SO$_2$ species, can be found in all samples. These species are originated from the electrolyte [91, 94]. In addition to the long chain polysulfides detected in the S2p spectrum of
the first discharge state, an additional sulfur peak was observed at 163.1 eV. This peak, which is sited within the range of Ti-S binding energy, can be attributed to the S-Ti-N bond. To confirm the TiN-Li₂S₈ interaction, 100 mg of TiN was mixed with 5 mL of 0.01 M catholyte solution and stirred (Fig. 4.9). The catholyte color changed from bright yellow-green to colorless within 30 min, which indicates that the polysulfides were adsorbed by TiN powder. The adsorbed higher order polysulfides were reduced by transfer of electrons from the TiN electrode and converted to
the lower order polysulfides ($\text{Li}_2\text{S}_2$ and $\text{Li}_2\text{S}$). In addition, as a result of reversible S-Ti-N binding interactions, the active material loss due to lower order polysulfides precipitation decreases.

**Fig 4.9.** SEM images of the TiN electrode: (a) after first discharge and (b) after first charge

**Fig 4.10.** Visualized adsorption of polysulfide on TiN nanopowder.

Catholyte solutions with 0.01 M $\text{Li}_2\text{S}_8$ were prepared by stirring appropriate amounts of $\text{S}_8$ and $\text{Li}_2\text{S}$ into TG$_3$ at 70 °C for 8 h. Then 0.1 g TiN power was added, mixed and stirred for 30 min.
The mixture was then centrifuged and separated inside the glove box in a different vial. As shown in Fig. 4.10, the first vial on the left, is the yellow-green catholyte solution, the middle vial is the colorless solution that was separated from the TiN powder. Catholyte color changed from bright yellow-green to colorless after half an hour, which indicates that the polysulfides were adsorbed by TiN powder.

4.4. Summary

In summary, we have shown that TiN is a promising electrocatalysts for advanced Li/dissolved polysulfide batteries. We demonstrate that changing the lower voltage limit from 1.5 V to 1.8 V at 0.1 C rate highly enhances the cycling performance of the Li-S battery due to decreasing the insoluble polysulfides formation on the TiN electrode. Furthermore, the existence of S-Ti-N bonding at the electrode surface observed by XPS analysis is indicative of strong interactions between polysulfides and TiN. This could effectively mitigate the insoluble lithium sulfide formation on the TiN electrode surface, which minimizes the active material and surface area loss and improves the capacity retention. The resultant TiN electrocatalyst deliver high capacity of almost 1,040 mAh g\(^{-1}\) sulfur after 100 cycles at 0.1 C rate.
CHAPTER 5 CHARACTERIZATION AND ELECTOCHEMICAL ACTIVITY OF NANOSTRUCTURED TRANSITION METAL NITRIDES FOR HIGH PERFORMANCE LITHIUM SULFUR BATTERIES

5.1 Introduction

Growing demand for EV and electronic devices requires energy storage systems with high energy density. Some drawbacks of conventional Li-ion batteries such as the low energy density, high cost and safety concerns demands for batteries beyond lithium ions. Li-S batteries are one the most promising energy storage systems due to their energy density and theoretical capacity, and low cost. However they suffer from several drawbacks such as: limited active material utilization due to the insulating nature of sulfur and discharge products, high self-discharge rate due to the dissolution of lithium polysulfide (LPS) intermediates in liquid electrolyte and redox shuttle reactions, and high rate of capacity fade attributed to the cathode structural degradation as a result of the volumetric changes that happens during charge and discharge [1, 35].

A wide variety of strategies including development of new electrolytes and additives to electrolytes [95, 96], cathode material development [32, 40, 42], and anode modifications [97, 98], have been explored extensively to address Li-S battery performance limitations. Among these strategies, suppressing polysulfides from dissolution by trapping polysulfides with physisorption or chemisorption are promising approaches for long life Li-S batteries [66, 99]. Metal oxides, metal sulfides, and hydroxide additives, such as TiS$_2$ and ZrS$_2$, have been investigated as polysulfide adsorbents [26, 28, 29, 54, 67]. They have been reported to reduce redox shuttle reactions, and exhibit a better cycle stability and capacity performance. On the other hand, our group investigated titanium nitride (TiN), as a new class of electro catalysts materials and demonstrated its superior performance of 726 mAhr$^{-1}$ after 100 cycles at 0.1 C rate
Thus, we expand our studies to different transition metal nitrides to gain a better understanding of the role of surface composition and morphology in enhancing the electrochemical performance of Li-S batteries.

In this work, Tungsten nitride (WN), Molybdenum Nitride (Mo₂N), and Vanadium Nitride (VN) were synthesized and the electrochemical performance and surface composition of electrodes composed of these metal nitrides were investigated for lithium sulfur batteries. In addition, the mechanism underlying (LPS) conversion reactions of metal nitrides were investigated. The WN electrode exhibited a higher capacity of 697 mAh g⁻¹, compared to 573 and 264 mAh g⁻¹ for VN and Mo₂N, respectively. This capacity which is in the range of the reported capacities for lithium/dissolved polysulfide systems, such as capacity of 789 mAh g⁻¹ and 600 mAh g⁻¹ after 100 cycles for Pt/graphene with 0.2 M Li₂S₈ catholyte concentration [72], and vertically-aligned carbon nanotubes with 0.3 M Li₂S₆ concentration [89], respectively. However, with a higher loading of WN electrode (9.5 and 12.5 g cm⁻²), higher capacities of 980 and 1,283 mAh g⁻¹ sulfur after 100 cycles at 0.1 C rate, were observed. The higher electrochemical performance of the WN electrode may be attributed to a strong reversible reaction between nitrides and polysulfide, which retains the sulfur species on the electrode surface, and minimizes the active material and surface area loss. X-ray photoelectron spectroscopy (XPS) analysis was performed to gain a better understanding of the mechanism underlying polysulfides redox reactions with different metal nitride electrode.
5.2. **Experimental**

5.2.1 Material nitride preparation

5.2.1.1 Tungsten nitride preparation

Ammonium tungstate \(((\text{NH}_4)_10\text{H}(\text{W}_2\text{O}_7)_6, \text{Aldrich, 99.99 \%})\), used as a precursor, was dissolved in 5 M hydrochloric acid solution (HCl Aldrich, 35%) and stirred at 25 °C for 1 h. The solution kept at 120 °C for 2 h, then cooled to room temperature, washed several times with ethanol and distilled water, and then filtered. The obtained yellow tungsten oxide powder was dried at 50 °C in a vacuum oven overnight. In order to produce tungsten nitride structures, it was heated up in a furnace under NH₃ flow to 700 °C over 11 h, held at 700 °C for 3 h and cooled down to room temperature, and subsequently passivated for 2 h in flowing Ar gas overnight.

5.2.1.2 Molybdenum nitride preparation

Ammonium molybdate tetrahydrate (Sigma Aldrich) was dissolved in 5 M HNO₃ (Sigma Aldrich) and stirred at room temperature for 1 h, following by a reaction in an autoclave at 160 °C for 3 h. The resulting molybdenum oxide was washed with water and ethanol and then dried at 80 °C in a vacuum oven overnight. Subsequently, it was heated up in a furnace under NH₃ flow to 700 °C over 12 h, maintained at 700 °C for 1 h and cooled down to room temperature, followed by flowing Ar gas overnight.

5.2.1.3 Vanadium nitride preparation

1.7 g ammonium metavanadate (NH₄VO₃ Sigma Aldrich), and 1.82 g oxalic acid dihydrate (C₂H₂O₄·2H₂O Alpha Aesar) were dissolved in 60 mL distilled water at room temperature with constant stirring for 12 h. The solution was then heated in an autoclave at 180 °C for 24 h. After centrifuging and washing several times with distilled water, the resulting
product was dried at 80°C in a vacuum oven overnight. The dried material was then heated to 800 °C under NH₃ flow and maintained at 800 °C for one hour.

5.2.2. Fabrication of electrodes and cell assembly

The electrode slurry was prepared by adding 10 wt% of Poly (vinylidene fluoride) PVDF, as binder and N-methyl pyrrolidinone (NMP) as solvent to the electrocatalyst materials (WN, VN, and Mo₂N). The slurry was coated on Al foil and dried at 80 °C under vacuum for 12 h.

Elemental sulfur S₈, lithium sulfide Li₂S, Bis(trifluoromethane)sulfonimide lithium salt LiN(SO₂CF₃)₂, LiTFSI, Triethylene glycol dimethyl ether (TG₃), were purchased from Aldrich and used as received. Catholyte solutions with 0.2 M Li₂S₈, 0.1 M LiTFSI, and 1 M LiNO₃ were prepared by stirring appropriate amounts of S₈ and Li₂S into TG₃ at 80 °C overnight. 8 μL of catholyte solution was added on the positive electrodes. Coin cells (CR2031) were assembled inside an Ar filled glove box, using a polypropylene separator (Celgard 2400), and lithium foil anode.

5.2.3. Characterization and electrochemical measurements

Phase purity of the positive electrode materials was characterized using a Rigaku Miniflex 600 X-Ray Diffractometer. Metal nitrides electrodes material morphology was observed with field emission scanning electron microscopy (JEOL 7600F, FESEM). The average particle size was calculated using about 100 particles found in an arbitrarily chosen area of the enlarged microscopic images. The specific surface areas of the electrode materials were measured by Braunauer-Emmet-Teller (BET) multimolecular adsorption method (Micromeritics Tristar II surface area/porosimeter). Galvanostatic discharge-charge tests were conducted using a Maccor Model 4200 Automated Test System between the voltage range of 1.5 to 3 V (vs. Li/Li⁺) at room temperature. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS)
measurements were made using a Gamry potentiostat reference 3000. The voltammogram was performed at a scan rate of 0.05 mV s\(^{-1}\), and voltage range of 3 to 1.5 V (vs. Li/Li\(^+\)). EIS were recorded between 1MHz and 0.1 Hz, and AC amplitude of 10 mV at room temperature.

5.3 Results and discussion

5.3.1 Structural characterization

5.3.1.1 Tungsten nitride

Morphology and structure of the prepared WN was analyzed using SEM (Fig. 5.1a), TEM (Fig. 5.1d), and XRD (Fig. 5.1g). The WN material exhibited a fairly uniform nano-plate structure with regular mesoporous. The average size and thickness of nano-plates was measured to be 290 and 23 nm, respectively. The XRD of the WN sample indicates a face-centered cubic (fcc) structure having diffraction peaks at 2\(\theta\) values of 37.6°, 43.8°, 63.7°, 76.4° and 80.5° corresponding to the (111), (200), (220), (311), and (222) planes, respectively (JCPDS # 75-1012). The d-spacing from inner to outer can be indexed to the same planes of VN cubic phase, which is in a good agreement with the XRD results (Fig.5.1g). The calculated crystal size according to the Scherrer equation is 73.8 Å. The BET surface area of WN was measured to be 16.7 m\(^2\) g\(^{-1}\) using BET sorptometry.

5.3.1.2 Vanadium nitride

The prepared VN exhibited pea shape nanoparticles, with the average particle diameter and length of 47 and 85 nm, respectively (Fig. 5.1b, 1e). X-ray diffraction spectroscopy (XRD) pattern of the as-prepared VN materials (Fig. 5.1h) shows diffraction peaks of 37.5°, 43.7°, 63.5°, 76.0°, and 80.0°. These peaks can be ascribed to the (111), (200), (220), (311), and (222) crystal planes with an fcc structure (JCPDS # 73-2038). The average crystallite sizes using Scherrer equation was determined to be 81.97 Å. The BET surface area of WN was measured to be 13.3
m² g⁻¹ using BET sorptometry.

5.3.1.3 Molybdenum nitride

Fig. 5.1c and 1f show the SEM and TEM images of the fairly uniform mesoporous nano rod shaped porous Mo₂N, respectively. The average particle diameter and length of nano-rod was calculated to be 850 and 75 nm, respectively. In the XRD pattern of the as-synthesized sample, the diffraction peaks of Mo₂N (JCPDS # 25-1366) at 2θ values of 37.4°, 43.4°, 63.1°, 75.7°, and 79.2° corresponds to a fcc Mo₂N structure with (111), (200), (220), (311), and (222) planes, respectively (Fig. 5.1i). The average crystallite sizes using Scherrer equation was determined to be 112.5 Å. BET surface area of WN was measured to be 10.2 m² g⁻¹ using BET sorptometry.

Fig 5.1. SEM image of (a) WN, (b) VN, (c) Mo₂N. TEM images and SAED patterns of (d) WN, (e) VN, (f) Mo₂N. Powder XRD pattern of (g) WN, (h) VN, (i) Mo₂N.

Although all materials show face centered cubic structure, they have varied size, shape, and surface area. WN has the smallest thickness and crystalline size. Moreover, WN and Mo₂N
have a porous structure surface, while VN has a quite smooth surface. In addition, the BET surface area of WN is higher than VN and Mo₂N.

5.3.2. Electrochemical performance

In order to have a better understanding of nitride electrodes activity towards the polysulfide conversion reactions, cyclic voltammetry was performed for cells with a 0.2 M Li₂S₈ catholyte concentration, at a scan rate of 0.05 mV s⁻¹ (Fig. 5.2). In general, reduction of Li₂S₈ to Li₂S occurs through a series of intermediate Li₂Sₓ species (2<x<8) at different potentials [1]. The higher voltage cathodic peak corresponds to the reduction of dissolved Li₂S₈ on the surface of the electrode to soluble higher order LPS Li₂Sₓ (4<x<6), and the lower voltage cathodic peak represents the further reduction of LPS to insoluble lithium sulfides (Li₂S₂ and Li₂S) [1].

The typical sulfur redox reactions with one oxidation and two reduction peaks were observed for cells with WN and VN electrodes. However, the cell with a Mo₂N electrocatalyst revealed much broader redox peaks compared to the other nitrides, which suggests a slower redox behavior toward lithium sulfide redox shuttle reactions. This could be due to the lower Mo₂N surface area and a morphology that causes higher polarization on the electrode surface. Furthermore, under the same experimental conditions, the current density of the cell with the WN electrode is clearly higher than VN and much higher than Mo₂N. According to the Randles-Sevcik equation: 

\[ i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2} \]

where \( i_p \) is the peak current, \( n \) is electron stoichiometry, \( A \) is electrode area, \( D \) is diffusion coefficient, \( C \) is concentration, and \( v \) is scan rate, this maybe attributed to the higher diffusion coefficient of Li ion in WN electrode which can be due to WN porous surface structure and higher surface area.

Another noticeable point that was observed is the potential difference between anodic and cathodic peaks of VN, which increases by cycling and Mo₂N, which is almost stable after the fist
cycle (unlike WN, that decreases). This potential increase, which is due to the higher polarization on the electrode surface is associated with the LPS accumulation on the VN and Mo$_2$N electrodes. Thus, redox reactions are less inclined to occur on the surface of these two electrodes. In general, the CV results demonstrated a better reversibility and lower polarization for the cell with the WN electrode.

**Fig 5.2.** Cyclic voltammograms at 0.05 mV s$^{-1}$ recorded for (a) WN, (b) VN, (c) Mo$_2$N.

Fig. 5.3. depicts the galvanostatic discharge-charge (GDC) profiles of the different electrodes at a 0.1 C rate, with 0.2 M Li$_2$S$_8$ catholyte concentration. They all demonstrated two reduction plateaus (conversion of Li$_2$S$_8$ to higher and lower order LPS). In the case of WN, both plateaus started to form at lower voltages (2.43 and 1.96 V), which is in very good agreement with the CV results. The VN catalyst demonstrated two plateaus at around 2.2 and 1.7 V respectively. The Mo$_2$N electrode barely shows any plateaus after the 10$^{th}$ Cycle.
**Fig 5.3.** GDC profiles in the voltage limit 1.5-3.0 V for (a) WN, (b) VN, (c) Mo$_2$N.

It appears that the capacity and cycle performance of the Li-S battery can be influenced by the type of nitride electrode (Fig. 5.4.a). A high initial capacity of 1,768 was observed for the WN electrode with a 8 mg cm$^{-2}$ electrode loading. This could be due to the high surface area of WN electrode and reversible insertion and extraction of ionic species. However, it was deactivated to 700 mAh g$^{-1}$ sulfur within 100 cycles. The Mo$_2$N and VN electrocatalysts also revealed initial capacities of 1,001 and 1,068 mAh g$^{-1}$ for the same loading of 8 mg cm$^{-2}$, which dropped to 573 and 264 mAh g$^{-1}$ after 100 cycles, respectively. Therefore, in order to get a better understanding of capacity fading, all metal nitride electrodes were separated from the coin cell and washed thoroughly with TG$_3$ solvent several times and subjected to SEM analysis. Fig. 5.4b-h. presents the SEM image of the nitride electrodes surface after 100 charges. A passivation layer, which is reported to mainly consist of insoluble LPS (Li$_2$S and Li$_2$S$_2$), can be observed for all electrodes. This layer appears to cover a few sections of WN and Mo$_2$N, and almost the majority
of the VN electrode surface. In addition, the WN electrode particle size is bigger as a result of particle agglomeration or WN morphological change due to redox reactions. In general, three major reasons appear to influence metal nitride capacity fade. First, an increase in internal resistance on the electrocatalyst surface due to the non-conductive nature of Li$_2$S and Li$_2$S$_2$ which reduces the Li ion diffusion into the nitride electrode. Second, surface area loss due to particle agglomeration, size change, and passivation layer formation; third, active material loss due to the quasi-reversible nature of polysulfide conversion reaction, which was shown by the existence of Li$_2$S and Li$_2$S$_2$ at the charge state.

![Chart and images](image_url)

**Fig 5.4.** (a) Cycling performance at 0.1 C rate, and SEM images of electrodes before cycling, (b) WN, (e) VN, (g) Mo$_2$N, and after cycling (c) WN, (f) VN, (h) Mo$_2$N.

Fig. 5.5a, shows the rate capability and coulombic efficiency of WN, VN, and Mo$_2$N electrodes at different C rates, and their efficiency. The C rate is based on the theoretical capacity of sulfur (C = 1,675 mAh g$^{-1}$ sulfur). The cells were first subjected to a low 0.1 C rate to obtain stable nominal capacity. Subsequent cycling was performed at higher current rates of 0.2,
0.5, and 1.0 C each for 5 cycles. Finally, it was reverted to 0.1 C for 6 additional cycles. Interestingly, metal nitrides capacity retention increases as the C rate increases. The results reveal the higher capacity performance for WN electrode for all rates. The WN, Mo$_2$N, and VN electrocatalysts revealed a capacity of 665, 347, and 145 mAh g$^{-1}$ at 1.0 C rate respectively. The specific capacity decreases with increasing cycle numbers. However, the electrode recovered most of its capacity when the current rate was returned back to 0.1 C. Although, changing the C rate affects coulombic efficiency for a cycle, it remains constant at almost 98% for the rest of cycles and different C rates.

![Graphs](image)

**Fig 5.5.** (a) Rate capability and coulombic efficiency of metal nitrides at different C rates, (b) capacity performance of WN electrocatalysts with different loadings.

The effect of electrocatalyst material loading on battery performance was studied for WN electrode (Fig. 5.5b). Electrode loadings of 8, 9.5, 12.5 mg cm$^{-2}$ were prepared and the capacity performance and cyclability of Li-S cells were examined with 8 $\mu$l of 0.2 M Li$_2$S$_8$ at 0.1 C rate. The cell with lower loading (8 mg cm$^{-2}$) presented lower capacity performance and lower capacity deactivation compared to the cells with 9.5 and 12.5 mg cm$^{-2}$ loadings. However, cells with 9.5 and 12.5 mg cm$^{-2}$ loadings revealed very high initial capacities of 3,907 and 4,355 mAh g$^{-1}$ sulfur, which deactivated to 980 and 1,283 mAh g$^{-1}$ sulfur after 100 cycles,
respectively. In order to investigate any possible reactions between electrolyte material and WN that may result to such a high capacity, WN cells with different loadings and electrolyte solution were prepared and examined at 0.1 C rate. The results show the capacity is affected by WN loadings (Fig. 5.6). In addition, the cell with catholyte solution presents both lower and higher voltage plateaus during discharge profile, indicating the reduction reaction of \( \text{Li}_2\text{S}_8 \) to lower order polysulfides, and one oxidation plateau associated with oxidation of lower order polysulfide to sulfur (Fig. 5.7a). However, the cell with electrolyte solution doesn’t show any plateaus, which indicate any redox reaction (Fig. 5.7b). The high capacity of WN could be as a result of high reversible insertion and extraction of ionic species.

**Fig 5.6.** Capacity performance of WN electrode with different loadings and electrolyte solution.
In order to obtain a better understanding of the underlying mechanism of lithium sulfide redox reactions, surface chemical environment of the electrodes was investigated by X-ray photoelectron spectroscopy (XPS). XPS was conducted on electrodes extracted from cells after first charged and discharged state and the deconvoluted spectra in the S2p region are presented in Fig. 5.8a-c.

Peak binding energies of 160.5 and 161.75 eV suggested Li$_2$S and Li$_2$S$_2$ were formed both in charge and discharge status of all electrodes [100, 101]. However, the presence of these peaks in charged state indicates poor reversibility of LPS redox reactions [72]. The higher intensity for the Li$_2$S and Li$_2$S$_2$ peaks of VN and Mo$_2$N suggests their lower reversibility compared to the WN electrodes. It is also in very good agreement with the detected passivation layer (Fig. 5.4f). Furthermore, the presence of Li$_2$S$_n$ (n≥4) at 162.7±0.1 eV [90-92] at discharge status of VN and Mo$_2$N electrodes is consistent with incomplete redox reactions of these two electrodes, which was suggested earlier by cyclic voltammetry results (Fig. 5.2).

Interestingly, in addition to the long chain polysulfides detected in the S2p spectrum of WN, a strong peak was detected at 163.5 eV of the discharged state. This peak, which was not
detected in VN and Mo₂N S2p spectrum, is sited within the range of W-S binding energy [102, 103], and can be attributed to the S-W-N bond. The existence of S-W-N upon discharge, which converts back to WN during charge, suggests the ability of WN to trapped polysulfides during discharge. This minimizes the active material and surface area loss, which happen due to insoluble LPS precipitation. The peaks with the binding energy of 167±0.2 eV were found in all samples, and can be attributed to the -S-O bonding in -SO₃ and -SO₂ species. These species are originated from the electrolyte [91, 94].

![Image](image.png)

**Fig 5.8.** Post-mortem analysis of the electrodes in charge and discharge states: deconvoluted XPS S2p spectra of the (a) WN, (b) VN, (c) Mo₂N. Original and fitted XPS data are represented with gray and orange lines respectively.

### 5.5 Summary

In summary, we prepared different transition metal nitrides (WN, VN, and Mo₂N) as electrocatalyst for the lithium sulfur battery. We also investigate the mechanisms underlying these metal nitrides polysulfide conversion reactions using XPS analysis. Among these materials, WN demonstrated the most promising cycling performance and a high capacity of 700 mAh g⁻¹ after 100 cycles. By increasing the WN loading to 9.5 and 12.5 mg m⁻² an improved capacity of 980 and 1,283 after 100 cycles were observed. The superior performance of WN could be due
the existence of S-W-N bonding at electrode surface, which indicates a strong interaction
between LPS and WN. This could effectively alleviate the insoluble LPS formation on WN
electrode surface, active material and surface area loss, and improve the overall performance of
the battery cell. This result is comparable with our previous study on using a TiN electrocatalyst
with 16 nm spherical shape nanoparticles and a face centered cubic face structure. TiN revealed a
high capacity of 726 mAh g\(^{-1}\) for 7 mg cm\(^{2}\) TiN loading after 100 cycles. Although these results
indicate that WN is a highly promising candidate for high performance Li-S batteries, other
structural modification could be made to further improve its cycling stability.
CHAPTER 6 VERTICALLY AlIGNED TITANIUM NITRIDE NANOTUBE AS ELECTROCATALYST FOR HIGH PERFORMANCE DISSOLVED POLYSULFIDE BATTERY

6.1. Introduction

In this study, TiO\textsubscript{2} nanotube were prepared using two steps anodization method on Titanium foil followed by a nitridation process in an ammonia atmosphere. The vertically aligned TiN nanotubes were investigated as a electocatalyst for dissolved polysulfide Li-S battery. The result shows the TiN nanotubes on metallic Titanium foil substrate exhibits a higher cycling stability. Therefore, a series of TiN nanotubes with average diameter size of 17, 45, and 83 nm have been used as a electrocatalysts, and the effect of nanotube size on Li-S battery performance has been investigated.

TiN nanoparticles was investigated as a new class of electocatalyst and demonstrated its superior performance of 726 mAh g\textsuperscript{-1} after 100 cycles at 0.1 C rate [104]. In addition, different transition metal nitrides were studied to gain a better understanding of the role of surface composition and morphology in enhancing the electrochemical performance of Li-S batteries. WN, Mo\textsubscript{2}N, and VN were synthesized and the electrochemical performance and surface composition of these electrodes composed of these metal nitrides were investigated for lithium sulfur batteries. The WN electocatalyst exhibited a higher capacity of 697 mAh g\textsuperscript{-1}, compared to 573 and 264 mAh g\textsuperscript{-1} for VN and Mo\textsubscript{2}N, respectively. Although these metal nitrides were shown a superior initial capacity, their capacity was deactivated very fast. The main reasons of capacity fade are morphological changes of metal nitride electrode and surface area loss as a result of volumetric changes and insoluble polysulfide precipitation, respectively. Here, it was tried to improve the capacity retention of Li-S cell by synthesizing a conductive electrode structure,
which can buffer tensions of volumetric expansion and reduces the surface area loss and insoluble polysulfide precipitations.

6.2 Experimental

6.2.1 Preparation of Titanium nitride nanotubes

A two electrodes electrochemical cell was used to prepare highly order TiO$_2$ nanotubes by a two steps anodization method. This set up has a Ti working electrode and Pt counter electrode. In order to obtain TiO$_2$ nanotubes with 17, 45, and 83 nm diameters, Ti foil (99.6 % purity, 1.0 mm thickness, GoodFellow) were anodized under 20, 30, 60 V, in an ethylene glycol (99.8% anhydrous, Sigma-Aldrich) solution containing 0.5 wt% NH$_4$F and 2 vol% deionized water. Subsequently, the TiO$_2$ aggregated layer was peeled off using ultrasonication for 1 min. Then, the second anodization step was started with the same solution and under the same voltages [70, 105]. The resultant TiO$_2$ nanotubes and Ti substrate were calcinated under ammonia in a tubular furnace to 250 °C, in 8 h, held for 40 min, then raised to 1000 °C, in 3 h and maintained for 1h. The furnace cooled down to room temperature followed by flowing 150 mL min$^{-1}$ Ar gas overnight.

6.2.2 Preparation of dissolved polysulfide and cell assembly

Elemental sulfur S$_8$, lithium sulfide Li$_2$S, Bis(trifluoromethane)sulfonimide lithium salt LiN(SO$_2$CF$_3$)$_2$, LiTFSI, Triethylene glycol dimethyl ether (TG$_3$), were purchased from Aldrich and used as received. A catholyte solution with 0.2 M Li$_2$S$_8$, 1 M LiTFSI, and 1 M LiNO$_3$ was prepared by stirring appropriate amounts of S$_8$ and Li$_2$S into TG$_3$ at 80 °C for 6 h. 8 μL of 0.2 M Li$_2$S$_8$ catholyte solution containing 0.41 mg sulfur was added onto TiN positive electrodes. In addition, a Polypropylene separator (Celgard 3501), and lithium foil anode were used to assemble coin cells (CR2032) inside an argon filled glove box.
6.2.3 Characterization and electrochemical measurements

Phase purity of the positive electrode materials was characterized using a Rigaku Miniflex 600 X-Ray Diffractometer. Morphological features of the TiN nanotubes electrode before and after cycling were observed with field emission scanning electron microscopy (JEOL 7600F, FESEM). Galvanostatic discharge-charge tests were conducted using a Maccor Model 4200 Automated Test System between the voltage range of 1.5 to 3 V (vs. Li/Li⁺) at room temperature. Cyclic voltammetry experiments were performed using a Gamry potentiostat reference 3000 at 0.1 mV s⁻¹ in the voltage range of 3 to 1.5 V (vs. Li/Li⁺).

6.3 Results and discussion

6.3.1. Structure and morphology

SEM images of the electrodes were recorded at high magnification and show the uniform distribution of the vertically aligned 17 nm diameter TiO₂ nanotubes (Fig. 6.1a-b). Fig. 6.2 presents TiN nanotube with 17 nm diameter. As shown in Fig. 6.1c and 6.2d, the obtained TiN retains its vertically aligned morphology of nanotube with clear open tips. The TiN nanotubes show a scraggly surface as a result of the lattice shrinkage, which happens during the structure transformation from TiO₂ to TiN.

Crystal structure of the prepared TiN analyzed by X-ray diffraction (XRD) (Fig. 6.2) presents five diffraction peaks of TiN (111), (200), (220), (311) and (222). The positions and intensities of TiN diffraction peaks can be indexed to the face-centered cubic phase structure of TiN (JCPDS file no. 38-1420). The XRD results presents that TiO₂ nanotube are completely transformed into TiN.
Fig 6.1. Cross sectional SEM image of (a) TiO$_2$, (c) TiN, Top view SEM image of (b) TiO$_2$, (d) TiN.

Fig 6.2. Powder XRD pattern of 83 nm TiN nanotube.
6.3.2 Electrochemical performance

In order to have a better understanding of TiN nanotubes electrode activity towards the polysulfide conversion reactions, cyclic voltammetry was performed on TiN nanotubes with 17 nm diameter size, 3 μm length, and a 0.2 M Li$_2$S$_8$ catholyte concentration, at a scan rate of 0.1 mV s$^{-1}$ (Fig. 6.4). The typical sulfur redox reactions with one oxidation and two reduction peaks were. In general, reduction of Li$_2$S$_8$ to Li$_2$S occurs through a series of intermediate Li$_2$S$_x$ species (2<x<8) at different potentials [1]. The higher voltage cathodic peak corresponds to the reduction of dissolved Li$_2$S$_8$ on the surface of the TiN nanotube to soluble higher order LPS Li$_2$S$_x$ (4<x<6), and the lower voltage cathodic peak represents the further reduction of LPS to insoluble lithium sulfides (Li$_2$S$_2$ and Li$_2$S) [1].

![Cyclic voltammograms recorded for 17 nm TiN nanotube with 0.2 M Li$_2$S$_8$ catholyte concentration, at a scan rate of 0.1 mV s$^{-1}$.](image)

**Fig 6.3.** Cyclic voltammograms recorded for 17 nm TiN nanotube with 0.2 M Li$_2$S$_8$ catholyte concentration, at a scan rate of 0.1 mV s$^{-1}$. 
In order to investigate the effect of TiN nanotube size on capacity performance and cycling stability of Li-S battery, different TiN electrodes with 17, 45, and 84 diameter sizes were prepared on Ti foil with 3.5 μm length (Fig.6.4). It is known that one of the factors determining electrocatalytic activity is the accessible surface area [60]. Therefore, after 100 cycles, the 17 nm diameter TiN nanotube electrode with higher surface area displays a higher discharge capacity of 270 mAh g\(^{-1}\) sulfur, contrasting with the 155 and 135 mAh g\(^{-1}\) sulfur discharge capacity of the 45 nm and 84 nm electrodes, respectively (Fig.6.5). Although the discharge capacity is appeared to be very stable at the end, they have a very low value as a result of their lower loading (almost 1mg cm\(^{-2}\)) compared to reported capacities.

**Fig 6.4.** Cross sectional SEM image of TiN nanotubes with diameter size of (a) 17 nm, (b) 45 nm, (c) 83 nm. Top view SEM image of TiN nanotubes with diameter size of: (d) 17 nm, (e) 45 nm, (f) 83 nm.
Fig 6.5. Cycling performance of Li-S cell with TiN nanotube grown on Ti foil with different diameters.

TiN nanotube with higher length can potentially have higher capacity performance and cycling stability as a result of their high surface area, which facilitates the sulfur utilization, and

Fig 6.6. Images of TiN with 83 nm diameter and different lengths: (a) TiO$_2$ 3 $\mu$m, (b) TiO$_2$ 8 $\mu$m, (c) TiN (3 $\mu$m left, 8 $\mu$m right).

TiN nanotube with higher length can potentially have higher capacity performance and cycling stability as a result of their high surface area, which facilitates the sulfur utilization, and
the ability of TiN nanotube to buffer the stress during volumetric expansion, respectively. Therefore, it was tried to grow a higher length of 17 nm diameter TiO$_2$ nanotubes by increasing the anodization time. However, TiN nanotube for over 5 μm nanotube length were peeled off from the Ti substrate, after the heat treatment process (Fig.6.6). In order to study the capacity performance of the prepared TiN nanotube with 8, 11, and 15 μm length, they were coated on Al foil. The capacity of TiN nanotube with 8 μm length is slightly higher than 11 and 15 μm (Fig 6.7). This could be due to the more difficult penetration of sulfur active material into the longer nanotubes, which reduce the active surface area. Although the initial capacity for all lengths is very high, the capacity performance of TiN coated Al foil was experienced a very high deactivation rate. This could be due to nonhomogeneity of coated TiN compared to vertically aligned nanotube structure on Ti foil and pulverize the nanotube structure.

![Fig 6.7. Cycling performance of Li-S cell with TiN nanotube coated on Al foil with different nanotube lengths.](image)
6.4 Summary

Vertically aligned TiN nanotube electrodes with different nanotube diameters and lengths were prepared. The effect of nanotube diameter size and length on discharge capacity and cycling stability of Li-S battery was studied. 17 μm nanotubes grown on Ti foil is shown to have a higher capacity performance as a result of higher active surface area and a good cycling stability. However, after coating TiN nanotube with different lengths on Al foil, capacity performance experienced high initial capacity along with a high deactivation rate. This could be due to non organized structure of coated TiN nanotubes and also longer length of nanotubes, which reduces catholyte penetration into tube structure. Although these results indicate that TiN nanotube is a highly promising candidate for high performance Li-S batteries, other structural modification could be made to further improve its cycling stability.
CHAPTER 7 CONCLUSION AND FUTURE WORK

7.1 Conclusion

The effects of Ni particle size and graphene support on the lithium polysulfide conversion reactions and Li-S battery performance have been studied. The results indicate the higher capacity performance of the 20 nm Ni electrode with higher surface area than 40 and 100 nm Ni nanoparticles. In addition, the 40 nm Ni electrode shows much higher cycling stability, which is possibly due to thinner passivation layer formation and less morphological changes of the positive electrode. As a result of the better dispersion of Ni nanoparticles on graphene support, large surface-volume ratio and synergetic effect of graphene and Ni, Ni/graphene electrode exhibited higher initial capacity and capacity retention than the graphene electrode.

TiN was introduced as a promising electocatalyst material for advanced Li/dissolved polysulfide batteries. Cycling stability of TiN electrode was enhanced by modification of the lower voltage limit from 1.5 V to 1.8 V at 0.1 C. Thus it decreases the insoluble polysulfides formation on the electrode. Furthermore, the existence of S-Ti-N bonding at the electrode surface observed by XPS analysis is indicative of strong interactions between polysulfides and TiN. This could effectively mitigate the insoluble lithium sulfide formation on the electrode surface, which minimizes the active material and surface area loss and improves the capacity retention. The resultant cells deliver high capacity of almost 1,040 mAh g\(^{-1}\) sulfur after 100 cycles at 0.1 C rate.

Different transition metal nitrides (WN, VN, and Mo\(_2\)N) was synthesized and used as electrocatalysts for lithium sulfur battery. The mechanisms underlying these metal nitrides polysulfide redox reactions were investigated using XPS analysis. Among these materials, WN demonstrated the most promising cycling performance and a high capacity of 700 mAh g\(^{-1}\) for 7 mg m\(^{-2}\) WN loading and after 100 cycles. By increasing the WN loading to 9.5 and 12.5
mg m$^2$ an improved capacity of 980 and 1,283 after 100 cycles were observed. The superior performance of WN could be due the existence of S-W-N bonding at electrode surface, which indicates a strong interaction between LPS and WN. This could effectively alleviate the insoluble LPS formation on WN surface, active material and surface area loss, and improve the overall performance of the battery cell. Although these results indicate that WN is a highly promising candidate for high performance Li-S batteries, other structural modification could be made to further improve its cycling stability.

7.2 Future work

The volume expansion of the cathode electrodes (almost 79%) can fracture the conductive structure and increase the polarization within the cell, which results in lower performance stability and rapid capacity deactivation. Pore size and structure of the conductive matrix can buffer the volume expansion. It has been demonstrated that electrocatalysts such as Pt, Au, and Ni enhance the electrochemical performance of Li-S battery. However, there is not any research investigating the effect of pore size and structure of these electrocatalysts on Li-S battery performance. New research in this direction on different electrocatalysts with different structure and pore sizes could provide researchers with a deep understanding, which helps them to design a conductive electrocatalyst structure that improve the cycling stability of the battery cell.

Metal nitrides such as TiN and WN have been shown to enhance the capacity retention of Li-S battery due to their ability of making a bond with polysulfide species. For higher loading of some of metal nitrides, such as WN, it was shown that capacity increases to over theoretical capacity. This could be due to some unknown reaction between electrolyte and metal nitride or due to ion transfer during charge/discharge process. Different electrochemical and
characterization technique should be executed to investigate these possibilities. In addition, different electrolyte composition should be studied to investigate the stability of electrolyte with metal nitrides within the selected voltage limit.

On the other hand, metal nitrides shown a high initial capacity. However they have a very high deactivation rate. Therefore, TiN nanotubes electrode with a higher surface area and ability to buffer the stress has been developed. In addition, it was shown that the higher length nanotubes exhibit less capacity due to more difficult catholyte penetration into nanotubes. However, preparation of longer length of TiN nanotube was not very successful due to separation of nanotube from Ti substrate. One of the approaches that can potentially enhance capacity performance is preparing a higher loading of TiN nanotube, which are aligned and attached to the conductive current collector substrate. This can be done by investigating different synthesize method or by optimizing the anodization method parameters. The other approach could be investigating the effect of catholyte compositions and concentration, that increase sulfur utilization and capacity of Li-S batteries. This could be done by studying different type of electrolyte solution with higher ionic conductivity toward Li ions, and lower viscosity, which could potentially increase the dissolved polysulfides penetration into conductive electrode structure, and enhance the Li ion diffusion consequently.

Finally, the issues regard to lithium anode should be studied. Li anode can be corroded by parasitic reactions of Lithium surface dissolved PS. It also can react with organic electrolyte solvents, which consumes lithium. They also form a passivation layer on the Li anode surface with a lower ionic and electronic conductivity, which increases the charge transfer resistance of the anode electrode. By applying an artificial layer on Li anode, which is ionically conductive as well, any parasitic reaction including redox shuttle reactions decreases. Although coating this
layer on Li will enhance Li-S battery performance, investigating this topic is very difficult due to high reactivity of Li. Future research should focus on Li anode protection or potential replacement.
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ABSTRACT

NANO-STRUCTURED ELECTROCATALYSTS FOR HIGH PERFORMANCE LITHIUM SULFUR BATTERIES

by

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Ni nanoparticles has been investigated as a carbon-free cathode material for dissolved polysulfide Li-S battery. A series of Ni nanoparticles with nominal particle size of 20, 40, and 100 nm have been used as electrocatalysts, and the effect of particle size on Li-S battery performance has been investigated. In addition, graphene has been chosen as a support to anchor the Ni nanoparticles, and the synergetic effect of carbon material and Ni nanoparticles on Li-S battery electrochemical performance has been studied. The results indicated there is a strong particle size effect. Ni/graphene electrode exhibits a capacity of 753 mAh g\(^{-1}\) sulfur after 40 cycles due to its high conductivity and electrocatalytic activity toward polysulfide reduction reaction. This capacity is significantly higher than similar studies.

Based on the understanding of the electrocatalytic effect of Ni and capacity fading mechanism, transition metal nitrides has been investigated as a new class of cathode materials. Titanium nitride (TiN) nanoparticle was studied as a novel cathode material for Li/dissolved polysulfide batteries. In addition, X-ray photoelectron spectroscopy (XPS) analysis was used to obtain a deeper understanding of the mechanism underlying polysulfide conversion reactions with TiN cathode, and during charge and discharge processes. TiN exhibited a superior
performance in a Li/dissolved polysulfide battery configuration.

Knowing the superior performance of TiN, the study was expanded to different transition metal nitrides to investigate the role of surface composition and morphology in enhancing the electrochemical performance of Li-S batteries. WN, Mo$_2$N, and VN were synthesized and the electrochemical performance, surface composition, and oxidation/reduction mechanism of these cathodes electrodes were studied for lithium sulfur batteries.

Understanding the fading mechanisms of dissolved polysulfide system for metal nitride cathodes, it was tried to enhance Li-S battery cycling stability. The effect of TiN nanotube size and length on cyclability of Li-S battery has been studied. A series of TiN nanotube with the average nanotube size of 20, 50, and 80 nm were growth and synthesized on Ti foil using anodization method. The electrochemical performance and capacity retention of these nanotubes with different length were studied.
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