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Electrochemical Performance of Titanium Disulfide and Molybdenum Disulfide Nanoplatelets

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Electrochemical Performance of Titanium Disulfide and Molybdenum Disulfide Nanoplatelets

A thesis submitted in partial satisfaction of the requirements of the degree Master of Science in Materials Science and Engineering

by

Andrew Francisco Siordia

2016
ABSTRACT OF THESIS

Electrochemical Performance of Titanium Disulfide and Molybdenum Disulfide Nanoplatelets

by

Andrew Francisco Siordia

Master of Science in Materials Science and Engineering
University of California, Los Angeles, 2016
Professor Bruce S. Dunn, Chair

Single layer crystalline materials, often termed two-dimension (2D) materials, have quickly become a popular topic of research interest due to their extraordinary properties. The intrinsic electrical, mechanical, and optical properties of graphene were found to be remarkably distinct from graphite, its bulk counterpart. In conjunction with newfound processing techniques, there is renewed interest in elucidating the structure-property relationships of other 2D materials
like the transition metal dichalcogenides (TMDCs). The energy storage capability of 2D nanoplatelets of TiS$_2$ and MoS$_2$ are studied here providing a contrast with investigations of corresponding bulk materials in the early 1970s. TiS$_2$ was synthesized into nanoplatelets using a hot injection route which provided a capacity of ~143mAh$^{-1}$ from thin film electrodes as determined by cyclic voltammetry measurements. Phase identification using X-ray diffraction, scanning electron microscopy, and transmission electron microscopy to complement the electrochemical performance and impurity identification is presented. MoS$_2$ thick films were created using a sulfonation reaction of synthesized MoO$_2$ and were found to have a capacity of 220mAh$^{-1}$ using galvanostatic cycling measurements. Energy and power densities of these TMDCs are presented and shown to exceed the performance of commercial electrochemical capacitors.
The thesis of Andrew Francisco Siordia is approved.

Yang Yang
Sarah H. Tolbert
Bruce S. Dunn, Committee Chair

University of California, Los Angeles
2016
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Chapter 1. Introduction & Objectives

Layered 2D materials have drawn significant attention over the last 5 decades due to their unique in-plane bonding which has led to the technological advancement of devices ranging from low resistance contacts to thermoelectrics. Specifically, van der Waals (vdW) materials exhibit a layered structure whose atoms are bound through out of plane dipole-dipole interactions. The layered configuration, as shown in Figure 1, provides a preferential biaxial shearing and electronic conduction along the basal plane. Electronic conduction along the c-axis of vdW materials is often an order of magnitude lower than along the basal plane due to the weak binding forces between basal planes. One prominent material subclass that exhibits vdW behavior is the TMDCs which consist of a row of transition metal atoms encapsulated by subsequent layers of chalcogens often resulting in a hexagonal close packed (hcp) morphology with either a trigonal prismatic or octahedral coordination.

The layered morphology of the TMDCs has enabled their so called vdW gap to host several cationic species such as the alkali and precious metals. Early electrochemistry on cationic insertion was performed on the bulk form of the TMDCs and it was found that the electronic band gap was tunable from semimetallic or semiconducting to metallic. Additionally, it was reported by Liu. et.al that a size dependence on the electronic energy gap of MoS$_2$ was prevalent when transitioning from a metallic single layer to semiconducting multilayer crystals. The ability to transition between semiconducting and metallic nature has the potential of being used as sensing devices, but also has the inherent utility of altering the atomic species within the host lattice through simultaneously storing ionic species through electron-ion exchange. Although storing ionic species within the vdW gap has been well established since the
1970s, the amount of energy stored was limited by the sluggish reaction kinetics of ion diffusion over microns of material under an applied potential.\textsuperscript{6-7,9}

Figure 1. TMDC schematics with coordination geometries from a side and top view, and close packed structure adapted from Reference F1 and F2. The 2H to 1T transition glides the sulfur atomic positions from a staggered to eclipsed position similar to a Newman projection.

One approach to circumvent the limited diffusion into the bulk was to process nanoscale materials which would allow diffusion of the ionic species much more readily. Chemical vapor deposition (CVD) has been proven as a reliable technique to prepare 2D vdW materials, but suffers from the ability to process nanomaterials in bulk. Alternative processing techniques to obtain 2D materials from the bulk were eventually discovered and are outlined in Figure 2. The simplest and arguably the most historically important technique is mechanical exfoliation which was successfully demonstrated with the well-known 2D carbon allotrope, graphene. Facile mechanical exfoliation was first accomplished through repeated pressing and removing of Scotch
tape onto Highly Oriented Pyrolytic Graphite (HOPG) which eventually led to large-scale solution processing routes of HOPG.\textsuperscript{10} The exfoliation of HOPG by Novoselov and Geim in 2004\textsuperscript{11} ignited a renewed interest in the TMDC materials due to the materials’ shared excellent electronic properties, exceptional mechanical flexibility, and partial optical transparency.\textsuperscript{12}

\textbf{Figure 2. Recent 2D materials development techniques with the most commonly associated applications.}

Access to bulk processing of the TMDC materials enabled a quicker and more facile pace of research where investigating the atomic scale tunability of materials’ intrinsic properties became more readily attainable than with slow growth methods such as CVD. Since the advent of large-scale processing routes of nanoscale layered materials, TMDC applications became easier to develop which include lubricants, transistors, and energy storage devices.\textsuperscript{13}
Nanoscale layered TMDCs have been studied for their size-dependent mechanical\textsuperscript{14-15}, catalytic\textsuperscript{16-17}, optical\textsuperscript{18-19}, and electronic\textsuperscript{20-22} properties. TiS\textsubscript{2} and MoS\textsubscript{2} are two of the most widely studied TMDCs due to their electronic and ionic conduction mechanisms, established processing techniques, and device applications revolving around energy storage. Specifically, both materials have been deemed as suitable candidates for various types of batteries and supercapacitors. Both devices operate under fundamentally different charge storage mechanisms. Batteries store energy through faradaic reduction and oxidation reactions whereas supercapacitors store energy through an electric double layer at the electrode-electrolyte interface. Since nanoscale TiS\textsubscript{2} and MoS\textsubscript{2} have been known to exhibit both battery and capacitor behavior, they have long been considered ‘hybrid’ materials which undergo different intercalation mechanisms that provide an array of energy and power density values.\textsuperscript{23-25}

The objectives of this research are to give insight towards the energy storage mechanisms of TiS\textsubscript{2} and MoS\textsubscript{2} when the feature size of the materials descends below 100nm, and to quantify their electrochemical performance in relation to commercial devices. Figure 3 depicts a Ragone plot which compares the energy and power densities for different electrochemical devices. Typically, battery materials exhibit a high energy density and low power density and sit on the bottom right of the Ragone plot. Supercapacitors tend to exhibit contrasting behavior where their energy density is low, but their power density is high. Establishing a wide range of materials to meet industry-dictated power and energy density design constraints has placed a strong emphasis in exploring the “white space” of the Ragone plot. Hybrid materials have the unique opportunity to fill in the range that has yet to be achieved by conventional batteries and supercapacitors individually, and an ideal high performance candidate would perform where the red star is located in Figure 3.
Figure 3. Typical Ragone plot of materials for electrochemical capacitors adapted from Reference F3. Thin film electrodes of time dependent syntheses of TiS\(_2\) (black) and MoS\(_2\) (blue) thick film button cells are overlaid for comparison with commercial devices.

Chapter 2. Background

2.1 Titanium Disulfide

TiS\(_2\) has been studied extensively for its hybrid electrochemical behavior which was most prominently outlined by Conway in 1991.\(^9\) Early work was devoted to studying the electrochemical behavior of bulk TiS\(_2\) and the intercalation kinetics were not studied as a function of the feature size of the material. Although the hybrid nature of TiS\(_2\) was outlined through early work, the energy storage capability of the dichalcogenide was most recently studied by Muller.\(^23\) Combined with Conway’s suggestion of a near linear trend of lithium
insertion with an applied potential and Wang’s contribution that the supercapacitive character of materials becomes apparent when reducing the feature size\textsuperscript{26}, Muller synthesized and characterized 50nm TiS\textsubscript{2} nanoplatelets. Furthermore, TiS\textsubscript{2} stores energy through alkali ion (Li\textsuperscript{+}, Na\textsuperscript{+}, etc.) insertion into the van der Waals gap according to the following:

$$\text{TiS}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiS}_2$$

(1)

where x represents the number of moles of lithium inserted into the TiS\textsubscript{2} structure. The resulting nanoplatelets were evaluated as half-cell devices and found to exhibit \textasciitilde74\% of the theoretical capacity when charging at 1mV/s through cyclic voltammetry. Several attractive features such as high reversibility, high-rate charge storage, minimal redox potential shift, and no phase change upon cycling were found for these materials which are characteristic of high energy and power density materials. Muller concluded that the results represented one of few size-effect studies that have been performed on the TMDCs and that there is significant potential for other TMDCs to fill the “white” space of the energy and power density spectrum. Although this groundbreaking research has brought to light a significant direction for energy storage materials, the optimization of the morphological dependent material properties is in its infancy which is dictated by the synthetic protocol.

2.1.1 Titanium Disulfide Protocol Limitations

The most recent advancement by Muller established the electrochemical and material characterization of the TiS\textsubscript{2} nanoplatelets, but it was unclear how effective the hot injection route successfully reproduced the reported phase and morphology. It is essential to establish a rigorous protocol for creation of these nanomaterials due to the heightened interest in their use as high performance energy storage materials. The hot injection route was an adaptation from the CdS\textsubscript{2}
quantum dot synthesis Murray et al. established in 1993 where precursors of a Cd source and separate sulfur sources were sequentially injected into a solvent that acted as a flux for the desired reaction to occur at increasing temperatures.\textsuperscript{27} It was emphasized that the environment of the reaction vessel be maintained as air free and the protocol has since been updated via solvent degassing methods\textsuperscript{28} and standardized Schlenk line cannula injection techniques.\textsuperscript{29} Muller’s approach made mention of an air free environment, but the transfer techniques that were employed easily introduce oxygen into the reaction vessel. The oxygen leads to undesirable metal oxides that bring uncertainty to what material was being benchmarked in his paper. Although creation of a more rigorous protocol is discussed further in Chapters 3 and 5, the reproduction of the results Muller has established is emphasized and a study of the reaction kinetics is reported here.

2.2 Molybdenum Disulfide

MoS\textsubscript{2} has several of the same attractive properties as TiS\textsubscript{2} and has been shown to be an analogous energy storage material with a unique storage mechanism. Like TiS\textsubscript{2}, MoS\textsubscript{2} stores energy through an electron-ion exchange reaction where the ion is inserted into the vdW gap due to an applied potential. Although MoS\textsubscript{2} lithiation between 1.1-3.0V has resulted in reversible ion exchange with the host vdW material, a detrimental conversion reaction occurs at 1.1V vs Li/Li\textsuperscript{+} leading to a decomposition of MoS\textsubscript{2} into Mo metal and Li\textsubscript{2}S. The decomposition mechanism has been proposed by the following lithiation and delithiation equations from 0.6-3.0V vs Li/Li\textsuperscript{+}.\textsuperscript{25,30}

**Lithiation**

\[
S + 2\text{Li}^+ + 2e^- \rightarrow \text{Li}_2S \ (\sim 1.8 \text{ V})
\]

(2)
\[
\text{MoS}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{MoS}_2 (~1.1 \text{ V}) \\
\text{Li}_x\text{MoS}_2 + (4-x)\text{Li}^+ + (4-x)e^- \rightarrow \text{Mo} + 2\text{Li}_2\text{S} (~0.6 \text{ V})
\] (3) (4)

**Delithiation**

\[
\text{Mo} + 2\text{Li}_2\text{S} \rightarrow \text{Li}_x\text{MoS}_2 + (4-x)\text{Li}^+ + (4-x)e^- (~1.2 \text{ V}) \\
\text{Li}_x\text{MoS}_2 \rightarrow \text{MoS}_2 + x\text{Li}^+ + xe^- (~1.6 \text{ V}) \\
\text{Li}_2\text{S} \rightarrow 2\text{Li}^+ + 2e^- + \text{S} (~2.3\text{V})
\] (5) (6) (7)

The decomposition of MoS\textsubscript{2} has been reported to be caused by the development of a lithium superlattice occupying the octahedral sites in the 2H Mo-S configuration.\textsuperscript{31} Upon increasing the amount of lithium in the host MoS\textsubscript{2} matrix above 0.1 moles the superlattice shifts occupation of the octahedral sites to the tetrahedral sites. To compensate for the induced distortion by the Li superlattice shift, the Mo-S lattice has a corresponding shift by changing the MoS\textsubscript{2} phase from 2H to 1T. The numerical denotation in each morphology represents the number of layers per repeat unit. The thermodynamically stable phase of MoS\textsubscript{2} is the 2H form which has a trigonal prismatic coordination as shown in Figure 1 and is classified as a semiconductor. The metastable phase is the 1T form which has an octahedral coordination and is classified as metallic. The irreversible phase transformation from 2H to 1T occurs under electrochemical cycling where the transition from semiconducting to metallic nature has been explained by the reduction of the MoS\textsubscript{2}, resulting in an extra electron occupying the trigonal prismatic isoelectronic coordination causing an octahedral distortion similar to the Jahn-Teller effect.\textsuperscript{24,32-33} Physically, the phase change occurs by a gliding mechanism of the Mo basal plane across the S basal plane which subsequently induces a strain on the host lattice.\textsuperscript{34} The induced strain can easily form
dislocations on the basal plane which can subsequently fracture and leave dangling sulfur bonds and open diffusion pathways for lithium ions.\(^\text{35}\) It is plausible that the intercalation of lithium at 1.8V preferentially adsorbs ions causing a formation of polysulfide chains which is outlined in Equation 2. Furthermore, the Li\(_2\)S is a byproduct of the 4 electron transfer reaction (Equation 4) which promotes the conversion reaction of MoS\(_2\) into Mo metal. The formation of Mo metal and Li\(_2\)S requires some electrons to be diverted from the charge transfer reaction causing sluggish reaction kinetics, which ultimately limit the overall performance of the MoS\(_2\). This mechanism for ion insertion provides for the formation of undesirable components which detrimentally contribute to the overall capacity of the MoS\(_2\).

The attractive feature in changing the semiconducting 2H MoS\(_2\) to the 1T metallic phase is a prototypical device where an applied potential increases the intrinsic conductivity without the need for dopants as occurs with traditional semiconductors. Facile tunable conductivity has several apparent applications in transistors, sensors, and medical devices, but as of today has not been extensively studied for single-material devices. Furthermore, the phase transformed MoS\(_2\) is still able to store lithium via insertion in the vdW gap which has intrinsically high ionic diffusivity as seen in many hybrid materials like TiS\(_2\). Each of these TMDCs have their own properties and electrochemical performance whose industrial application and fundamental mechanistic study is far-reaching, and this report focuses on the latter.

**Chapter 3. Materials & Methods**

**3.1 Titanium Disulfide Synthesis**

2D-TiS\(_2\) nanoplatelets were synthesized through a hot injection route which is depicted in Figure 4.\(^\text{23}\) Titanium (IV) chloride (4.8 mmol, 0.91g), was added to oleylamine, (C\(_{18}\)H\(_{35}\)NH\(_2\), 22.4 mmol, 6g) at 150°C in a 50 mL three-neck round-bottom flask under Ar\(_2\) flow. Oleylamine
was heated at 140°C under vacuum for 15 min to remove excess oxygen and water using a heating mantle under a reflux apparatus. Titanium chloride was injected dropwise over 2 minutes under the oleylamine and orange colored precipitates formed immediately along the sidewalls and base of the flask. The injection cannula was prevented from coming into contact with air by injecting through a double septum. The mixture was allowed to react for 15 minutes to saturate the Ti$^{4+}$ ions in solution and the temperature of the reaction was brought up to 300°C. Carbon disulfide (16 mmol, 0.97 mL) was injected into the reaction solution, whereupon the color of the solution turned blue-black. The reaction occurs via in situ generation of H$_2$S, from CS$_2$, as an intermediate reactant and is depicted in Figure 4.
Figure 4. TiS$_2$ synthesis schematic which shows the most reactive byproducts being H$_2$S and RNH$_2$. Deprotonated oleylamine forms HCl gas leaving Ti$^{4+}$ in solution to react with CS$_2$ to form sulfonated oleylamine and TiS$_2$ nanoplatelets.

Once CS$_2$ was injected, three separate syntheses were timed for 6, 7, and 10 minutes where the reaction was stopped by removing the heating mantle and cooling to room temperature. An excess of butanol was added to precipitate the TiS$_2$ nanoplatelets that were recovered by centrifuging the solution. The nanocrystals were washed with hexane and methanol to remove the excess oleylamine and sulfur. The resulting 2D nanocrystals were dispersed in 2-propanol for ease of processing devices and characterization. Dry TiS$_2$ nanoplatelets were recovered from solution by drying in a vacuum oven at 110 ºC for 8 hours. Two additional syntheses with the same working parameters as the 10 minute synthesis were carried out to illustrate the volatility and consequential variability in material performance.

### 3.2 Titanium Disulfide Characterization Techniques

Powder X-ray Diffraction was performed in a Rigaku Miniflex 2 Desktop X-Ray Diffractometer using a Cu-Kα source ($\lambda$=1.54Å). 35mg of each of the different time-dependent TiS$_2$ powders were separately placed onto a glass slide with an insert for the loaded mass. The θ-2θ scans were then performed over the course of 10 minutes in a range of 10-80 degrees 2θ.

SEM (FEI Nova NanoSEM™ 230) and TEM (FEI Technai T12 TEM) images were obtained to examine the effect that reaction time has on the morphology of the TiS$_2$ nanoplatelets. 10µL of 1g/L TiS$_2$ in ethanol solution was dropcast onto a mirror polished aluminum stub for each of the three time-dependent solutions. 20µL of 1g/L TiS$_2$ in 2-propanol was dropcast onto a Ted Pella 200 mesh holey carbon TEM grid on top of Whatman filter paper to absorb the excess solvent and was dried overnight.
Thin film working electrodes were formed by dropcasting approximately 20µg of TiS$_2$ onto oxygen plasma treated stainless steel foil in an area of 1cm$^2$ and dried under vacuum at 120ºC overnight. Electrochemical experiments were carried out using the Bio-Logic VMP3 Potentiostat in a 3 neck flask where the working electrode was immersed in 1M LiClO$_4$ in EC:DMC electrolyte with lithium counter and reference electrodes. Cyclic voltammetry was used to investigate the capacity and kinetics of TiS$_2$ between 1.4 and 3.0 V. All electrochemical testing was performed in an Ar-filled glovebox.

### 3.3 Molybdenum Disulfide Synthesis

Preparation of MoS$_2$ nanoplatelets begins with the formation of MoO$_2$ nanoplatelets through a hydrothermal reaction. 5mL of ethanol was added dropwise to 270mg of MoCl$_5$ in a 40mL glass vial. HCl vapor and vaporized ethyl groups immediately formed and the mixture was allowed to sit for 1 minute where the resulting solution was a dark red liquid. 15mL of deionized water was added dropwise and the solution turned a rich orange color. MoO$_2$ seed crystals were formed in solution which was then placed into an 80mL high pressure vessel (Parr) and heated at 180ºC for 6 hours to grow the crystals into nanoplatelets. The resulting MoO$_2$ nanoplatelets were then washed twice with deionized water and once with ethanol using centrifugation at 5000rpm for 20 minutes. Finally, the nanoplatelets were dried overnight in a vacuum oven at 60ºC. In collaboration with Professor Sarah Tolbert from UCLA, the MoO$_2$ powder was then sulfonated at 600ºC for 6 hours using a closed loop tube furnace with H$_2$S gas which created MoS$_2$ nanoplatelets. The nanoplatelet morphology remained the same through the sulfonation process and is represented in the SEM images in Figure 5.
Figure 5. SEM images at 5keV of MoO$_2$ nanoparticles before (left) and after (right) the sulfonation reaction which converts the oxide into MoS$_2$ nanoparticles. Reaction used H$_2$S gas balanced with N$_2$ gas at 600°C for 10 hours which was allowed to cool down to room temperature.

Figure 6. MoS$_2$ nanoplatelet button cell schematic (left) with approximate diameter of 2cm. The cathode was a dried slurry with a 75:15:10 wt% ratio of MoS$_2$:CB:CMC. The corresponding anode is lithium foil which was made larger than the cathode by 2.5 times the area.

3.4 Molybdenum Disulfide Electrode Fabrication

Thick film electrodes were formed using a mixture of MoS$_2$ powder, Carbon Black (CB), and Carboxymethyl cellulose (CMC). The thick slurry had a mass ratio of 75:15:10 of MoS$_2$:CB:CMC with an active material mass loading of approximately 1mg/cm$^2$. The working electrode was fabricated by uniformly coating the slurry onto stainless steel foil via doctor blade. Thereafter, the working electrode was allowed to dry in air at room temperature and placed into a standard button cell as seen in Figure 6 using lithium foil as the anode, a Celgard glass fiber separator, and 1M LiPF$_6$ in EC:DMC as the electrolyte. New button cells were created for each
electrochemical characterization step using the Bio-Logic VMP3 Potentiostat. Cell assembly and galvanostatic testing were performed in an Ar-filled glovebox.

Chapter 4. Results

4.1 Titanium Disulfide

4.1.1 X-ray Diffraction

Figure 7 denotes the diffraction peaks which correspond to the (001), (101), and (110) planes in the TiS$_2$ hexagonal lattice where the (001) peak intensity corresponds with the c-axis lattice parameter and was referenced to a TiS$_2$ standard from the Match! software database. The calculated c-axis lattice parameter for each synthesis was 5.69Å which agrees with both the literature value$^{38}$ and the previous work.$^{23}$ As the synthesis time decreased, the diffraction peak intensity for the (001) plane (c-axis lattice parameter) decreased substantially indicating nonpreferential growth in the vertical direction. Furthermore, the intensity of the {110} peaks correspond to the a and b lengths in the hcp lattice where the sharp peak indicates growth in the lateral dimensions is the preferred growth direction. Each peak agrees within 0.2° 2Θ with the corresponding TiS$_2$ materials reported by Muller and was also matched with ICDS 26861.
Figure 7. θ-2θ X-ray diffraction spectra time dependent TiS$_2$ with respective peaks illustrated. Scan time was approximately 10 minutes.

Figure 8. SEM images at 5keV of time dependent syntheses: (A) t=6min, (B) t=7min, (C) t=10min, and at (D) 100,000X of (C). Figure D shows the hexagonal shape of the platelets (outlined).
4.1.2 Electron Microscopy

SEM and TEM images were used to characterize the morphology of the TiS$_2$ nanoplatelets prepared using different reaction times. The SEM images shown in Figure 8 indicate a consistent hexagonal morphology with an increase in crystallite size when the reaction time is increased to 10 minutes. This effect is most easily seen in Figure 8B where most of the nanoplatelets are significantly under 1µm, nearing 100nm. In Figure 8C, the particles have a consistent hexagonal morphology with the particle size approaching 250nm. Figure 9 depicts a representative TEM image that confirms the size of the nanoplatelets from the 10 minute synthesis is approximately 110nm. Not shown here is that the size of the crystallites increases with reaction time. One important note is that some diffraction effects like bend contours from buckled regions or line defects where the lined-textured regions are apparent in the image. Additionally, mass-thickness contrast is exhibited in the darker regions of Figure 9 due to

![TEM image](image_url)
nanoplatelet aggregation, but the contrast at the edge of the nanoplatelets is nearly constant suggesting that individual nanoplatelets were created.

4.1.3 Electrochemistry

Electrochemical characterization was carried out to identify how closely the kinetics of the newly synthesized materials compared with previous work.\textsuperscript{23} Figure 10 illustrates the cyclic voltammograms of the 3 time dependent syntheses of TiS\textsubscript{2} which utilized boiled oleylamine. Redox peaks at approximately 1.9V and 2.3V are present at 1mV/s, but are suppressed at higher sweep rates where the ion diffusion is limited which agrees with Muller’s findings.\textsuperscript{23} The most significant point is that the redox peak with nearly matching peak separation is seen at 2.3V in both the previous work and the 7minute reaction synthesis. The discharging capacities at a cycling rate of 1mV/s were 45mAh\textsuperscript{-1}, 110mAh\textsuperscript{-1}, and 142mAh\textsuperscript{-1} for the 6, 7, and 10minutes TiS\textsubscript{2} reactions. Capacities were calculated by integrating the internal area of the CV and averaging that value across 5 cycles. Energy density and power density values as half cells are plotted in Figure 3 to compare with commercial electrochemical devices which are on par the previous work where the energy and power density of the 6minute synthesis was approximately 220Wh/kg and 500W/kg, respectively.\textsuperscript{23} The 10 minute synthesis was the most crystalline and demonstrated the highest capacity of all the time dependent syntheses. This reaction time was used for all further syntheses of TiS\textsubscript{2} materials since electrochemical performance was emphasized.
Figure 10. Cyclic voltammograms of TiS$_2$ 6 minutes, 7 minutes, and 10 minutes syntheses using boiled oleylamine which illustrates redox peaks at about 2.3V and 1.9V. As time is increased the redox peaks become suppressed, but the weight normalized capacity is increased.

Although time played a key role in determining the crystallinity of the nanoplatelets, the reaction is quite volatile and often produces undesirable products. Figure 11 shows a comparison of the previous 10 minute synthesis (black) with two separate syntheses using oleylamine that was dried over 3Å molecular sieves. Figure 11A depicts Reference 23’s cyclic voltammograms which are compared with the present work’s cyclic voltammograms which are depicted in Figure 11B. Samples from each synthesis underwent 5 cycles at a scan rate of 1mV/s. The “TiS$_2$/TiO$_2$ Mix” (black) curve formed large quantities of TiO$_2$ in both the sidewall of the reaction vessel and
Figure 11. Cyclic voltammograms of TiS$_2$ of reference 20 (left) and current work (right). The “TiS$_2$/TiO$_2$ Mix” scan demonstrates that a mixture suppresses the electrochemical activity of TiS$_2$. The “TiS$_2$ Dry” scan utilized molecular sieve dried oleylamine to remove oxide formation. The TiS$_2$ + Impurity scan used boiled oleylamine which resulted in a noticeable impurity. All scans were performed at 1mVs$^{-1}$ in both reference 20 and the current work. The previous work is adapted from Reference 23.

in the mixture. TiO$_2$ is the most common byproduct within this reaction when excess moisture or oxygen is present in the reaction.$^{23,39}$ Dried oleylamine was used to circumvent TiO$_2$ formation, and the corresponding products’ performance are depicted as the “TiS$_2$ Dry” (red) scan. A reduction peak at 2.3V becomes apparent with a corresponding oxidation peak that has a peak separation of approximately 100mV. Furthermore, a reduction peak appears at 1.85V upon initial cycling, but disappears with as the materials were subsequently cycled. The “TiS$_2$ + Impurity” scan used the same dried oleyleamine as the “TiS$_2$ Dry” synthesis, but yielded a material with varying redox peaks as the cycles were increased which was uncharacteristic of previous syntheses. The additional reduction peaks in both the red and blue curves are discussed in further detail in Chapter 5. The box shape in each of the syntheses from 1.9-2.2V is typical of supercapacitor behavior which is easily exemplified when viewing Figure 12, where the normalized capacity of each material is shown as a function of sweep rate. Figure 12 depicts the 6 minute, 7 minute, 10 minute, and “TiS$_2$ Dry” performance in comparison with the results
presented in Reference 23. At slow sweep rates the capacity of the all materials is the highest with the “TiS$_2$ Dry” having the closest matching capacity with that of the previous work done by Muller. The time dependent syntheses which did not utilize dry oleylamine are also depicted for comparison. The energy and power density of “TiS$_2$ Dry” was calculated to be 223Wh/kg and 515W/kg at a sweep rate of 1mV/s, which exceeds the performance of commercially available electrochemical capacitors and batteries.

Figure 12. Rate capability of TiS$_2$ time dependent syntheses and TiS$_2$ Dry synthesis as compared with 50nm and 100nm work in Reference 23. SEM insert is an image of the “TiS$_2$ Dry” nanoplatelets which are approximately 94nm in diameter with a hexagonal shape two dimensional morphology.
4.2 Molybdenum Disulfide

4.2.1 Electrochemistry

Electrochemical behavior of the MoS$_2$ nanoplatelets was studied using galvanostatic cycling to
elicit the button cell performance. Galvanostatic cycling of the MoS$_2$ was conducted between 1.0
and 3.0 V at 1C, 5C, 10C, 20C, 40C, 60C, and 100C where a cycling rate of 1C (2.3mAcm$^{-2}$)
charges the button cell to the theoretical capacity of MoS$_2$ (167mAhg$^{-1}$) in 1 hour and 100C
(103mAcm$^{-2}$) charges the cell in 36s. 10 charge-discharge cycles were performed at each
sequentially increasing C rate to study the intercalation kinetics which are displayed in Figure
13. The MoS$_2$ underwent the typical voltage plateau at approximately 1.2V which is indicative

![Figure 13. Galvanostatic cycling of MoS$_2$ thick film nanoplatelets where the current density is 2.3mAcm$^{-2}$ and 103mAcm$^{-2}$ at 1C and 100C. Cycling the cell at 1C took 1 hour and at 100C took 36s. Upon the initial cycle at 1C a voltage plateau at 1.2V indicates the phase change from 2H to 1T for all subsequent scan rates.](image-url)
of the semiconducting-to-metallic phase transformation after the initial cycle at 1C. The effect that cycle number has on capacity retention is shown in Figure 14 where 89% of the capacity was retained after increasing the lithiation rate up to 100C and returning to 1C. Figure 15 displays the long-term cyclability where the cell underwent 3000 charge-discharge cycles at a rate of 20C and retained 81% of the nominal cell capacity with a nearly 100% coulombic efficiency.

![Figure 14. Rate capability of MoS$_2$ thick film button cells upon sequential cycling indicating high rate intercalation.](image)

![Figure 15. Extended life cycling at 20C demonstrating capacity retention up to 3000 cycles.](image)
5.1 Titanium Disulfide

5.1.1 Impurity: Titanium Dioxide

Although characterization of the electrochemical properties of nanoscale TMDCs is in its infancy, many of these materials hold promise as favorable energy storage compounds. Time dependent syntheses of TiS$_2$ via a hot injection route were performed to better understand the influence that size, phase, and crystallinity has on the lithiation kinetics of the material. The SEM and TEM images showed the hexagonal structure of the TiS$_2$ nanoplatelets with sizes and crystallinity that varied as a function of time. Complementing the electron microscopy, x-ray diffraction gave insight on the phase and crystallinity of the materials and that the 1T hexagonal structure was achieved. Although TiO$_2$ was visibly present in the products of the TiS$_2$ reaction, x-ray diffraction confirmed that no appreciable amount of crystalline TiO$_2$ was present in the powder. However, this does not remove the possibility that the apparent impurity could be comprised of sulfur and titanium as well as amorphous TiO$_2$.

TiS$_2$ synthetic parameters played a key role in determining the structure and the electrochemical performance of the hybrid material. Generally, nanoplatelet size was controlled by the concentration of precursors (TiCl$_4$ and CS$_2$) in solution (oleylamine) and reaction time. In a previous study, FT-IR and EDS analyses were performed after washing the nanoplatelets to ensure that all excess oleylamine was removed from the solution.$^{23}$ When the reaction time increases, nanoplatelets agglomerate and coalesce, resulting in larger hexagonal 2D-nanocrystals. Two possible mechanisms can occur in this case; one is a dissolution/recrystallization (Ostwald ripening) and the other is an epitaxial growth, driven by relaxation of stress created by misorientation at the attachment interfaces.$^{40}$ The growth of 2D-TiS$_2$ polycrystalline nanocrystals
can be explained in the same way by epitaxial growth under (001) orientation control. Due to concern over surface reactions\(^\text{39}\), fresh batches of 2D-TiS\(_2\) were used in the characterization studies to achieve good reproducibility.

Careful observation of the synthetic protocols provided insight on how the synthesis time affected both the morphology and nanoplatelet size. Side reactions during the addition of precursors, even with the appropriate stoichiometry, could result in a loss of product or even the formation of unwanted byproducts. Addition of the TiCl\(_4\) produces numerous orange precipitates which are likely a combination of Ti\(^{4+}\) ions which reacted with excess oxygen and short chain amines from the decomposition of oleylamine in a high temperature environment.\(^\text{39,41}\) When the CS\(_2\) is injected, H\(_2\)S gas is formed as an intermediate gas that can carry an excess of sulfur away leading to a change in stoichiometry, and possibly, crystallinity. Another measure of uncertainty in this synthesis is due to having some volumetric transfer leakage through a violent reaction with the atmosphere prior to injection into the reaction vessel. TiCl\(_4\) reacts violently with any source of oxygen and produces mostly anatase TiO\(_2\) which is often demonstrated when making pigments by elevating the chloride above its melting point in the presence of oxygen.\(^\text{42}\) When the injection cannula come into contact with air, TiO\(_2\) and HCl gas form immediately, leading to a seeded impurity within the reaction vessel where the subsequent injection of CS\(_2\) can introduce a new source of oxygen and make the formation of TiO\(_2\) more likely. The injection steps were isolated as the root cause of TiO\(_2\) formation by eliminating every other oxygen source through a combination of boiling and drying the oleylamine 3Å molecular sieves.

Impurities are often of concern in reactions and it is evident that an impurity is created during the formation of TiS\(_2\). Since the reactants of the synthesis commonly produce TiO\(_2\), the most common phases’ diffraction patterns and reduction peaks and were compared with the
literature and ICSD 36408 and 85495.\textsuperscript{23,36} No set of peaks from TiO$_2$ anatase, brookite, rutile, or TiO$_2$-b phase matched with any peaks represented in Figure 7. The cathodic reduction peaks were also compared with the results in Figure 11, but each reduction peak has been reported to be between 1.3 and 1.7V.\textsuperscript{26,43-45} It is clear that the impurity that is evident from the reduction peak at 1.85V is not from an oxide, but from an alternative material with the reacted elements of titanium and sulfur.

### 5.1.2 Impurity: Titanium Trisulfide

One possible impurity candidate is TiS$_3$ since the synthesis was designed to have excess sulfur and TiS$_3$ has been noted to form along with TiS$_2$ in reactions that reach up to 300ºC without post-annealing, as in the work done presently.\textsuperscript{46} Furthermore, TiS$_3$ and TiS$_2$ have similar crystal structures in that the unit cell of TiS$_2$ can be described as sulfur occupying overlapping corners of 2 truncated octahedra with the shared point as titanium. This formation is most easily seen in Figure 1 as the 1T phase with a corresponding vdW gap. Although TiS$_3$ is a hexagonal unit cell, it differs from TiS$_2$ in that the corner sharing octahedra are no longer truncated which extends the structure in 3D, effectively eliminating the layered morphology that TiS$_2$ exhibits.\textsuperscript{47} The similarities in crystal structure allow a more favorable environment for the TiS$_3$ to form especially when titanium is put into contact with a sulfur source around 300ºC.\textsuperscript{46} Crystalline TiS$_3$ has the (001) peak appear at about 11º 2Θ and is not clearly seen in Figure 7, but amorphous TiS$_3$ shares similar electrochemical activity as the crystalline form. Amorphous TiS$_3$ has been shown to have its highest reaction rate potential range at 1.8-2.2V.\textsuperscript{48} Figure 16 shows that as cycles increased, the reduction peak potential shifted from 2.3V to 1.85V which is within the range of the reported data by Matsuyama. Matsuyama showed that as the amorphous TiS$_3$ was charged galvanostatically, a plateau occurred at approximately 1.9V which is indicative of a
reduction reaction. The “TiS₂ Dry” synthesis shows a similar phenomenon in that the peak at 1.9V disappears as the material is cycled which may indicate that TiS₃ was initially present and subsequently destroyed through ion diffusion. However, the specific peak potentials where the reduction of TiS₃ occurred in the present work was unclear due to a continuously decreasing shift in the potential.

![Graph showing cyclic voltammogram](image)

**Figure 16. “TiS₂ + Impurity” cyclic voltammogram from Figure 11 where the redox peak at 2.3V gradually disappears and a peak becomes more pronounced at 1.9V, which corresponds to the redox peak of amorphous TiS₃.**

This decreasing shift in reduction potentials could also be due to a phase change of the TiS₃ material since TiS₂ is known not to exhibit any change from the 1T phase upon lithiation.⁴⁹
The instability of the TiS$_2$ nanoplatelets from the hot injection synthetic route has been reported due to the high surface area that can react with excess sulfur or oxygen.\textsuperscript{39} Park postulates that the TiS$_2$ nanoplatelets may even undergo a sulfur exchange with oxygen at room temperature. It is possible from an energy standpoint, that the TiS$_3$ can release the excess sulfur or even convert to TiS$_2$ when under an induced potential just to maintain a more favorable system. The only evidence that supports this speculation is that under successive cycling the supposed TiS$_3$ reduction peak shifts from 2.3V, which is characteristic for TiS$_2$, to 1.85V as cycling was increased. Suggestion for following up these experiments are covered in Chapter 7.

5.1.3 Hybrid Insertion

Electrochemically, TiS$_2$ behaves as a hybrid material with both properties of a battery and a supercapacitor. The TiS$_2$ nanoplatelet half cells demonstrated battery-like behavior through the faradaic redox peaks at 2.3V, but also had the box shape of the CV to resemble that of a supercapacitor. Furthermore, electrochemical characterization of the material was able to show that the crystallinity (i.e. synthesis time) played a large role in diminishing the capacity of the materials, making it a clear fact that having high crystallinity is important for energy storage materials. This phenomenon can be explained by the degradation of material on the substrate and the filling of vacant redox sites from the inhomogeneous synthesis of the TiS$_2$ nanoplatelets. However, the shape of the CV shows both capacitive and battery-like behavior indicating that TiS$_2$ can be classified as a hybrid material. The capacity of the half cells decreased as sweep rates were increased indicating that a mixture of diffusion and surface controlled reactions are occurring for the Li$^+$ to intercalate into the TiS$_2$.

A b-value analysis of the “TiS$_2$ Dry” synthesis was used to quantify if the lithiation process was diffusion or surface controlled, where b is from the following equation:
\[ i = av^b \]

(9)

If the \( b \) value approaches 0.5, the lithiation process is characteristic of a diffusion controlled reaction and if it is closer to 1 it is surface controlled reaction. The \( b \) values are depicted in Figure 17, where at high potentials the reaction is a mixture of diffusion and capacitive processes which agrees with the values presented by Muller.²³

![Figure 17. Anodic b value determination of “TiS₂ Dry” synthesis indicating diffusion controlled processes near 2.3V and under 1.9V following Equation 9. Capacitive processes dominate between 1.9V and 2.3V and above 2.4V.](image)

Another similarity is that both Reference 23’s work and this work have a \( b \) value approaching 0.5 at 2.3V where the diffusion controlled faradaic redox reaction occurs. A \( b \) value of 0.61 was found from the slope of the intercept of \( \log(i_{\text{max}}) \) vs \( \log(v) \) where \( v \) is the sweep rate and \( a \) is
a constant. Additionally, both studies have nearly capacitive processes between 2.0 and 2.3V. The only notable difference is that upon reaching 1.9V, the current work reverts to a diffusion controlled process whereas the previous work argues that it is purely capacitive. This disparity is possibly due to the TiS$_2$ nanoplatelets having residual TiS$_3$ which have a reduction peak at 1.9V which would agree with the b value transitioning towards 0.5. Additionally, the nanoplatelets have shown to have a disordered structure along the c-axis as the feature size was decreased. The disorder along the c-axis and the layered nature of the dichalcogenides lends itself to a higher likelihood of lithium diffusion events which could destroy the materials upon excessive cycling. Even with the disparity in the b values of the materials at low potentials, both the current and previous work agree with the characteristic capacitive nature at intermediate potentials and diffusion processes dominating at the 2.3V reduction potential.

5.2 Molybdenum Disulfide

5.2.1 Influences on Electrochemical Performance

The electrochemical performance of the MoS$_2$ nanoplatelet button cells can be attributed to the incorporation of carbon black, the semiconducting to metallic phase transformation, and 30nm nanoplatelet feature size. The mechanism by which energy is stored in MoS$_2$, a layered complex, has been attributed to stages of intercalation as a result of charge transfer reactions. Typically, intercalation occurs through an increased driving force (i.e. applied potential) stimulating electron transfer between host and guest species.$^{50}$ Ions can be considered elastic dipoles which have dipole-dipole interactions with neighboring guest species which will lower the system’s overall energy by reducing the induced lattice strain from the intercalated species. In addition to an applied potential driving ion diffusion into 2H MoS$_2$, utilizing a highly conductive network to increase the intercalation rate further enhances the ion diffusion into the
semiconducting dichalcogenides. CB has been used as a highly conductive additive that increases the utilization of active material and lowers the internal resistance of the cathode, effectively increasing the overall capacity of cathode materials. The button cells utilized a 15wt% addition of conductive CB to improve upon the intrinsic electrical conductivity of the MoS$_2$ ($10^{-4} \Omega^{-1} \text{cm}^{-1}$) where the slurry composition was 75:15:10 of MoS$_2$:CB:CMC. Evidence has been shown that upon lithiation of MoS$_2$ the dichalcogenide changes from the 2H to 1T phase which subsequently increases the electrical conductivity of the host material. The increased conductivity of the host materials was one of the features responsible for maintaining ion diffusion pathways, which can be attributed the extended cycle life of the materials. Similarly, the MoS$_2$ nanoplatelets have shown a similar effect in that they have an 81% capacity retention even after 3000 cycles. Furthermore, Cook expanded upon the underlying benefit behind the fast diffusion pathways in that the nanometer-scale feature size of the MoS$_2$ limited long range diffusion which is also the same mechanism here that enables the nanoplatelets to nearly reach the theoretical capacity of MoS$_2$ (167mAh$^{-1}$).

5.2.2 Electrochemical Performance

The present work utilized MoS$_2$ that has the same feature size as Cook, and the individual contributions towards a capacity increase were studied collectively using galvanostatic mode. Figure 13 depicts various C rates of the cycled MoS$_2$ button cells where the intercalation rate was increased up to 100C. With the exception of the cycles performed at 1C, the spread among cycles was minimal, indicating appreciable stability even though the capacity significantly decreased at higher rates. At a cycling rate of 1C the total mass normalized capacity of the thick film electrodes was approximately 220mAh$^{-1}$ and decreased to 90mAh$^{-1}$ as the C rate was increased to 100C with 6 cycles for each rate. The spread of the 1C discharge curves is due to the phase
transformation occurring at the characteristic voltage plateau around 1.1-1.2V vs Li/Li$^+$. The rate capability of the MoS$_2$ nanoplatelets can be seen in Figure 14 where the cell underwent increasing C rates with a subsequent return to a slower rate of 1C. The difference between both the initial and final scans at 1C demonstrated a 90% retention of the weight normalized capacity at approximately 200mAh$^{-1}$ which can be seen in Figure 18. The shape of the charge curve has no appreciable change and, if the 1$^{st}$ cycle is ignored, the discharge curves look similar upon reaching 0.8V. The spread in the initial scan is due to the material undergoing the phase transformation and can be seen to have negligible spread in the final scan since the amount of 1T MoS$_2$ has already been formed. The voltage plateaus that are often indicative of redox peaks in

![Diagram](image)

Figure 18. Initial and final 1C galvanostatic scans from Figure 14 showing the same shape in both charge and discharge curves. The spread in the initial galvanostatic scans is due to the 2H to 1T phase transformation of the MoS$_2$ nanoplatelets.
MoS$_2$ systems are still apparent between 1.7-2.0V. Electrochemical performance of the button cell is presented in Figure 3 alongside commercial capacitors. The weight normalized energy and power density of the MoS$_2$ nanoplatelets exceeds the commercial performance where a rate of 1C shows 440 Wh/kg and 440W/kg.

**Chapter 6. Conclusions**

TMDCs have continuously proven the promise of vdW materials becoming potential replacements in devices that utilize graphene. Since graphene has long been considered a highly limited resource the TMDCs have offered an array of material properties to potentially become a substitute for the material. The work done presently surveyed TiS$_2$ and MoS$_2$ nanoplatelets and compared their electrochemical performance to the industry standards of both batteries and capacitors. Fundamental studies on the dichalcogenide’s structure and phases provided a means to understand how the electrochemical performance was improved upon from the previous work in the field. The energy storage capability of the TMDCs was attributed to charge transfer reactions which were quantified through monitoring the kinetics of lithiation of the TMDC. TiS$_2$ did not exhibit a phase change, but had an issue of impurity formation causing inconsistencies in accurately measuring the electrochemical performance of the materials. TiO$_2$ impurities were determined to be at most a minor contribution to the performance, but TiS$_3$ impurities could have possibly diminished the overall performance which has already been shown in 2015. The shape of the cyclic voltammograms displayed capacitive and battery-like behaviors which were quantified using a b value analysis that verified that the materials had hybrid energy storage behavior. Although the impurities detracted from pure TiS$_2$’s material performance, the typical hybrid material behavior remained intact which provided for superior electrochemical performance compared with commercial devices.
MoS$_2$ underwent a phase change that increased the electrical conductivity which, in turn, had a positive effect on the capacity of the materials. The capacity retention of the MoS$_2$ took advantage of the fast kinetics of the material in that the button cells were able to undergo thousands of cycles without a significant decrease in performance. The materials were shown to not only take advantage of the metallic phase increasing the capacity, but also the feature size playing a key role in the high performance. Short diffusion paths were achieved which enabled both the MoS$_2$ and TiS$_2$ nanoplatelets to nearly reach the theoretical capacity at relatively high discharge and charge rates. The performance of the TMDCs was then quantified and plotted on Figure 3 to show that both have higher electrochemical performance than commercial devices.

**Chapter 7. Suggestions for Future Work**

Although TiS$_2$ and MoS$_2$ nanoplatelets were shown to exceed commercial energy and power densities through their unique morphology and formulation, some characterization still must be completed to verify the materials’ phase and performance. The production of TiS$_2$ would benefit from using flexible cannula for injection to aid in preventing oxide formation. Moreover, the synthetic protocol could use a nonstoichiometric recipe to aid in forming more TiS$_2$ since the excess sulfur forms an impurity. Since TiS$_3$ was formed during synthesis, a post anneal could transform it to TiS$_2$ and increase the crystallinity of the materials. Furthermore, XPS studies could prove beneficial in identifying the binding energy of the Ti-S bonds in both of the sulfides. Beyond the synthetic routes, *in-situ* and *ex-situ* X-ray diffraction along [001] of the charged TiS$_2$ materials would give information about how the c-axis lattice parameter will have shifted upon insertion. *In situ* TEM would complement the diffraction results and could provide a means for monitoring the charge transfer reactions which induce staged intercalation of lithium. Furthermore, creating thick film electrodes of TiS$_2$ and cycling them galvanostatically would
help establish the rate capability of the materials for a more direct comparison to commercial
devices. As for the MoS$_2$, the device performance has been well studied and could benefit from
cyclic voltammetry to indicate the exact redox potentials that show the onset of phase
transformation. One further step would be determining the cell’s survivability as a battery under
extreme temperatures and extensive cycling environments with a cycle life in the 10,000 range.
Overcoming these extreme parameters could put this material into a favorable position for
industrial commercialization and poses the possibility of being the start of a new route of
synthetic methods for energy storage materials.
References


**Figure References**

