ELECTROCHEMICAL STUDIES OF METAL DICHALCOGENIDE-POLYMER COMPOSITE ELECTRODES IN 1,2-DIMETHYL-3-PROPYL-IMIDAZOLIUM TETRAFLUOROBORATE AND 1-ETHYL-3-METHYL-IMIDAZOLIUM TETRAFLUOROBORATE

Thomas E. Sutto  
NRL, Code 6170, Chemistry Division  
Washington D. C., 20375

Paul C. Trulove  
Air Force Office of Scientific Research  
801 Randolph Str. Room 732  
Arlington, VA 22203-1977

Hugh C. De Long  
Chemistry Department  
US Naval Academy  
Annapolis MD 21402

ABSTRACT

A comparative electrochemical study of DMP BF₄ and EMIBF₄ using layered metal sulfide- PVdF-HFP polymer composite electrodes was undertaken to investigate their use in place of graphite in the DIME Battery System. TiS₂ and TaS₂ were chosen since both are known to readily intercalate large heterocyclic compounds. MoS₂ was chosen since it is similar in many ways to the other metal sulfides, but it does not lend itself to the intercalation of large guest species. Results indicate that MoS₂ was too difficult to electrochemically intercalate, and exhibited no charge/discharge behavior. TaS₂, on the other hand, underwent spontaneous intercalation, and subsequent exfoliation, resulting in low efficiencies. TiS₂ exhibited a high efficiency for both cation (80%) and, remarkably, anion (65%) intercalation. Time delayed discharging indicated that the BF₄⁻ anion does suffer from chemical degradation within the sulfide layers over time, unlike that observed for BF₄⁺ in graphite.

INTRODUCTION

Recently, it has been shown that batteries can be built from a simple two component system, graphite rods and the molten salts (1). These Dual Intercalating Molten Electrolytes Systems, DIME systems, 1-ethyl-2-methyl-imidazolium tetrafluoroborate (EMIBF₄) and 1,2- dimethyl-3-1-propyl-imidazolium tetrafluoroborate (DMP BF₄) act as both the electrolyte, as well as providing the imidazolium cation and BF₄⁺ anion which behave as the reversibly intercalating ions of a simple battery. In an attempt to further investigate, and possibly optimize these DIME systems, an
investigation into the electrochemical behavior of layered metal sulfide electrodes was undertaken.

The three layered metal sulfides chosen, TiS₂, TaS₂, and MoS₂, although very similar in structure, (2) exhibit very different types of behavior towards intercalation (3). Although all three are layered sulfides, TiS₂ and TaS₂ fall into the Cdl₂ structural type. These are considered classic layered materials, where the metals are found in simple octahedra composed of sulfur. In essence, each layer in these compounds can be viewed as an a-b-a sandwiching of three graphite layers, where the outer layers are sulfur, and the inner layer is the metal, both in simple hexagonal arrays. However, MoS₂ differs in that the metal centers lie in trigonal prismatic coordination spheres. This results in significant interlayer bonding from one metal layer to the neighboring sulfur layers from other metal-sulfur sheets. Thus, MoS₂ is extremely difficult to intercalate, while TiS₂ and TaS₂ readily undergo intercalation by various solvated alkali metals, and, more importantly, extremely large organic molecules, such as substituted pyridines, pyrroles, and long chain aliphatic amines.

It is this latter aspect of TiS₂ and TaS₂, which makes these materials extremely interesting in terms of the DIME System. Although previous work primarily has focused on using the layered sulfides as host materials for Li or Na intercalation (4), they will be studied here for their ability to readily intercalate and de-intercalate the molten electrolytes EMIBF₄ and DMPIBF₄. Finally, in order to compare these three layered metal sulfides, it is important to note how the electronic structure of the materials should affect both the intercalation process and the final products of intercalation. The layers of TiS₂ are very similar in a way to graphite since simple electron counting indicates that Ti⁴⁺ leaves no unpaired d-electrons for metallic conduction, and indeed behaves as a semi-metal, just as graphite does. Therefore, in many ways, TiS₂ should behave similarly to graphite. On the other hand, TaS₂, in which the tantalum is ideally d¹, does possess unpaired d-electrons, which lend themselves to creating metallic, and at sufficiently low temperature, superconductive properties. Additionally, this one unpaired electron makes TaS₂ favor cation intercalation much more readily than TiS₂, and should intercalate much more readily. In terms of intercalation behavior, this makes these layered metal sulfides much more amenable to accommodate positively charged species. In fact, it should be noted; however, that simple, thermodynamically driven intercalation of both of these materials is limited to only cation intercalation. Finally, as previously stated, MoS₂ is extremely difficult, relatively speaking, to intercalate, and it cannot readily intercalate solvated alkali metals, substituted heterocyclic compounds or long, aliphatic amines. In fact, only under extreme reaction methods does it readily intercalate alkali metals. Therefore, these three materials should illuminate the intercalative behavior of the DIME's.
EXPERIMENTAL

Preparation of the initial salts, EMICl and DMPICl

1-ethyl-3-methyl-imidazolium chloride was prepared as previously reported (5). The preparation of 1,2-dimethyl-3-n-propyl-imidazolium chloride was altered from that previously reported in order to produce a higher yield and a purer product (6). The starting materials: 1,2-dimethyl-imidazole (98%) and 1-chloropropane (98%) were purchased from Aldrich, as was the acetonitrile (99.5% anhydrous). The 1,2-dimethylimidazole (m.p. 38 °C) was melted at 50 °C under flowing nitrogen in a drying oven. Typically, 500 g of 1,2-dimethyl-imidazole, a 25% molar excess of 1-chloropropane, and 50 ml of acetonitrile were placed in a thick-walled, single neck, 2-liter round bottom flask fitted with a reflux condenser. Excess 1-chloropropane was added to limit the amount of unreacted 1,2-dimethyl-imidazole in the final product. The solution was degassed several times with dry nitrogen, gradually heated to 75 °C, and allowed to reflux for 4 days under nitrogen pressure. Cooling the solution produced a tan-white precipitate and a yellow-red supernatant. 300 ml of ethyl acetate was added to the round bottom flask to precipitate all of the 1,2-dimethyl-3-n-propylimidazolium chloride, and the material was filtered and washed with five 100 ml washings of ethyl acetate in order to remove all of the unreacted 1,2-dimethyl imidazole. The solid material was dissolved in a minimum amount of hot acetonitrile and recrystallized twice by adding a large excess of ethyl acetate. This removed nearly all of the unreacted 1,2-dimethyl imidazole. For the final recrystallization, the solid product was again dissolved in a minimum amount of boiling acetonitrile and allowed to slowly crystallize out as the solution cooled over 24 hours. The solid material from each recrystallization was washed with ethyl acetate. The final product was a white crystalline material, which exhibited a very slight tan tint. Finally, the 1,2-dimethyl-3-n-propyl-imidazolium chloride was heated to 155 °C under an active vacuum (10⁻³ torr) for 2 days to remove the volatile contaminants.

Preparation of the BF₄ salts

The preparation of 1-ethyl-3-methyl-imidazolium tetrafluoroborate and 1,2-dimethyl-3-n-propyl-imidazolium tetrafluoroborate was done by direct reaction of the respective chloride salt with NH₄BF₄ (Aldrich, 99.98%) in acetonitrile. In this solvent, the substituted imidazolium chloride salts are highly soluble in acetonitrile, and NH₄BF₄ is only marginally soluble in acetonitrile (7). However, the secondary product, NH₄Cl, is not soluble in acetonitrile, and this fact provides the driving force for this reaction. This reaction step was performed in a dry box, under dry nitrogen, in order to limit the possible inclusion of water into the final product. For a typical reaction, one mole of the substituted imidazolium chloride salt was placed in a 1-liter reaction flask fitted with a threaded Teflon plug and dissolved in a minimum amount of acetonitrile. To this solution, a 10% molar excess of NH₄BF₄ was added. The flask was sealed and allowed to stir at room temperature for 4 days. Upon completion of the anion exchange, the solid material (NH₄Cl and unreacted NH₄BF₄) was removed by vacuum filtration using a glass frit of medium pore size. Subsequently, to the remaining molten salt/acetonitrile...
solution, 30 g of decolorizing carbon and 30 g of basic alumina were added and the solution was allowed to stir at room temperature in the sealed reaction flask for two days. The carbon black and alumina were then removed by successive filtration; through a medium pore size glass frit, a 1 micron filter disc (Whatman, PTFE Membrane) and finally a 0.45 micron filter disc (Whatman, PTFE Membrane). For the final step in the purification process, the molten salts were heated to 65 °C under an active vacuum (10⁻³ torr) for 2 days to remove any trace water or acetonitrile. The final molten salts were clear and nearly colorless, with a slight yellow tint to the EMIBF₄ and a slight tan tint to the DMPIBF₄.

Preparation of the Metal Sulfide-Polymer Composite Electrodes

Metal sulfide-polymer composite electrodes were prepared from 1 μ sized synthetic TaS₂, TiS₂, and MoS₂ (99.9995% Aldrich) and poly-vinylidene-difluoride hexafluorophosphate (PVdF-HFP Kynar -2801-00 from Elf Atochem). The metal sulfide-polymer electrodes were prepared based upon the metal sulfide to polymer mass ratios of 1:1, 2:1, 3:1, 4:1, 5:1, and 6:1 (Percent metal sulfide for each-50%, 66%, 75%, 80%, 84%, and 85.5%; respectively). Composite electrodes made with the composition of 1:2 (33% metal sulfide) were found to be too non-conductive to be used as electrodes, and samples of composition 7:1 (87.5% metal sulfide) failed to maintain structural integrity and readily came apart in the molten salts.

The composite electrodes were prepared by mixing the metal sulfide and the polymer in the appropriate weight ratios. For each composite, the combined weight of the dry powders was 2 grams. The dry powders were placed in a 30 ml sample vial, and stirred until the material appeared a homogenous color. 15 ml of 4-methyl-2-pentanone (98%, Aldrich) was added to dissolve the polymer. The sample vial was sealed and stirred vigorously with a stir bar as the solution was slowly heated up to 60 °C. After approximately 2 hours of heating, the mixture became extremely viscous. The sample was removed from the heat, poured into a 2.5" diameter Al weighing boat, and air cured at room temperature for 24 hours. Samples were placed in a vacuum oven and dried an additional 36 hours under an active vacuum (approximately 10⁻³ torr) at 60 °C.

For all samples, the metal sulfide-polymer composites formed as strong, slightly flexible discs, approximately 2-3 mm thick. For all subsequent electrochemical measurements, the metal sulfide-polymer composites were cut into strips 0.5 cm wide, 1.5 cm long and approximately 0.2 cm thick. Electrical contact for these strips was made by clamping the top 0.5 cm of the strip with a flat mouthed copper alligator clamp, and only the bottom 0.7 cm of the strip was placed in contact with the ionic liquid.

Electrochemical Measurements

Cyclic voltammetry was measured using either an EG&G PAR 273A or 263A potentiostat/galvanostat and M270 ver.4.30 software. The reference electrode was Ag/AgBF₄ using a reference solution of 0.01M AgBF₄ in the respective molten salt. The
A reference electrode was separated from the cell by a wetted Vycor tip (Bioanalytical Non-Aqueous Reference Electrode). A ¼ “diameter graphite rod (Aldrich, 99.9995%, hardness 50) was used as the counter electrode. The surface area ratio of working to counter was 1:5. A 15 ml glass vial fitted with a Teflon cap (three ¼” holes) was used as the cell. All data was collected in a dry box under dry nitrogen. In order to measure the cyclic voltammetry of a 100% metal sulfide electrode, the metal sulfides were compressed for 2 hours in a 1/2” I.R. dye. The pellet was then clamped to a soldered copper connector and approximately 1/2 of the pellet was immersed in the molten salt. Charge-Discharge Experiments were also performed on an EG&G PAR 273A or 263A Potentiostat/galvanostat and M270 ver.4.30 software. For all samples, the charging current was adjusted such that the surface current density was approximately 0.8 mA/cm². Since only the bottom 0.7 cm of the strip was placed in the molten salt, the surface area was approximately 1.0 cm², so a charging current of 0.8 mA was applied. In all cases, the discharging current was 1/2 of the charging current. Finally, the working to counter surface area ratio was 1:5. Thus, 2.5 cm of a 1/4” diameter graphite rod was inserted into the molten salt as the counter electrode.

RESULTS AND DISCUSSION

Figure 1 shows the typical cyclic voltammograms observed for MoS₂ and TaS₂. Although only the cyclic voltammograms in EMIBF₄ are shown, both TaS₂ and MoS₂ behaved similarly in either molten salt. As can be seen, MoS₂ exhibited no electrochemical intercalation, and behaved as a simple resistor. TaS₂, on the other hand, exhibited some intercalation and deintercalation. However, due to its rapid exfoliation into solution, few details can be observed. Figures 2 and 3 show the intercalation behavior of TiS₂ in EMIBF₄ and DMPIBMF₄, respectively. In either molten salt, oxidative and reductive behavior similar to that observed for graphite rods can be seen. However, in both cases, the pure metal sulfide did rapidly exfoliate into solution. These cyclic voltammograms, therefore, only indicate the lack of MoS₂ reactivity, and the rapid exfoliating and intercalating behavior of TiS₂ and TaS₂.

Figure 4 shows the typical charge discharge behavior of the DMP⁺ cation, for the 4:1 TiS₂ (80% TiS₂) polymer composite electrode. Figure 5 shows the charge/discharge behavior of the BF₄⁻ anion for the 5:1 TiS₂ (83.3% TiS₂). For the anodic charging, the difference between the charging and discharging plateaus was -2.10 V to 1.05 V upon discharging. For the cathodic charging, no clearly defined charging plateau could be observed, although the approximate end point for charging reached a maximum value near 0.75 V. During discharging of the BF₄⁻, a plateau was typically observed near 0.20 V, and after discharging was completed, a final plateau of -0.25 V was observed. For both anodic and cathodic charge-discharge cycles, the system was considered discharged when the measured potential was equal to the median potential between the initial and final discharge potential plateaus.

The charge/discharge behavior of the BF₄⁻ anion in TiS₂ is somewhat surprising. Typically, these layered metal sulfides are known only for their ability to intercalate cation species. However, if the molten salt readily intercalates between the metal sulfide...
layers, then the excess molten salt, already present in the van der Waals Gap, serves to prevent direct interaction between the electron rich sulfur layers, and the negatively charged species. This may explain the lack of a well-defined anodic charging plateau. Discharging from this molten salt intercalated TiS₂ may occur as shown in the following equation (Equation 1).

\[
[\text{EMI}]_x[\text{BF}_4]_x\text{TiS}_2 \rightarrow ([\text{EMI}]_x[\text{BF}_4]_{x-1}) + \text{TiS}_2 + \text{BF}_4^-
\]  

[1]

Therefore, the overall ability of the molten salt to intercalate into these layered systems allows for this novel case of negatively charged guest species. Indeed, anion efficiencies of over 70% were observed for the 6:1 TiS₂-polymer electrode in DMPuBF₄, and 48% for the 5:1 TiS₂-polymer electrode in EMIBF₄. Figure 6 shows the peak charge/discharge efficiencies observed for all of the TiS₂ and TaS₂ polymer composite electrodes. Typically, a total of 20 charge/discharge cycles were run, and a constant value for the efficiency was observed after 4 or 5 cycles, which is the value reported.

Figure 7 shows a series of time delayed cation and anion charge/discharge experiments. For either ion, the TiS₂ polymer composite electrode was charged for 15 minutes, and the discharge cycle (at 1/2 the charging current) was delayed anywhere from 0 minute to 480 minutes. The data obtained for a simple graphite rod is also shown. As can be seen, the cation charge/discharge behavior is similar for both types of electrodes. However, for BF₄⁻, the TiS₂ maintained a much higher efficiency than the graphite rod as the time between charging and discharging increased, providing clear evidence that in the DIME System, the BF₄⁻ anion is not stable in a graphite matrix. This can be directly attributed to the interactions of fluorinated boron compounds in graphite (8,9,10).

**CONCLUSION**

Although previous work has typically referred to the intercalation of the substituted imidazolium ring into graphite, the highly disoriented nature of this guest species has made a detailed x-ray structural study of the intercalation products extremely difficult. However, the results of the electrochemical studies of these three different metal sulfide layers provides strong evidence that intercalation is occurring. For TiS₂, TaS₂ and graphite, exfoliation of these materials into the molten salt electrolyte is commonly reported (1). Unfortunately, without x-ray structural data, the argument can be made that the charging effects observed arise from insertion of the guest species into the graphite particles, without true insertion between individual layers occurring. For these three metal sulfide systems studied, only MoS₂ is considered to be nearly impossible to intercalate with large organic guest species. If only insertion between the individual grains of the layered materials was occurring, then similar charging effects should have been observed for MoS₂. However, this lack of charge/discharge efficiency for MoS₂, while TiS₂ and TaS₂ exhibit charging effects similar to graphite, clearly indicates that the charge/discharge efficiencies of the DIME systems arise from insertion of the substituted imidazolium ring into the van der Waals gap between the layers.

In general, the success of the TiS₂ composite electrodes also points out an alternative to the graphite electrode for the DIME System. The cation efficiencies are...
somewhat below that observed for graphite. However, the anion charge/discharge behavior clearly indicate that these, or possibly other layered sulfides, or possibly other layered dichalcogenides merit further investigation for possible application in the DIME Battery System.

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Figure 1. Cyclic voltammograms of TaS$_2$ and MoS$_2$ electrodes in EMIBF$_4$. Scan rate 20 mV/s, initial scan direction cathodic.

Figure 2. Cyclic voltammogram of TiS$_2$ electrode in EMIBF$_4$. Scan rate 20 mV/s, initial scan direction cathodic.
Figure 3. Cyclic voltammogram of TiS₂ electrode in DMPIBF₄. Scan rate 20 mV/s, initial scan direction cathodic.

Figure 4. DMPIT⁺ charge discharge behavior at a 4:1 TiS₂-polymer composite electrode in DMPIBF₄. Charging at 1.0 mA/cm², discharging at 0.5 mA/cm².
Figure 5. BF$_4^-$ charge discharge at a 5:1 TiS$_2$ polymer composite electrode in DMPBF$_4$. Charging at 1.0 mA/cm$^2$, discharging at 0.5 mA/cm$^2$.

Figure 6. Cation discharge efficiencies for TiS$_2$ and TaS$_2$ in EMIBF$_4$ and DMPBF$_4$. Charging at 1.0 mA/cm$^2$, discharging at 0.5 mA/cm$^2$.
Figure 7. Time delayed discharge efficiencies of DMPI$^+$ and BF$_4^-$ for the 85% TiS$_2$ PVD composite electrode and graphite rod electrodes.