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R.D. Rauh, R.A. Boudreau, M.E. Langmuir, T.L. Rose, M.A. Parker, and A.N. Scoville

July 1982

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INVESTIGATION OF INTERCALATED COMPOUNDS FOR PHOTOELECTROCHEMICAL ENERGY STORAGE

FINAL REPORT
February 23, 1981 - February 22, 1982

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July, 1982

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SUMMARY

Layered chalcogenides of general formula MX₂ were investigated for the storage of electrical energy generated by photoelectrochemical solar cells. These storage materials can be highly economical and have excellent volumetric energy densities allowing direct incorporation into flat plate photovoltaic modules. Two approaches were evaluated: 1) intercalation electrodes such as CuₓTiS₂ which can be charged by a separated regenerative photoelectrochemical cell; 2) "active" photointercalation/photodeintercalation cells in which the storage step is effected directly by irradiating a layered semiconducting photoelectrode.

A cell of the first kind was demonstrated consisting of an n-GaAs photoelectrode and TiS₂ intercalation electrode. The intercalant was Cu in an acetonitrile-tetrabutylammonium chloride electrolyte. During the charging reaction, CuCl₂⁻¹ was oxidized to CuCl₄⁻² at the n-GaAs photoanode and reduced to CuₓTiS₂ at the cathode. The best results were obtained with TiS₂ which had been pressed onto Ta exmet. The cell was charged under tungsten lamp irradiation of 40 mW/cm² until the TiS₂ was 36% utilized. The spontaneous discharge cycle was continued until 64% of the stored charge was recovered. The major problem encountered in the cycling experiments was deterioration of the physical structure of the TiS₂ electrode, although the system itself appears to be chemically reversible between 0<x<0.6.

A new electrode bonding procedure based on presintered MX₂/Teflon/graphite mixtures was developed which produced much more robust electrodes. Use of VSₑ₂ as the intercalation material resulted in a spontaneous intercalation rate of Cu in aqueous solutions which was almost 6 times that obtained for TiS₂.

Studies of "active" photointercalation devices were made on four single crystal semiconducting layered dichalcogenides: HfS₂, HfSe₂, ZrSe₂, and ZrS₂. These were prepared as single crystals by iodine vapor transport. The photoelectrochemical properties of the four compounds were measured in electrolytes with different redox potentials. HfS₂ and ZrSe₂ showed both p- and n-type photoresponse indicative of nearly intrinsic, highly compensated type material. No photoresponse was observed with the ZrS₂ crystals. Cu was spontaneously intercalated into HfS₂ in aqueous solution. As the intercalation progressed towards 0.5 equivalent/mole passed, the photovoltage and photocurrent increased and the crystal showed pronounced n-type character. After passage of more current, the crystal became more metallic with resulting decreases in photoresponse. Similar results were obtained for spontaneous intercalation of Li in HfS₂ crystals in propylene carbonate electrolytes.
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1.1 INTRODUCTION

Layered compounds are assuming an important position as materials for energy storage and solar energy conversion. The largest and most useful group of these compounds is the metal dichalcogenides, having the general formula MX2 (e.g., TiS2, WSe2, etc.). Their structure is largely two-dimensional; in analogy to graphite, the metal and chalcogenide atoms are ordered into separate planes. Electrical properties are anisotropic, with conduction highly favored in the direction parallel to plane stacking. The compounds tend to be metals, semimetals or semiconductors, depending on the d electron population of the central metal and its hybridization gap.

The purpose of this program was to investigate applications of intercalation compounds to photoelectrochemical energy storage. Two approaches were investigated. In the first approach, which we refer to as a passive intercalation photoelectrochemical storage cell, the layered compounds are metallic and act only to store the electrical energy produced by a conventional regenerative photoelectrochemical cell. During the contract period a number of half-cell experiments were run with TiS2, VSe2, HfSe2, and TiSe2 as passive intercalation electrodes using Cu, Fe and Ni as the intercalant. Experiments were run in both aqueous and CH3CN solutions utilizing counter electrodes of the material to be intercalated. These cells provided the information necessary to select usable cell couples giving net photoelectrochemical energy storage in a reversible intercalation system. Using this information, a photoelectrochemical cell of the following configuration was used to demonstrate intercalation energy storage

\[
\begin{array}{c|c|c|c}
\text{n-GaAs} & \text{CH3CN}^+ & \text{CH3CN}^- & \text{TiS}_2 \\
\hline
\text{CuCl}_2^{-1} & \text{CuCl}_2^{-1}
\end{array}
\]

This cell was charged by irradiating the n-GaAs with a tungsten lamp source and then spontaneously discharged. The cycle returned 64% of the stored energy. The major problem encountered in the cycling experiment was physical deterioration of the TiS2 electrode pressed onto the Ta Exmet screen.

The second approach uses an active intercalation cell which involves direct photointercalation or photodeintercalation of the energy storing electrode. The photointercalation approach has been described recently by Tributsch, and direct photointercalation has been demonstrated for ZrSe2 (1). The device would accomplish both photoconversion and storage at the illuminated, intercalating electrode, which must have semiconducting properties. If MX2 is a p-type semiconductor, the intercalation can be promoted photoelectrochemically with the appropriate choice of the intercalant, A. The reduction of A+ to A(MX2) must occur at low enough voltage relative to V(A+2/A+) (50.7V) to be accomplished by the photoelectrode.
Single crystal semiconducting layered dichalcogenides of HfS$_2$, HfSe$_2$, ZrS$_2$ and ZrSe$_2$ were grown by iodine vapor transport. The photoelectrochemical properties were measured in a variety of intercalating and non-intercalating electrolytes. HfS$_2$, HfSe$_2$ and ZrSe$_2$ showed both p- and n-type photoresponse, indicative of nearly intrinsic, highly compensated type material. No photoresponse was observed for ZrS$_2$. Doping with arsenic or excess chalcogenides either had no effect or led to poorer electrical characteristics. Spontaneous intercalation of Cu, Fe and Li initially produced increased photovoltage and photocurrent responses reflecting more pronounced n-type character. For all the intercalants, the photoresponse was lost when the chalcogenides were intercalated to mole fractions greater than 0.4, indicating the formation of a degenerate semiconductor or metallic phase.
2.1 SYNTHESIS AND PHOTOELECTROCHEMICAL EVALUATION OF MX\textsubscript{2} SINGLE CRYSTALS

2.1.1 Single Crystal Growth of Dichalcogenides

2.1.1.1 HfS\textsubscript{2}

Single crystals of HfS\textsubscript{2} were grown by iodine vapor transport of HfS\textsubscript{2} powder (99.9%) obtained from Cerac. In the first run, approximately 1g of the powdered compound was sealed under vacuum in a quartz tube (1.6 cm i.d., 20 cm length) along with 5 mg I\textsubscript{2}/cm\textsuperscript{3} tube volume. The tube was placed in a two-zone tube furnace with a linear temperature gradient of about 5\textdegree{}C/cm. The charge zone was maintained at 900\textdegree{}C. After 6 days, a large number of microcrystals had formed in the growth zone. Since a few were large enough for preliminary electrochemical characterizations, the growth was terminated. These crystals were red-purple and had a layered structure with hexagonal geometry. The crystals were rinsed in methanol to remove I\textsubscript{2} and dried in air during which they showed no evidence of oxidation.

A second run was made with 0.5g of HfS\textsubscript{2} powder and a temperature profile with a sharp gradient between the growth and charge zones. The charge zone was 890\textdegree{}C and the growth region 825\textdegree{}C. After 60 hours, large crystals with areas of 0.4 to 0.6 cm\textsuperscript{2} were found in the growth region.

Arsenic Doped HfS\textsubscript{2}. An attempt was made to prepare by iodine vapor transport HfS\textsubscript{2} crystals doped with arsenic. The dopant choice was based on the successful doping of WSe\textsubscript{2} crystals with antimony to give p-type crystals (2). Arsenic metal (0.05 mole ratio) was added to 0.5g of HfS\textsubscript{2} in the quartz reaction ampule. The tube was placed in an oven with a temperature profile having a sharp gradient between the charge and growth zones. The charge zone was 890\textdegree{}C and the growth region 825\textdegree{}C. After 60 hours, significant material had transported but only small, well-shaped crystals were formed. No increase in the crystal size was obtained when the reaction was allowed to run an additional 100 hours. The small crystals were rinsed in methanol and dried. There was no obvious physical difference between doped and undoped crystals.

Cu\textsubscript{x}HfS\textsubscript{2}. Attempts to grow Cu intercalated HfS\textsubscript{2} crystals by iodine vapor transport were begun using the method of Boswell et al. (3). Cu metal, HfS\textsubscript{2} and I\textsubscript{2} were sealed under vacuum in a quartz tube. Initial attempts at growing the crystals with the charge and growth zones at 890\textdegree{}C and 815\textdegree{}C, respectively, produced no transport after three days. These temperatures had resulted in large crystal growth of HfS\textsubscript{2} in the absence of Cu. Increasing the temperature of the charge zone by 110\textdegree{}C and reducing the temperature difference between the two zones to 50\textdegree{}C (growth zone 950\textdegree{}C) resulted in growth of a few large crystals. Unfortunately, the heating element for the charge zone burned out before the transport was completed, and the crystals already grown were back transported.
Next the tube was placed in the furnace with the charge zone at 1065°C with a temperature difference of 30°C between zones. This was maintained for one week. However, no significant crystal growth was observed. At some point during the heating process, copper sulfides may have formed impeding formation of the intercalated HfS$_2$.

2.1.1.2 ZrSe$_2$

Crystals of zirconium diselenide were grown at Professor Aaron Wold's laboratory at Brown University. To facilitate preparation of crystals, the H-tube glass and quartz transfer vessel shown in Figure 1 was used. The device allows quantitative transfer of the iodine from the sealed capillary tube after the starting materials have been added and the tube evacuated to remove residual air and water vapor. The tube was filled with 0.1 mole of Zr and a stoichiometric amount of Se. Iodine (5 mg/cm$^3$) was added as the transport agent, and the tubes were sealed under vacuum. The temperature of the charge zone was held at 850°C; the growth zone was 40°C lower. After 10 days, approximately 20% of the material had transported and several large, well-formed crystals had formed in the growth zone. These crystals were metallic silver in appearance and had a layered structure with hexagonal geometry. The room temperature resistivity, measured by the 4-point probe technique with the current flowing perpendicular to the c-axis, i.e., in the plane of the layers, was found to be $\approx 10^{-4}$ ohm-cm.

In a second growth experiment, zirconium was mixed with a slight excess of Se to hinder the Zr from occupying Se vacancies during crystal growth. The charge zone was held at 950°C and the growth zone maintained at 900°C for nine days. These higher temperatures were used since there are some indications that higher growth temperatures lead to crystals with improved photovoltaic properties. Several large "rosettes" or clusters of crystals with an area $\approx 0.5$ cm$^2$ were formed as well as many smaller crystals.

Optical metallographs of two of these crystals are shown in Figure 2. In general, the surface of the ZrSe$_2$ crystals is very irregular with many smaller crystals growing on the surface of the larger crystal. In a few instances, large area crystals showed no surface defects. The resistivity of one of the larger ZrSe$_2$ crystals measured by the 4-point probe method gave a value of $10^{-3}$ ohm-cm perpendicular to the c-axis.

2.1.1.3 ZrS$_2$

Zirconium sulfide crystals were also grown at Brown University as described above. The H-tube was filled with 0.1 mole of Zr and a stoichiometric amount of sulfur with I$_2$ as the transport agent. The sulfide was initially heated with the charge zone at 900°C and a temperature gradient of 80°C. After 7 days, no transport had occurred, so the reaction zone was raised to 975°C with a 60°C temperature gradient. This regime was maintained for 3 days with no improvement in transport. However,
Fig. 1. H-tube transfer vessel for preparing samples for crystal growth by I₂ vapor transport (designed by R. Kershaw and A. Wold, Brown University). Scale about 1:5; overall height ~75 cm.
Fig. 2. Optical micrographs of ZrSe$_2$ crystals (50X).
large crystals had grown on the mass of ZrS<sub>2</sub> in the reaction zone. These crystals were irregularly formed and smaller crystals were attached to the face of each larger crystal.

2.1.1.4 HfSe<sub>2</sub>

Single crystals of HfSe<sub>2</sub> were prepared at EIC by I<sub>2</sub> vapor transport beginning with the powdered compound and a 0.1 mole ratio excess of Se. The excess Se should hinder the Hf from occupying Se vacancies which may arise during the crystal growth. The HfSe<sub>2</sub> crystals were grown from a charge of 0.5g of HfSe<sub>2</sub> and 0.01g Se. The sealed quartz tube was placed in a tube furnace having a temperature gradient of 2.4°C/cm between the charge and growth zones. The charge zone was maintained at 1065°C and the growth zone at 1035°C.

After one week, small (1-2 mm<sup>2</sup>), well-shaped crystals had formed in the growth zone. The silvery-black crystals were washed in methanol and dried. Metallographs of the crystals are shown in Figure 3. The HfSe<sub>2</sub> crystals are predominantly free of surface irregularities. Some of the areas showed red and blue coloration which is thought to be due to films formed by oxidation of the surfaces of the crystals.

2.1.2 Photoelectrochemical Evaluation of MX<sub>2</sub> Crystals

2.1.2.1 Fabrication of Electrodes with Single Crystals

Generally, electrodes were made from the dichalcogenide crystals by cementing one surface with conducting silver epoxy to a nickel disk which was spot-welded to a Ni wire. After the epoxy cured, the electrode was threaded through a length of capillary tubing and sealed in place with GC Electronics epoxy so that only the surface perpendicular to the c-axis was exposed to the electrolyte. For some electrodes, however, ohmic contact was made on one edge of the crystal to expose a larger area of the edges to the electrolyte. This method of mounting should improve the intercalation rates since intercalation occurs at the edges of the crystals.

2.1.2.2 Electrochemical Response of Single Crystal Electrodes

Single crystal electrodes were tested in a photoelectrochemical cell in a variety of aqueous and nonaqueous electrolytes. A three-electrode cell configuration was used. The photoresponse was measured when the crystal was illuminated by a tungsten-halogen lamp with an intensity of 80 mW/cm<sup>2</sup>. The direction of voltage shift was used to determine the type for most of the samples. Some crystals, however, had negligible photovoltages; for these samples, the type was sometimes apparent from the measured photocurrents.

The most extensive measurements were done with the HfS<sub>2</sub> crystals. The results are summarized in Table 1. Figure 4 shows a representative
Fig. 3. Optical micrographs of HfSe$_2$ crystals. Darker areas of crystal indicate regions of oxidation (50X).
Table 1. Photoelectrochemical response of HfS$_2$ single crystal electrodes in different electrolytes.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$E^0$ (V vs. SCE)</th>
<th>No. Electrodes Tested</th>
<th>Area (cm$^2$)</th>
<th>Photovoltage (mV)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M NaOH (aq)</td>
<td>-1.0</td>
<td>6</td>
<td>0.5–0.24</td>
<td>-6 to -30</td>
<td>n</td>
</tr>
<tr>
<td>S$^{-2}$/S$^2_2$</td>
<td>-0.72</td>
<td>1</td>
<td>0.24</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0.5M NaCl (aq)</td>
<td>-0.65</td>
<td>3</td>
<td>0.11–0.24</td>
<td>-9 to +3</td>
<td>n,p</td>
</tr>
<tr>
<td>Fe$^{II}$/Fe$^{IV}$ (CH$_3$CN)</td>
<td>-0.60</td>
<td>1</td>
<td>0.09</td>
<td>-9</td>
<td>n</td>
</tr>
<tr>
<td>PQ$^{2+}$/PQ$^{2+}$ (CH$_3$CN)</td>
<td>-0.60</td>
<td>2</td>
<td>0.07;0.09</td>
<td>0 to +1</td>
<td>p</td>
</tr>
<tr>
<td>0.1M HCl (aq)</td>
<td>-0.3</td>
<td>3</td>
<td>0.11–0.24</td>
<td>1 to +15</td>
<td>p$^2$</td>
</tr>
<tr>
<td>Cu$^{+2}$/Cu$^{+}$ (aq)</td>
<td>+0.1</td>
<td>2</td>
<td>0.11</td>
<td>+11 to +14</td>
<td>p$^2$</td>
</tr>
<tr>
<td>Cu$^{+2}$/Cu$^{+1}$ (CH$_3$CN)</td>
<td>+0.35</td>
<td>2</td>
<td>0.11;0.24</td>
<td>+2 to +56</td>
<td>p</td>
</tr>
<tr>
<td>Fe$^{III}$/Fe$^{+2}$ (aq)</td>
<td>+0.51</td>
<td>2</td>
<td>0.11;0.24</td>
<td>-29 to +8</td>
<td>n,p</td>
</tr>
<tr>
<td>I$^{-}$/I$_3^-$   (CH$_3$CN)</td>
<td>+0.6</td>
<td>2</td>
<td>0.07;0.09</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

$^1$The $E^0$ redox values given for the NaOH, NaCl and HCl solutions are for the H$^+/H_2$ couple.

$^2$Results for HfS$_2$ crystals grown in presence of As.
Fig. 4. Current-voltage curve for single crystal HfS$_2$ illuminated by 80 mW.cm$^{-2}$ light from tungsten-halogen lamp. Electrolyte was 0.1N NaOH, scan rate 25 mV.sec$^{-1}$. Dark current indicated by chopped signal.
cyclic voltammogram of an illuminated crystal. The HfS₂ crystals generally showed a change in type from n to p as the redox couple of the electrolyte became more positive. In some cases, different crystals gave either a p- or an n-type response in the same electrolyte. Large dark currents and both anodic and cathodic photocurrents characterized many of the crystals. These results are consistent with the Fermi level of the HfS₂ crystals lying about mid-gap. As seen from Table 1, the crystals grown in the presence of As showed essentially the same photoelectrochemical behavior as those grown in the absence of As.

A few measurements were made on the HfSe₂.1, ZrSe₂ and ZrS₂ crystals. No photoresponse was observed for the ZrS₂ crystals. The results for the other two crystals are given in Table 2. Only p-type response was observed for the HfSe₂.1 crystals. The ZrSe₂ showed both types of behavior as was observed for the HfS₂ crystals. Most of the literature results report n-type behavior for the group IV-B dichalcogenides (1,4,5), although Tributsch observed p-type photoresponse for some ZrSe₂ samples (1). The Zr and Hf diselenides grown with a slight excess of selenium were very unstable in aqueous electrolytes. A selenium film formed on the surface of the crystals with the passage of any anodic current. This film passivates the semiconductor and governs the subsequent electrochemical behavior. No photoresponse could then be observed for these crystals in aqueous electrolytes.

Table 2. Summary of photovoltage behavior of HfSe₂.1 and ZrSe₂ crystals in aqueous electrolytes.

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Area (cm²)</th>
<th>Electrolyte</th>
<th>E°²</th>
<th>Range Vph(mV)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfSe₂.1</td>
<td>0.05-0.24</td>
<td>0.1M NaOH Cu⁺²/Cu⁰</td>
<td>-1.0</td>
<td>0 to 8</td>
<td>p</td>
</tr>
<tr>
<td>(6)</td>
<td></td>
<td>Cu⁺²/Cu⁰</td>
<td>+0.10</td>
<td></td>
<td>p</td>
</tr>
<tr>
<td>ZrSe₂</td>
<td>0.05-0.12</td>
<td>0.1M NaOH</td>
<td>-1.0</td>
<td>-16 to +60</td>
<td>n,p</td>
</tr>
<tr>
<td>(4)</td>
<td></td>
<td>0.1M HCl Fe⁺³/Fe⁺²</td>
<td>-0.30</td>
<td>+1 to +16</td>
<td>p</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe⁺³/Fe⁺²</td>
<td>+0.51</td>
<td>-1 to +1</td>
<td>n,p</td>
</tr>
</tbody>
</table>

¹Number in parenthesis is number of crystal samples tested
²E° are the redox values for 2H⁺/H₂ for NaOH and HCl solutions vs. SCE.
3.1 PASSIVE INTERCALATION CELLS

3.1.1 General System Considerations

Passive intercalation cells for photoelectrochemical storage make use of an intercalating counter electrode for energy storage. The electrolyte in these cells must contain ions of the intercalant which can be cycled reversibly between two upper oxidation states, e.g., \( A^{+2/+1} \). Thus, the reaction at the photoanode would be

\[
A^{+1} \xrightarrow{hv} A^{+2} + e^-
\]  

(1)

At the intercalating counter electrode, the reduction of \( A^+ \) would occur, viz:

\[
A^+ + \frac{1}{x} MX_2 + e^- \rightarrow \frac{1}{x} A_xMX_2
\]  

(2)

For the sum of half reaction (1) and (2), \( \Delta G \) would be greater than zero, but attainable at the voltage delivered by the photoelectrode. Any excess power delivered by the cell could be extracted directly as electricity. In practice, this type of cell would require an ion exchange membrane separating the anode and cathode compartments, to prevent the self-discharge reaction

\[
A^{+2} + \frac{1}{x} A_xMX_2 \rightarrow 2A + \frac{1}{x} MX_2
\]  

(3)

When discharge of the cell is desired, a metallic or carbon electrode in the photoanode compartment would act as the substrate for the reduction of \( A^{+2} \) while oxidation of \( A_xMX_2 \) occurs at the counter electrode.

The electrochemical requirements for such a system involving a one electron transfer are illustrated in Scheme I.

Here it is seen that \( V(A^{+n}/A^{+n+1}) \) has a voltage positive of the \( A^{+n}/O \) reaction. This relationship is a general requirement for intercalation; otherwise, \( A^{+n} \) would spontaneously deintercalate and \( MX_2 \) would act merely as a substrate for the \( A^{+n}/O \) reaction. For example, the intercalation of Li into TiS\(_2\) takes place some 2V positive of the Li\(^{+1}/0\) potential. Therefore,
we note the following requirements for an intercalation storage device driven by light:

- The couple $A^{n+1}/A^n$ must be very soluble in the electrolyte and must stabilize the photoanode against oxidative decomposition.
- The intercalation of $A^n$ into $MX_2$ must be spontaneous with respect to the $A^n/O$ reaction.
- For a cell that operates without external bias, $\Delta V_{\text{cell}}$ (under illumination) $> V_{\text{stor}}$.

We have identified several metal ion redox systems that have potential to fulfill the above requirements. Two of these are the $Cu^{2+}/Cu^{+1}$ and the $Fe^{3+}/Fe^{2+}/O$ redox systems. Each can be employed in a storage cell having energetics encompassed in Scheme I, although the potentials are strongly coupled to the solvent and ligands surrounding the ions and to the intercalation compound employed for storage.

The intercalation electrode will be combined with a n-GaAs photoelectrode to form the passive photoelectrochemical cell (PEC) with storage. Considerable work has been done at EIC with the n-GaAs/Cu$^{2+}/Cu^{+1}$ system in acetonitrile (ACN)(6). The important characteristics of this system are summarized briefly here.

The redox potential of the $Cu^{2+}/Cu^{+1}$ couple in acetonitrile is strongly influenced by the complexing strength of the anion present in solution. In the presence of noncomplexing anions such as perchlorate or tetrafluoroborate, the $Cu^{2+}/Cu^{+1}$ redox couple does not stabilize n-GaAs against lattice decomposition in acetonitrile. In the presence of chloride ion, which complexes both ions, stable photocurrents are obtained. To date, the best photoelectrochemical cell parameters achieved with this electrolyte at 80 mW/cm$^2$ light intensity (tungsten-halogen lamp) are: short circuit current density = 19 mA/cm$^2$, open circuit voltage = -0.73V vs. Cu(II)/Cu(I)/Pt, maximum power 3.78 mW/cm$^2$ at -0.35V, and light to electrical power conversion efficiency of 4.8%. The electrolyte in this case was 0.4M Cu(I), 0.05M Cu(II) in 1M tetrabutylammonium chloride (TBAC) in acetonitrile. In this solution, the stable Cu(I) species is CuCl$_2^{-1}$ and Cu(II) is 90% CuCl$_4^{-2}$ and 10% CuCl$_3^{-1}$.

The potential of the n-GaAs PEC under these conditions is suitable to drive the intercalation reaction of Cu(I) into TiS$_2$, as shown in Scheme II:
provided the iR drop between the electrodes is not excessive. The capacity and intercalation rate of the TiS$_2$ electrode must be matched to the average current density supplied by the photoelectrode. It is also necessary to avoid the self-discharge reaction:

$$\text{Cu}_x\text{TiS}_2 + \text{Cu(II)} \rightarrow 2\text{Cu(I)} + \text{TiS}_2$$

(4)

by providing a cation exchange membrane between the photoelectrode and the storage electrode compartments.

### 3.1.2 Fabrication of Pressed Powder Electrodes

Teflon-bonded MX$_2$ electrodes were fabricated. For the first electrodes tested, the MX$_2$ was thoroughly mixed with 10-15% Teflon powder and 0-15% AGM graphite. The mixture was pressed on 1 cm$^2$ Ni or Ta Exmet screens at about 6000-10,000 lbs for 2-3 minutes. The finished electrodes contained 0.08-0.09 g of MX$_2$.

Because these electrodes tended to deteriorate during the cycling experiments, a new procedure was developed to fabricate paste electrodes with more structural integrity. A slurry of AGM graphite and TFE 30 Teflon dispersion in H$_2$O was heated at 110°C overnight to remove the H$_2$O and then sintered at 250°C under argon for two hours. This sintering process forms a fine network of Teflon in graphite. The semiconductor powder was then incorporated into the putty-like Teflon mixture using CH$_3$CN as a solvent to form a thick paste. The paste was spread onto Ta screen and then pressed between paper towels at 15,000 lbs for 5 minutes. Finally, the electrodes were held under vacuum for several hours to remove all of the solvent.

Hafnium diselenide and zirconium diselenide pressed pellet electrodes were prepared from powders of the compounds obtained from Cerac. Approximately 0.25 g of the compound was loaded into a circular, tempered, steel die, 8 mm in diameter, and pressed in a Carver press. The cylindrical
Fig. 5. Plot of open circuit voltage and average current density during spontaneous intercalation of Cu into TiS$_2$:Teflon electrode in aqueous CuSO$_4$ solution.
Table 3. Cell parameters for spontaneous intercalation of Cu into dichalcogenides in aqueous electrolytes.\(^1\)

<table>
<thead>
<tr>
<th>Dichalcogenide</th>
<th>(V_{OC}) (V vs Cu/Cu(^+))</th>
<th>(J_{SC}) (mA/cm(^2))</th>
<th>Charge Passed (coulombs)</th>
<th>% Utilization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>VSe(_2)</td>
<td>0.135</td>
<td>0.089</td>
<td>2.7</td>
<td>0.5</td>
</tr>
<tr>
<td>TiSe(_2)</td>
<td>0.161</td>
<td>0.025</td>
<td>3.5</td>
<td>0.02</td>
</tr>
<tr>
<td>TiS(_2)</td>
<td>0.225</td>
<td>0.05</td>
<td>0.4</td>
<td>0.015</td>
</tr>
<tr>
<td>HfS(_2)</td>
<td>0.184</td>
<td>0.08</td>
<td>0.4</td>
<td>0.022</td>
</tr>
</tbody>
</table>

\(^1\)0.05M Cu solution; copper flag used as counter electrode. All electrodes had an area of 0.5 cm\(^2\) and a loading of \(\approx 7 \times 10^{-5}\) moles of MX\(_2\).
pellets had shiny metallic surfaces. Pellets were also prepared from a 90% ZrSe$_2$/10% graphite mixture under the same conditions as the pure materials. The pure pellets were very resistive (10$^5$-10$^6$ ohm-cm) as expected for undoped, packed powder samples. The addition of C to the ZrSe$_2$ reduced the resistivity of the pellets by three orders of magnitude.

3.1.3 Intercalation of Cu into Dichalcogenides in Aqueous Electrolyte

The intercalation of Cu into a TiS$_2$ pressed powder electrode in aqueous solutions of 0.5M CuSO$_4$ was chosen as the first test system. Whittingham has reported that Cu$^{+2}$ can be electrochemically reduced onto TiS$_2$ from aqueous solution, resulting in Cu$_x$TiS$_2$, although no details were given (7). Scrosati and co-workers have also reported continuous cycling of Cu$_x$TiS$_2$ between $x=0.4$ and 0.8 (8). A TiS$_2$:Teflon electrode pressed onto Ni Exmet was studied in a two-electrode cell with a copper flag as the counter electrode. The electrodes were shorted through a Keithley picoammeter, and the current was continuously monitored on a strip chart recorder. At periodic intervals, the open circuit potential was measured after allowing one-half to one hour for equilibration. During the intercalation the open circuit voltage vs. Cu$^+$/Cu reference dropped from 0.20V to 0.025V and the current density dropped from 0.52 mA/cm$^2$ initially to 0.06 mA/cm$^2$. A plot of the changes in these parameters during the intercalation is given in Figure 5.

Assuming all the charge passed resulted in intercalation of Cu, the mole fraction of Cu in the TiS$_2$ could be calculated. The calculated mole fraction of Cu in the TiS$_2$ was 0.87 when the intercalation was stopped. As a check, the amount of copper lost from the copper electrode at the end of the reaction was measured by atomic absorption spectroscopy and indicated that 20% less copper had reacted than calculated from the current measurement. The agreement, however, is within the experimental uncertainty of the two measurements.

A study was done of the comparative reaction rates of Cu intercalation into four intercalation materials: VSe$_2$, TiSe$_2$, HfS$_2$ and TiS$_2$. Pressed powder electrodes made with the improved paste technique were used. The area of all the electrodes was 0.5 cm$^2$. The loading of the electrode was adjusted so that they all contained $\approx 7 \times 10^{-5}$ moles of the dichalcogenide. The cell consisted of the intercalation electrode and copper foil for the counter electrode. There was no deterioration of the pressed electrodes even with the passage of current equivalent to the intercalation to Cu$_{1.3}$MX$_2$. The current and open circuit voltage was monitored as described above.

The cell parameters for the four dichalcogenides are given in Table 3. The intercalation of the selenides was continued to Cu$_{1.3}$MSe$_2$, while the slower sulfide intercalation was stopped when Cu$_{0.8}$MS$_2$ was reached. The VSe$_2$ material retains the highest rate of intercalation over the longest period of time. Moreover, the voltage shows a less precipitous
drop during intercalation than did the other materials investigated. The short circuit current, $J_{SC}$, and the $V_{OC}$ for the VSe$_2$ electrode is plotted in Figure 6.

It was of interest to check if the high intercalation rate observed for Cu into VSe$_2$ in aqueous sulfate solutions would also be obtained for the Cu(I)Cl$_2^-$ in CH$_3$CN. The results of spontaneous intercalation of VSe$_2$ in 0.4M CuCl in 1M tetrabutylammonium chloride in CH$_3$CN is given in Figure 7. The loading is slightly higher for this electrode than the one for which the results are shown in Figure 6. Even with the higher load taken into account, however, a very high current density for intercalation is obtained, although the decrease with intercalation is somewhat more marked than in the aqueous sulfate solution. The current is again an order of magnitude larger than observed with TiS$_2$ after correcting for the electrode size and loading (vide infra, Figure 8). The voltage drop with intercalation was much steeper in CH$_3$CN than in the aqueous solution but began at a much larger value of 0.43V compared to 0.14V in aqueous solution. VSe$_2$, therefore, appears to be a promising material for coupling with the GaAs photoelectrochemical cell, but no experiments with the n-GaAs/VSe$_2$ full cells were done during the contract period.

3.1.4 Intercalation of Copper into TiS$_2$ in Acetonitrile

The spontaneous intercalation of Cu into TiS$_2$ in ACN was measured in an electrolyte of 0.1M CuClO$_4$ and 0.1M tetrabutylammonium perchlorate (TBAP) using the same experimental setup as for the spontaneous intercalation in aqueous solution. Plots of the potential and the current density vs. the mole fraction of Cu intercalated (based on the current passed) are given in Figure 8. Significantly, a larger voltage drop is observed in ACN than in the aqueous electrolyte (compare Figures 8 and 5). In both electrolytes, the region where the voltage is relatively constant with increasing mole fraction begins at 0.2 mole fraction Cu. The spontaneous current in the aqueous solution is about a factor of 5 higher than in the acetonitrile solution. The current density was less than 10 $\mu$A/cm$^2$ when the intercalation was stopped.

In order to obtain some estimate of the charging rates at which the TiS$_2$ electrodes could be intercalated as well as the reversibility of the intercalation-deintercalation reaction, galvanostatic recycling of the TiS$_2$:Teflon pressed powder (no carbon) electrodes was studied. The cycling runs were made at a current density of 0.3 mA/cm$^2$ in the cell:

\[
\begin{array}{c|c|c|c}
\text{TiS}_2 & 0.1M \text{CuClO}_4 & \text{TiS}_2 & 1M \text{TBABF}_4 & \text{Cu} \\
\hline
\text{1M TBABF}_4 & \text{Cu} & \text{in CH}_3\text{CN} & \\
\end{array}
\]

where TBABF$_4$ is tetrabutylammonium tetrafluoroborate. Initially, two coulombs of charge were passed and the rapid drop in potential from +0.625 to +0.25V vs. Cu$^{+1}$/Cu$^0$ was completely reversible. For the amount of charge passed, only a small fraction of the TiS$_2$ in the
Fig. 6. Plot of equilibrated open circuit voltage (left axis) and current density (right axis) during spontaneous intercalation of Cu in aqueous electrolyte into VSe$_2$ pressed powder electrode.
Fig. 7. Spontaneous intercalation of Cu in acetonitrile electrolyte into VSe$_2$ pressed powder electrode. Equilibrated open circuit voltage is plotted on left axis and current density on the right axis.
Fig. 8. Plot of open circuit voltage and average current density during spontaneous intercalation of Cu into TiS$_2$:Teflon:graphite electrode, 0.1M TBAP in ACN.
electrode could have been intercalated. Allowing the potential to drop to +0.15V by passing an additional 2 coulombs, showed that the initial drop in voltage was no longer reversible and that the charge passed was dedicated to plating and stripping CuO at the surface only. After passage of 6 coulombs, only stripping of Cu from the surface occurs on reversal. An electrode which had passed 11 coulombs of reduction current was dis-assembled and examined. The surface had changed in appearance, but the interior was the same as the starting material. The lack of capacity of the electrode for reversible intercalation may have been due to unfavorable morphology of the electrode and/or to a current density which exceeded the diffusion rate of Cu into the TiS2 lattice.

Earlier studies at EIC have shown that n-GaAs photoelectrode is not stabilized in perchlorate-acetonitrile solutions with the Cu^{+2}/+1 couple (4). Stable photocurrents are obtained, however, in chloride solutions. Since the proposed prototype passive intercalation cell will use GaAs as the photoelectrode, several experiments were run to evaluate the intercalation of Cu into TiS2 in a chloride-acetonitrile electrolyte.

A cyclic voltammogram of a cell with a pressed TiS2:Teflon:graphite electrode is given in Figure 9. The electrolyte was 0.5M CuCl in acetonitrile with 1M tetrabutylammonium chloride as supporting electrolyte. The cell was a two-electrode system with a copper flag serving as the reference and counter electrode. The initial $V_{OC}$ of the cell was 0.576V vs. Cu^{+1}/O. The cathodic current at potentials positive of the Cu^{+1}/O potential indicates that the reduction of the Cu(I) chloride complex to CuO occurs more easily on TiS2 than on Cu itself and that intercalation of Cu into the TiS2 is probably proceeding.

The cell potential was then held at +0.2V which is positive enough to insure that no direct plating of Cu metal on the electrode surface is possible. The current was monitored and the open circuit potential measured periodically, as discussed above. The reaction was allowed to proceed until the current in the stirred cell fell to zero and the $V_{OC}$ became constant. A portion of the electrode material was analyzed for Cu, Ti and total inert solids, i.e., C and Teflon. The Cu to Ti ratio would correspond to an intercalated compound with the stoichiometry of Cu$_{0.6}$TiS$_2$. The x-ray diffraction pattern of the electrode material did show additional diffraction lines from those expected for pure TiS2 or Cu, but the exact degree of intercalation could not be determined.

The spontaneous intercalation of Cu into TiS2 was tested with four pressed powder electrodes in the chloride electrolyte described above. Three of these were TiS2 pressed onto Ni Exmet and the fourth was pressed onto Ta screen. The cell parameters are summarized in Table 4. The TiS2 electrodes on Ni screen had similar open circuit voltages and all gave similar behavior on charging. One of these electrodes (#57-6) was discharged after being stored in dry Ar for several weeks. The electrode
Fig. 9. Cyclic voltammogram of TiS$_2$:Teflon:graphite electrode in 0.5M Cu(I), 1M TBAC in ACN.
Table 4. Cell parameters for spontaneous intercalation of Cu into TiS<sub>2</sub> in CuCl-ACN electrolyte.

<table>
<thead>
<tr>
<th>Electrode No.</th>
<th>Charge or Discharge</th>
<th>( V_{OC} ) (V vs Cu&lt;sup&gt;0&lt;/sup&gt;/Cu&lt;sup&gt;+&lt;/sup&gt;)</th>
<th>( J_{SC} ) (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>Charge Passed (coulombs)</th>
<th>% Utilization</th>
</tr>
</thead>
<tbody>
<tr>
<td>57-5</td>
<td>C</td>
<td>0.45</td>
<td>0.7</td>
<td>5.0</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.29</td>
<td>0.2</td>
<td>1.0</td>
<td>4.7</td>
</tr>
<tr>
<td>57-6</td>
<td>C</td>
<td>0.47</td>
<td>0.15</td>
<td>4.6</td>
<td>21</td>
</tr>
<tr>
<td>57-3</td>
<td>C</td>
<td>0.48</td>
<td>0.65</td>
<td>3.6</td>
<td>22</td>
</tr>
<tr>
<td>#5</td>
<td>C</td>
<td>0.62</td>
<td>3.1</td>
<td>13.2</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.14</td>
<td>-</td>
<td>2.2</td>
<td>3.6</td>
</tr>
</tbody>
</table>

<sup>1</sup>Electrodes pressed onto Ni Exmet of area 2 cm<sup>2</sup> except #5 which was pressed onto Ta screen and had an area of 6.4 cm<sup>2</sup>. 
was returned to the same electrolyte and potentiostatted at its original rest potential before intercalation (0.45V vs. Cu\(^0\)). The current was recorded versus time. From time to time the process was halted, and the open circuit potential was measured after ½ hour equilibration in the stirred solution. At first, it appeared to behave as expected for de-intercalation and the equilibrated \(V_{OC}\) rose to 0.4V. After passage of about 1 coulomb, the pressed electrode fell apart and the experiment was terminated.

The TiS\(_2\) electrode on Ta screen had a larger open circuit voltage and greater change in voltage upon intercalation than the electrodes on Ni screen. The change in equilibrated open circuit voltage and current for the charge and discharge are shown in Figure 10. A 21.4% utilization of TiS\(_2\) was obtained during charge. Discharge proceeded as expected; however, the current fell off rapidly and the reaction was stopped after only 3.63% of the Cu was recovered. The TiS\(_2\) was observed to have fallen off the screen. While the reversibility of the reaction was proven, a more robust chalcogenide electrode will have to be developed for use in long term cycling experiments.

### 3.1.5 Intercalation of Ni and Fe into TiS\(_2\)

One of the possible configurations of a passive intercalation cell might use two intercalation electrodes with different redox potentials as an "intercalation battery." Some preliminary experiments were performed with Ni and Fe intercalation onto TiS\(_2\) in CH\(_3\)CN to measure their redox potentials. Anhydrous NiCl\(_2\) was dissolved in CH\(_3\)CN to give a pale blue solution due to formation of the NiCl\(_4^{-2}\) complex ion. The reduction potential for the complex to Ni is \(0.637\)V vs. the Ag\(^+\)/Ag\(^0\) reference. Reduction to Ni on the TiS\(_2\) electrode occurred \(+0.15\)V anodic of the NiCl\(_4^{-2}\)/Ni\(^0\) potential. Cyclic voltammetry, however, showed that the reduction potential occurred at increasingly anodic potentials with successive sweeps which is atypical for intercalation reactions.

The intercalation of Fe into TiS\(_2\) was done with two different Fe complexes in CH\(_3\)CN solution. A saturated solution of K\(_4\)Fe(CN)\(_6\) in CH\(_3\)CN and 0.5M tetrabutylammonium tetrafluoroborate was prepared. The Fe concentration in the solution was only about \(4 \times 10^{-5}\)M. The redox potential for the Fe(CN)\(_6^{-4}\)/Fe\(^0\) couple was \(-0.35\)V vs. the Ag/Ag\(^0\) reference. The potential for the reduction on the TiS\(_2\) electrodes began at \(+0.26\)V vs. the Fe foil used as the counter electrode. After 80 minutes, the voltage had dropped to zero and the current leveled off at 10 \(\mu\)A. From the current passed, about \(0.5 \times 10^{-6}\) moles of Fe had been reduced (intercalated?), corresponding to a mole fraction of Fe in the TiS\(_2\) of only \(2.5 \times 10^{-4}\). When the cell was left at open circuit overnight, the open circuit potential rose to \(+0.20\)V. The small currents may indicate that the intercalation reaction is being limited by the low concentration of Fe(II) in solution.
Fig. 10. Plot of voltage (left scale) and current (right scale) as function of time for charging and discharging TiS$_2$ electrode on Ta Exmet. Note that the plot of charging current has been reduced by a factor of four.
The other Fe complex investigated was Fe(II)Cl\textsubscript{x}2-x. A saturated solution of Fe(ClO\textsubscript{4})\textsubscript{2} in CH\textsubscript{3}CN with 1M tetrabutylammonium chloride was prepared to give a pale yellow solution of 0.25M iron. Since the Fe(II) complex is colorless, the yellow color is attributed to the presence of the Fe(III) species. The results of a spontaneous intercalation of Fe into TiS\textsubscript{2} in this solution is shown in Figure 11. The initial current was large, 0.3 mA/cm\textsuperscript{2}, but decayed very rapidly to <0.08 mA/cm\textsuperscript{2}. The initial Voc of 0.4V vs. Fe(II)Cl\textsubscript{x}2-x/Fe\textsuperscript{0} dropped rapidly along with the current. As the reaction proceeded, the electrolyte at first became paler and then darker becoming a dark brown after 300 minutes. A black deposit was also observed forming the Fe counter electrode. It appears, therefore, that Fe(III) was being formed during the reaction.

Several cyclic voltammograms were run on a solution of 5 x 10\textsuperscript{-3}M Fe(ClO\textsubscript{4})\textsubscript{2} dissolved in CH\textsubscript{3}CN with 0.02M tetrabutylammonium chloride and 0.1M tetrabutylammonium tetrafluoroborate. The cyclic voltammograms showed that some Fe(III) complex was present and that the Fe(III)Cl\textsubscript{x}3-x/Fe(II)Cl\textsubscript{x}2-x reduction potential was at -0.27V vs. Ag\textsuperscript{+}/Ag\textsuperscript{0} reference. The reduction potential of Fe(II)Cl\textsubscript{x}2-x to Fe\textsuperscript{0} was about -0.58V vs. Ag\textsuperscript{+}/Ag\textsuperscript{0}.

3.1.6 n-GaAs/TiS\textsubscript{2} Full Cells

Three experiments were done with the passive intercalation cell:

\[
\begin{array}{c|c|c|c}
\text{n-GaAs} & 0.4M \text{CuCl} & 0.4 \text{CuCl} & \text{TiS}_2 \\
 & 0.05M \text{CuCl}_2 & \text{1M TBAC} & \text{1M TBAC} \\
 & \text{ACN} & \text{ACN} & \\
\end{array}
\]

The following general procedure was used for all the experiments. The Pyrex cell designed to make complete cell measurements is shown in Figure 12. One compartment holds the n-GaAs semiconductor electrode and a Pt electrode for use in discharging the cell. A Pyrex window allows illumination of the GaAs. The TiS\textsubscript{2} intercalating electrode is in the other compartment along with a Cu wire reference electrode. The two sides of the cell are joined by an O-ring joint between which is clamped an ion exchange membrane which will keep the oxidized Cu(II) ions formed in the semiconductor compartment from reaching the intercalated TiS\textsubscript{2} electrode and causing spontaneous deintercalation.

A transparent perfluorosulfonic acid membrane was used (Dupont, Nafion N-125). The membrane was 0.13 mm thick and had a resistance of 25 ohms/cm\textsuperscript{2} in CH\textsubscript{3}CN, 1M TBAC. The membranes were converted to the tetrabutylammonium form by soaking in a 1M solution of TBAC in ACN for several days and stored in dry ACN until used.
Fig. 11. Plot of open circuit voltage and average current during spontaneous intercalation of Fe into TiS$_2$:Teflon:graphite electrode in 0.25M Fe(CIO$_4$)$_2$ solution in ACN with 1M TBAC as supporting electrolyte.
Fig. 12. Pyrex cell for full cell intercalation experiments with $n$-GaAs/Ti$_2$S$_2$. 
The charging cycle was done by illuminating the GaAs electrode with a tungsten lamp at an insolation of 40 mW·cm^{-2}. The semiconducting electrode was short-circuited to the TiS_{2} electrode. Both sides of the cell were stirred during the reaction. The current, monitored by a Keithley picoammeter, and the potential of the TiS_{2} vs. the Cu reference electrode were simultaneously plotted vs. time with a two-pen strip chart recorder.

Deintercalation using the Pt electrode was accomplished by connecting the TiS_{2} electrode to the Pt electrode in the GaAs compartment through a 47 ohm load resistor. The load resistor was used to limit the discharge current.

Cycling experiments were run with three sets of TiS_{2} electrodes, one using a Ni screen and two on Ta screens. The intercalation electrodes were pressed powders of Teflon:graphite:TiS_{2} in the ratio 10:10:80. The first two electrodes were cycled once and the third, two full cycles. Table 5 summarizes the charge and discharge parameters for each cell.

For the first test, two TiS_{2} electrodes pressed onto Ni Exmet were used as the intercalating electrode. The charging cycle proceeded normally and was stopped when the current decreased to 0.05 mA. The discharge was then begun, as described above. As the discharge proceeded, a green solution began to appear in the TiS_{2} compartment. The current passed on discharge exceeded the current passed during the charge cycle and the reaction was stopped. The absorption spectrum of the green solution indicated that Ni chloride complexes were present and that the excess discharge current was due to oxidation of the Ni Exmet. (The potential for anodic oxidation of Ni in 1M TBAC must be positive of the Cu(II), Cu(I)/Pt potential.)

To avoid the problem of the Ni oxidation, the TiS_{2} electrode in the second experiment was prepared using a Ta screen. The intercalation of the TiS_{2} electrode was driven by the GaAs photocurrent to 6.8% utilization of the TiS_{2}. During intercalation the potential of the TiS_{2} electrode vs. the Cu reference dropped about 0.2V. The TiS_{2} was then discharged until negligible current (0.024 mA/cm^{2}) was being passed. From the current passed during intercalation, only 7% of the Cu was removed during the discharge before the rest potential of the TiS_{2} had returned to its value prior to the intercalation cycle. No further cycling could be done with the TiS_{2} electrode because a significant fraction of the TiS_{2} had fallen off the Ta Exmet.

A third intercalation electrode was constructed again using TiS_{2} pressed onto Ta screen. This electrode was pressed at a higher pressure to minimize the disintegration of the electrode during cycling. Two charging and discharging cycles were completed before the TiS_{2} electrode fell apart. In the first cycle, the 29.8 C passed resulted in a 36% utilization of Cu storage capacity of the TiS_{2}. The discharge cycle was run until 64% of the charge passed in the charging step was recovered.
Table 5. Cell parameters for full-cell passive intercalation of TiS$_2$.\(^1\)

<table>
<thead>
<tr>
<th>Electrode Area</th>
<th>Charge (C) or Discharge (D)</th>
<th>Potential During Cycling (V, TiS$_2$ vs. Cu)</th>
<th>Illuminated Full Cell Voc (V, GaAs vs. TiS$_2$)</th>
<th>Charge Passed (C)</th>
<th>% Utilization$^2$ TiS$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiS$_2$ on Ni (4 cm$^2$)</td>
<td>C</td>
<td>0.387</td>
<td>-0.245</td>
<td>1.4</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.147</td>
<td>-</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>TiS$_2$ on Ta (2.9 cm$^2$)</td>
<td>C</td>
<td>0.648</td>
<td>-0.553</td>
<td>4.0</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.486</td>
<td>-</td>
<td>-</td>
<td>6.6</td>
</tr>
<tr>
<td>TiS$_2$ on Ta (6.5 cm$^2$)</td>
<td>C1</td>
<td>0.624</td>
<td>-0.567</td>
<td>30</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>D1</td>
<td>0.261</td>
<td>-0.164</td>
<td>19</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>0.663</td>
<td>-0.598</td>
<td>2.6</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>0.192</td>
<td>-0.555</td>
<td>1.8</td>
<td>2.2</td>
</tr>
</tbody>
</table>

$^1$Full cell n-GaAs$_{[CuCl_4]^{-2}}$[CuCl$_2$]$^{2-}$TiS$_2$. The n-GaAs photoelectrode had an area of 0.27 cm$^2$ and was illuminated by a tungsten-halogen lamp with an intensity of 40 mW·cm$^{-2}$.

$^2$Calculated as the weight of Cu intercalated or deintercalated compared to weight of Cu in Cu$_{1.0}$TiS$_2$ assuming all the charge passed was used to reduce or oxidize Cu.
A yellow color in the TiS₂ compartment after the discharge indicated some Cu(II) was formed. The Cu(II) resulted from oxidation of the Cu(I) species in the compartment, not from migration of leakage through the membrane of the Cu(II) in the GaAs compartment of the cell. As the second charging cycle progressed, the yellow color began to disappear as Cu(II) was reduced to CuₓTiS₂ or as it reacted with the Cu⁺ electrode to give Cu(I). The current during this cycle rapidly decreased and the charging was stopped after only 2.3% of the TiS₂ was intercalated. The second discharge cycle recovered 71% of the stored charge. At the completion of the second cycle, most of the TiS₂ had fallen off the screen and a gas bubble had formed inside the Celgard surrounding the electrode.

The current-voltage curves for the full cell and the two half cells were measured before and after the first charge and discharge cycle and after the second discharge for the third intercalation electrode that was tested. The results are presented in Figures 13 and 14. Figure 13 shows the shift in the cell potential associated with the intercalation of Cu into the TiS₂ electrode after the charging cycle. The recovery of the initial current-voltage curve after the first discharge confirms the reversibility of the passive intercalation cell. After the second charge-discharge cycle, the open circuit voltage returned to the initial value but there was a substantial decrease in the current density evident in the i-V scan. The lower current density leading to broadened curve is attributed to the factor of 10 decrease in the current density of the TiS₂ due to deterioration of the structure of the intercalating electrode.

Figure 14 shows the half cell photocurrent curves at various stages during the cycling. The shift in potential of the intercalated TiS₂ electrode (curve 2) and the sensitive behavior of the electrode after discharging (curve 3 and curve 4) are clearly evident. As expected, no significant differences in the i-V curves of the GaAs half cell were observed as a result of the cycling experiments. Plots of the expected full cell i-V curves obtained by combining the two half cell curves agree very well with the observed curves in Figure 13. The measured full cell curve is shifted slightly positive of the calculated curve with increasing current by an amount which can be attributed to the combined iR drop through the electrolyte and the membrane between the TiS₂ and GaAs electrodes.

Although the cycling experiments have shown that the passive intercalation reaction is reversible, problems remain to be solved. Among these are the production of Cu(II) in the TiS₂ compartment due to over-discharge vs. Pt/Cu(II), Cu(I). The major problem, however, is the physical deterioration (disintegration) of the intercalating electrode. As the TiS₂ is intercalated, the crystal lattice expands and during deintercalation it contracts. If there is no pressure exerted on the TiS₂ particles, the electrode loses internal integrity and it also separates from the Exmet support. The improved pressed electrodes made with the Teflon-graphite paste (see Section 3.1.2) should provide improved
Fig. 13. i-V curves for illuminated full cell at different stages of charging-discharging cycling (scan rate = 20 mV·sec⁻¹, light intensity = 40 mW·cm⁻²).
Fig. 14. i-V curve for illuminated n-GaAs half cell at different stages of charging-discharging cycling (A = 0.3 cm², scan rate = 20 mV.sec⁻¹, light intensity = 40 mW.cm⁻²). Curves 1-3 are cathodic i-V curves for the TiS₂ half cell.
stability, but no electrodes of this type were tested in the full cell configuration. Construction of an electrode compartment to provide pressure on the electrode during operation would also help preserve the integrity of the intercalation electrode.
4.1 ACTIVE INTERCALATION CELLS

4.1.1 General Considerations

In an active intercalation storage cell, a single illuminated semiconductor electrode simultaneously drives the storage reaction and acts as the storage vehicle. In the simplest mode of reaction a p-type electrode acts as a photocathode to promote intercalation, or an electrode made from an n-type material acts as a photoanode to promote photodeintercalation. The counter electrode can merely be a metal electrode of the same material as the intercalant and acts as a source or sink for the metal ions during the charging cycle. In more elaborate designs, an active intercalation cell could involve intercalation at one electrode and deintercalation at the other, viz:

\[
MX_2 + A_xM'_2 \xrightarrow{\text{hv}} A_xMX_2 + M'_2 \Delta G > 0
\] (5)

A third type of cell would utilize the change in voltage which occurs as the mole fraction of the intercalant varies. This cell would operate like an electrochemical concentration cell:

\[
2A_xMX_2 \xrightarrow{\text{hv}} A_{x+y}MX_2 + A_{x-y}MX_2
\] (6)

The properties required of the intercalating semiconductor have been discussed by Tributsch (1). Three of the most fundamental requirements are:

- The band gap of the semiconductor must be compatible with the solar spectrum, i.e., 1.0-2.0 eV.
- The change in the electrode potential with intercalation must be large enough to permit significant energy storage.
- The semiconducting properties of the material must be retained when the material is intercalated.

From the rather limited work that has been done, the dichalcogenides of Hf and Zr appear to possess these required properties. The photoelectrochemical properties of ZrS\(_2\) have recently been reported (4). Most of the materials show n-type behavior although some p-type reactions with ZrSe\(_2\) have been observed. Significantly, the intercalation of Cu and Fe into ZrS\(_2\) and HfS\(_2\) at low concentrations of intercalant does not eliminate their semiconducting properties (9,10).

4.1.2 Spontaneous Intercalation of Cu into Single Crystal HfS\(_2\)

The spontaneous intercalation of Cu into HfS\(_2\) was measured by short-circuiting a single crystal HfS\(_2\) electrode (#78-1) to a Cu counter electrode.
in 0.05M aqueous CuSO₄ solution. The direction of current flow was consistent with reduction of Cu²⁺ at the semiconductor electrode. The average current density (4-6 μA/cm²) was an order of magnitude higher than the current densities for HfS₂ crystals intercalated in nonaqueous electrolytes. A reduction in the cathodic current was obtained when the crystal was illuminated at the onset of the intercalation. After the passage of 0.02 C of charge, however, illumination of the crystal enhanced the current by as much as 50% at some periods of the intercalation. After 10 days, 1.1 coulombs of charge had been passed.

Periodically, the intercalation was interrupted to measure the open circuit voltage, photovoltage, and i-V response. A plot of the open circuit voltage and photovoltage during the course of the intercalation is given in Figure 15. The open circuit voltage between the HfS₂ and Cu reference electrodes decreased from its initial value of 0.1V to about 0.030V after passage of ~0.2 coulombs and stayed at this value during the rest of the intercalation. As the intercalation progressed, a small negative photovoltage was measured. The voltage continued to increase to a maximum of ~36 mV at 0.2 mole fraction of intercalated Cu and then decreased to near zero.

The anodic photocurrents at several stages during the intercalation are shown in Figure 16. The photocurrents increased during the initial intercalation and then decreased, following the same general trend as the photovoltage. The anodic and cathodic dark currents steadily increased as more copper was intercalated. The trend towards more metallic behavior with increasing mole fractions of intercalated Cu is similar to the behavior reported for ZrSe₂ intercalated with iron (11). The atomic absorption analysis gave a Cu mole fraction of 0.38 for the CuₓHfS₂ sample, in good agreement with the value expected from the current passed during intercalation.

The x-ray spectra of intercalated and nonintercalated HfS₂ were measured at Brown University using the Gandolfi method. Table 6 shows the results obtained for the principal lines, along with the literature values.

No expansion of the HfS₂ lattice of the intercalated sample was observed. The CuₓHfS₂ sample, however, did show three additional strong lines which match those expected from a mixed Cu(I)-Cu(II) oxide. The amount and location of the oxide is not known. It may simply be the result of air oxidation of the Cu intercalated near the surface of the HfS₂ crystal.

4.1.3 Intercalation of Lithium into HfS₂

Because of the high rates and rechargeability reported for Li intercalation in TiS₂, an experiment with Li intercalation into HfS₂ was done. Since Li is an excellent electron donor, it exists mostly as Li⁺ in LiₓTiS₂
Fig. 15. Change in the $V_{OC}$ and photovoltage for HfS$_2$ single crystal as function of mole fraction of Cu intercalated. Photovoltage measured at tungsten-halogen light intensity of 80 mW·cm$^{-2}$. 
Fig. 16. Photocurrents measured in the HfS$_2$/Cu$^{+2}$(aq) system for various stages of intercalation indicated by number of coulombs passed. Illumination intensity = 80 mW/cm$^2$, scan rate = 25 mV/sec$^{-1}$. 
Table 6. X-ray spectra data for HfS$_2$ and Cu$_x$HfS$_2$.

<table>
<thead>
<tr>
<th>HfS$_2$ (SCG-78)</th>
<th>Cu$_x$HfS$_2$ (SCG-78-1)</th>
<th>HfS$_2$ (literature)</th>
<th>6CuO·Cu$_2$O (literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>d(Å) I/I$^o$</td>
<td>d(Å) I/I$^o$</td>
</tr>
<tr>
<td>5.85</td>
<td>70</td>
<td>5.77</td>
<td>70</td>
</tr>
<tr>
<td>3.14</td>
<td>80</td>
<td>3.14</td>
<td>80</td>
</tr>
<tr>
<td>2.76</td>
<td>100</td>
<td>2.76</td>
<td>100</td>
</tr>
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<td>-</td>
<td>2.46</td>
<td>15</td>
</tr>
<tr>
<td>2.14</td>
<td>90</td>
<td>2.15</td>
<td>90</td>
</tr>
<tr>
<td>1.81</td>
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<td>1.81</td>
<td>20</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>129</td>
<td>5</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>0.87</td>
<td>4</td>
</tr>
</tbody>
</table>

1Extra lines are associated with copper oxides as seen by comparison to 6CuO·Cu$_2$O data.
2Joint Committee on Powder Diffraction Standards, #3-0879.
3Joint Committee on Powder Diffraction Standards, #28-244.

giving it a high mobility in an electric field which in part may explain the high reported rates of intercalation. Furthermore, by donating its electron to the valence band of the semiconductor, Li acts as an n-type dopant increasing the electronic conductivity of the semiconductor.

Cyclic voltammograms of HfS$_2$ crystals were taken with Li metal reference and counter electrodes and 1M LiClO$_4$ in propylene carbonate as the electrolyte (Figure 17). The experiments were run in a dry box. The open circuit voltage in the dark was +2.67V vs. Li/Li$^+$. A small positive photovoltage of 20 mV was obtained when the crystal was irradiated with a tungsten lamp at 80 mW/cm$^2$. Cathodic photocurrents of ~0.1 mA/cm$^2$ were observed with much smaller (0.02 mA/cm$^2$) anodic photocurrents.

Since the current density was very small (0.8 µA/cm$^2$) when the cell was potentiostatted at +2.0V vs. Li/Li$^+$, the intercalation was allowed to proceed spontaneously. The current was monitored with the picocammeter as described previously. The average current density for the spontaneous reduction was 8-16 µA/cm$^2$ which is a factor of two higher than for Cu intercalation in HfS$_2$ in aqueous electrolytes. When the shorted crystal was irradiated, an increase in the cathodic current was observed.

During the intercalation, the V$_{oc}$ dropped rapidly from +2.67V to 0.94V vs. Li$^+$/Li and then slowly decreased to 0.48V by the end of the experiment. After 0.3 mole fraction Li was intercalated, the photocurrent was markedly decreased and it was essentially zero at 0.4 mole fraction Li. This behavior is consistent with that observed for Cu intercalation in HfS$_2$ discussed above. Significantly, Berthier et al. (13) also reported a non-metal to metal phase transition for Li$_x$ZrSe$_2$ at x = 0.4.
Fig 17. Cyclic voltammogram of HfS$_2$ electrode in 1M LiClO$_4$ in propylene carbonate.
The intercalation was terminated after 0.35 C of charge had passed corresponding to 0.47 mole fraction lithium intercalated. After soaking in the electrolyte for several days, the open circuit voltage had risen to +2.1V vs. Li/Li⁺, indicating that during intercalation most of the Li remains in the top layers of the crystal. A cyclic voltammogram taken after the intercalation is qualitatively the same behavior as before intercalation, but the shift in the peak potential and the \( V_{OC} \) indicated that intercalation has occurred. There was no photoeffect on the intercalated crystal, again suggesting the likelihood of a degenerate semiconductor or a phase transition to a metal.

4.1.4 Potentiostatic Intercalation of Cu into other Dichalcogenide Single Crystals

Attempts were made to intercalate Cu potentiostatically into HfS₂, ZrSe₂ and HfSe₂ from 0.05M aqueous CuSO₄ solutions. A three-electrode cell was used with a copper wire and a copper foil as the reference and counter electrode, respectively. The potential was held slightly positive of the Cu plating potential on Cu to assure that all the reduction current arose from the intercalation reaction. Periodically, the reaction was stopped and the open circuit potential between the working and reference electrode was measured.

The Cu intercalation in HfS₂ was done at a potential of 0.05V vs. Cu⁰/Cu⁺². The average current density was \( \sim 15 \mu A/cm² \) which was higher than that obtained for the spontaneous intercalation. The higher current is probably due to a different surface morphology for the crystal used in the potentiostatic measurements. The crystal area was smaller and, therefore, less likely to have pinholes or other defects which reduce the reaction rate. The \( V_{OC} \) decreased from 0.111V to 0.05V vs. Cu⁰/Cu⁺² during the intercalation in good agreement with the spontaneous experiment. The intercalation was stopped after the \( V_{OC} \) reached the applied potential; the total charge passed was 0.22 coulomb corresponding to 0.28 mole fraction of Cu intercalated into the HfS₂.

The Cu intercalation in ZrSe₂ was done in the same manner as for HfS₂ except that the cell had a optically flat window positioned over a metallograph to monitor the changes in crystal morphology during intercalation. The cell was initially potentiostatted at 0.05V positive of the Cu plating potential. After 15 hours, during which 0.1 C of charge was passed, the current had decreased to 0.05 mA/cm², and the \( V_{OC} \) was +0.05V vs. Cu⁰/Cu⁺²; therefore, the applied voltage was decreased to +0.025V vs. Cu⁰/Cu⁺² and the reaction allowed to proceed. After 24 hours, the current again significantly decreased (0.025 mA/cm²) and the reaction was terminated. The amount of charge passed corresponded to 0.25 mole fraction Cu intercalated. As was expected from the metallic behavior of the cyclic voltammograms in passive electrolytes, no photoresponse was observed during intercalation. As the intercalation on ZrSe₂
progressed, a film of elemental selenium formed on the crystal surface. The irreversible formation of selenium and, therefore, the deterioration of the crystal itself is the major drawback to the use of MSe\textsubscript{2} crystals in intercalation reactions in aqueous electrolytes.

An attempt was made to potentiostatically intercalate copper into HfSe\textsubscript{2.1} crystals. The initial \( V_{OC} \) was +0.218\,V vs. Cu\textsuperscript{0}/Cu\textsuperscript{2+}, and the cell was potentiostatted at +0.05\,V vs. Cu\textsuperscript{0}/Cu\textsuperscript{2+}. The intercalation proceeded at an average current density of \( \approx 13 \, \mu A/cm^2 \) for 3 hours before the current abruptly dropped to zero. The \( V_{OC} \) after equilibration was -0.16\,V vs. Cu/Cu\textsuperscript{2+} and Cu metal appeared to have deposited on the crystal surface. Because of this anomalous behavior, further intercalation of this HfSe\textsubscript{2} crystal was not attempted.
REFERENCES


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