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Intercalation Chemistry and Energy Storage

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The reaction between lithium and titanium disulfide is used to show the relationship between intercalation chemistry and electrochemical energy storage. The maintenance of crystalline structure with only a 10% lattice expansion perpendicular to the sulfide sheets allows high rates of reaction with lithium and complete reversibility of the reaction. The behavior of TaS_2 and VSe_2 are compared with that of TiS_2. Many oxides and other chalcogenides of the early group transition metals are also able to react with lithium to form ternary compounds, but none of these have to date shown the high reversibility of titanium disulfide.

Introduction

The phenomenon of intercalation in its application to the calendar, such as the quadrennial intercalation of February 29, is fully reversible. Similarly in its chemical usage, which has been associated most commonly with the insertion of guest species between the layers of a crystalline host lattice, the reaction must be reversible through appropriate chemical or thermal treatment. An intercalation reaction is a special case of a topochemical process. Thus, by definition, an intercalation reaction fulfills one of the requirements of an anode/cathode couple for a secondary cell, that of reversibility. The other cathode requirements for a reaction of the type $xM + BY \rightarrow M_xBY$ are:

- a high free energy of reaction;
- little change in free energy over the composition range, i.e., x;
- a wide range of x;
- little structural change on reaction;
- high diffusivity of the M ion in the BY structure;
- good electronic conductivity; and
- no solubility in the electrolyte.

This paper will discuss the key features of intercalation reactions and their application to electrochemical energy storage. Most effort has been expended on the reaction between lithium and titanium disulfide, and that reaction will be used as the base case here.

Experimental

All the materials used here were prepared by direct reaction between the elements in sealed tubes. They were anlyzed for stoichiometry by oxidation on a DuPont thermogravimetric system and for phase and structure with a Philips X-ray diffractometer using Cu$K\alpha$ radiation; in the latter the samples were protected from the atmosphere by a Mylar film (*1*). The reaction of the TiS_2, and other compounds, with lithium was performed using two techniques, *n*-butyl lithiation (*2*) and electrointercalation (*3*); these are described in detail in the next paper. For electrochemical cell construction, the

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cathode material was mixed with 10 wt% Teflon, pressed at 300°C into an expanded metal grid, and surrounded by a polypropylene separator and a sheet of lithium metal. The whole was then immersed in the electrolyte solution, which was usually lithium perchlorate dissolved in dioxolane. The testing was done in a Vacuum Atmospheres glove box using Princeton Applied Research potentiostats equipped with coulometers, programmers, and voltage limiting devices.

Results and Discussion

The Lithium–Titanium Disulfide Reaction

The reaction between lithium and titanium disulfide is continuous over the entire composition range, $x\text{Li}+\text{TiS}_2 \rightarrow \text{Li}_x\text{TiS}_2$ for $0 \leqslant x \leqslant 1$. This has been shown (*4*) by the variation in both the *c* lattice parameter (that perpendicular to the basal plane) and the emf of the cell $\text{Li}/\text{Li}_x\text{TiS}_2$ with lithium content as shown in Fig. 1. This finding is of major importance for battery utilization because there is no need to expend energy in nucleating a new phase either on the initial reaction or on the deintercalation. The expansion of the sulfide lattice found on lithiation was not entirely expected as the vacant octahedral sites in the van der Waals layers are ~0.7 Å in radius, almost identical to those of a fully ionized lithium ion. That an expansion was observed suggests that the lithium was not fully ionized; this is consistent with the decreasing free energy of reaction shown by the cell emf. Nuclear magnetic resonance studies showed a continuously increasing ^7Li Knight shift with lithium content, indicative of residual 2*s* electron density (*5*). This behavior can be explained by the conduction band in the TiS_2 becoming progressively more filled as the lithium content increases, thus raising the Fermi level and decreasing the energy difference between this electron level and that in lithium metal. In addition, the intercalation energy must also be reduced by the electrostatic repulsive forces between the lithium ions; these forces have recently been shown to be sufficiently large to cause ordering of the ions at room temperature (*6*).

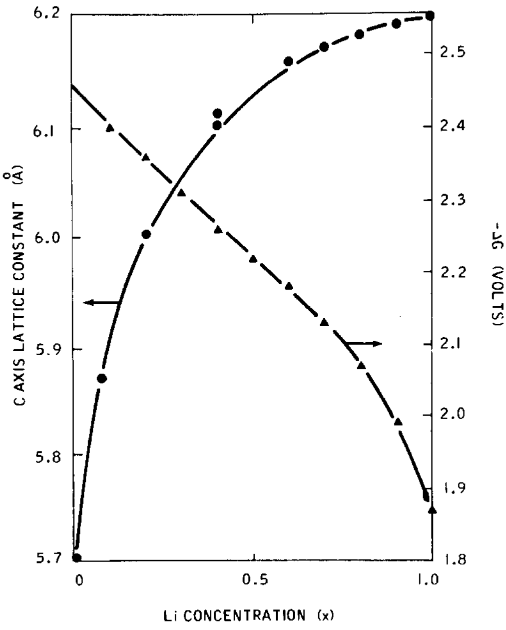

FIG. 1. The variation of the *c* lattice parameter and the lithium cell emf for $\text{Li}_x\ \text{TiS}_2$ with *x*.

Titanium disulfide shows a range of nonstoichiometry on the metal-rich side of the TiS_2 composition (*7*). These excess titanium atoms reside in the van der Waals layer thus both pinning the TiS_2 layers together and occupying sites. that lithium would normally fill. Figure 2 shows the *c* lattice expansion for the highest lithium content material, $\text{Li}_{1-y}\text{Ti}_{1+y}\text{S}_2$ (*1*). This smaller lattice expansion significantly reduces the lithium mobility and hence the usefulness of the material for battery applications (*8*). In addition the extra titanium causes a slight reduction in the energy of intercalation; this is expected from the decreased electronegativity of the lattice.

Of the requirements listed for a cathode, titanium disulfide has now been shown to fulfill all those relating to energy and degree

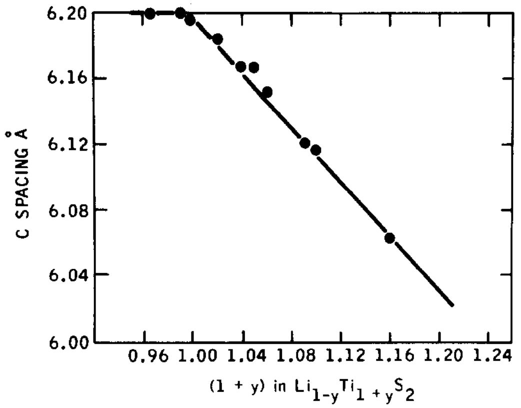

FIG. 2. The variation of the c lattice parameter of $Li_{1-y}Ti_{1+y}S_2$ with y.

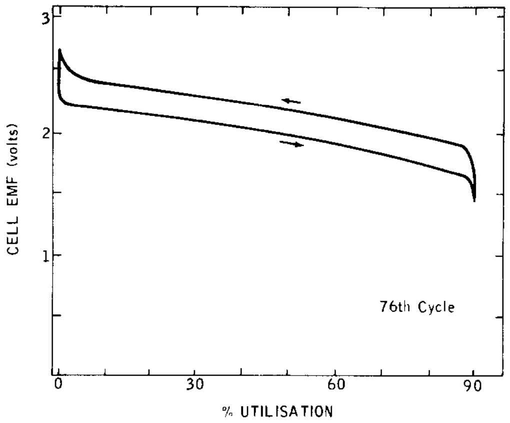

FIG. 3. The 76th cycle of an Li/TiS_2 cell at 10 mA/cm^2.

of reaction, and the structure remains essentially unchanged during reaction. The conductivity of titanium disulfide is that of a semimetal by virtue of an accidental overlap between the valence and conduction bands (*9*). On intercalation the conductivity should increase, and indeed that has been found for compacted powders (*10*); no data are, however, available for single-crystal material. Thus there is no need in this case to admix into the cathode structure a conductive diluent, such as graphite. There is also no evidence that these layered disulfides are soluble in the organic electrolytes used, so there is no self-discharge due to reaction of dissolved species with the lithium anode. The high diffusivity and reversibility of the lithium reaction were most easily measured in an actual cell. This is accomplished by measuring the cell voltages, during intercalation and deintercalation at a constant current density, and comparing them to the values under zero current drain (thermodynamic values). Results at 10 mA/cm^2 are shown in Fig. 3 (*8*); comparison with the data of Fig. 1 and the closeness of the two curves of Fig. 3 indicate that the reaction is both highly reversible and occurs at a high rate. These curves are indicative of a true intercalation reaction, being reproducible cycle after cycle. The difference in voltage between the forward and reverse reactions is predominantly due to resistance losses in the electrolyte.

The data of Fig. 1 give a free energy for the reaction $Li + TiS_2 \rightarrow LiTiS_2$ of 206 kJ/mole. This can be translated into a theoretical (weight of anode and cathode only) energy density for a battery of 480 hr/kg. In practical systems this will be reduced by a factor of 4 to 5 to around 100 W hr/kg. A current density of 10 mA/cm^2 in turn converts to a power density of 100 W/kg when the cell is constructed using thin plates (*11*). These values are comparable to those now envisioned for the high-temperature Li/S and Na/S batteries being developed for electric vehicle propulsion. Initial applications of the ambient-temperature Li/TiS_2 cells are likely to be in the electronics area where lifetime batteries are required. This is accomplished by combining the reversible cell with a small solar array.

Other Layered Dichalcogenides

Most emphasis has been placed on titanium disulfide because it is the lightest in weight as well as the most economical of the layered disulfides. However, many of the other dichalcogenides are potentially interesting in electrochemical cells. It is anticipated that by the appropriate choice of metals and chalcogens batteries can be tailored to almost any application requiring cell voltages in the range of 1 to 3 V and current densities from a few microamperes to tens of milliamperes per square centimeter. In addition the change of potential with state of charge can be controlled from almost zero in the case of VSe_2 to more than a volt for TaS_2. These two extreme cases will be discussed below; most of the other dichalcogenides show behavior more reminiscent of TiS_2 (*8*).

Figure 4 compares the thermodynamics of intercalation of lithium and sodium into titanium and tantalum disulfide (*4, 12–14*). A number of features are apparent in this figure. First, the variation in cell emf is much higher in the case of TaS_2. The reason for this is not clear but may be associated with the electronic band structure of this 2H modification. We are presently undertaking studies on the IT form which is isostructural with TiS_2 to see if this is indeed the case. Second, the sodium cells have a lower voltage just as expected from the lower electropositive character of sodium relative to lithium. Third, a number of breaks are observed in the Na/TiS_2 curve; these are associated with structural changes which cause the regions of nonstoichiometry to be limited in breadth. The site symmetry of the sodium ion which can be either octahedral or trigonal prismatic (*15*) dictates that the sulfide layers must shift relative to one another. These structural changes require energy and in addition will cause physical degradation of the cathode structure, and so are undesirable in a battery system. Indeed, only limited cycling capability is found in Na/TiS_2 cells. Although the Na/TaS_2 curve appears linear, a closer examination of the data suggests that here also structural changes are occurring. This is what would be expected from the size of the sodium ion (*8, 16*).

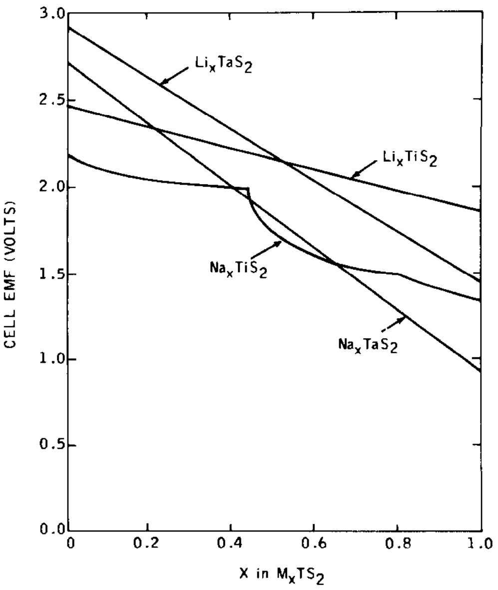

FIG. 4. Thermodynamics of intercalation of lithium and sodium into TiS_2 and TaS_2.

Vanadium diselenide represents a particularly interesting case, because there is little, if any, change in emf with composition, and two lithium ions are readily incorporated into the structure (*8, 17*). The data are shown in Fig. 5. The highly distorted lattice of VSe_2 is probably the reason for the emf behavior. VSe_2 which has vanadium in an octahedral site, like TiS_2, has a crystallographic c/a ratio of 1.821, almost identical to that of $NbSe_2$, 1.817, where the niobium is in trigonal prismatic coordination. The c/a ratios of TiS_2 and $TiSe_2$ are 1.672 and 1.698. On lithium intercalation the c/a ratios become almost identical for all the octahedral materials, e.g., $LiTiS_2$ 1.793, $LiVSe_2$ 1.773. Presumably the removal of this distortion in VSe_2 must occur in a concerted manner, not gradually. The second lithium is also incorporated at a constant potential, suggesting again a two-phase behavior in this regime. The lithium atoms in Li_2VSe_2 must reside in tetrahedral sites because there are insufficient octahedral sites, only one per transition metal. The switch in site symmetry possibly precludes any significant nonstoichiometric region, as these sites are expected to be of higher energy than the larger higher-

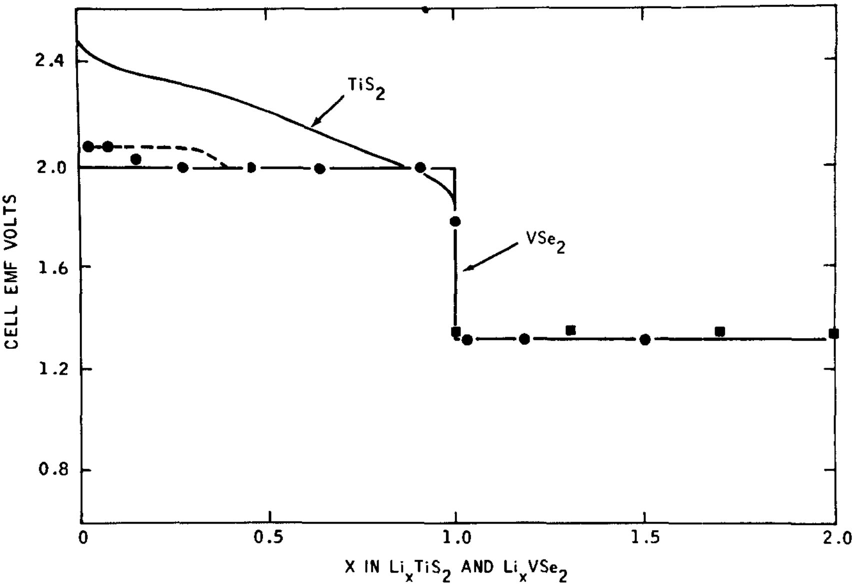

FIG. 5. Comparison of emf behavior of TiS_2 and VSe_2 in lithium cells.

coordinated ones. The behavior at very low lithium contents is not fully understood but may be suggestive of an ordered structure; this is under further investigation now. Cells of VSe_2 have been successfully cycled, but it is doubtful whether both voltage plateaus can be utilized in commercial applications. Full details of the other dichalcogenides are given elsewhere (*8*).

The Transition Metal Trichalcogenides and Oxides

Two trichalcogenides, TiS_3 and $NbSe_3$, have been studied in detail in lithium batteries (*18*) because of their ability to react with three lithium atoms. These reactions have now been shown (*4, 19*) to take place in two steps: e.g.,

$$TiS_3 + 2\,Li \rightarrow Li_2TiS_3,$$

$$Li_2TiS_3 + x\,Li \rightarrow Li_{2+x}TiS_3$$

$$\text{for } 0 < x < 1.$$

In the first step the polysulfide bond is broken whereas in the second the reaction is more like that of TiS_2. When the reaction is allowed to go to completion only the last lithium is reversible. The cell voltages under load and for zero current drain are shown in Fig. 6. These curves clearly show the two-phase and single-phase behavior in the two composition regions. The titanium in TiS_3 is in trigonal prismatic coordination, an unstable environment when the sulfur atoms are oxidized to S^{2-}. It is therefore likely that the TiS_6 groups become distorted toward the octahedral configuration on reaction and

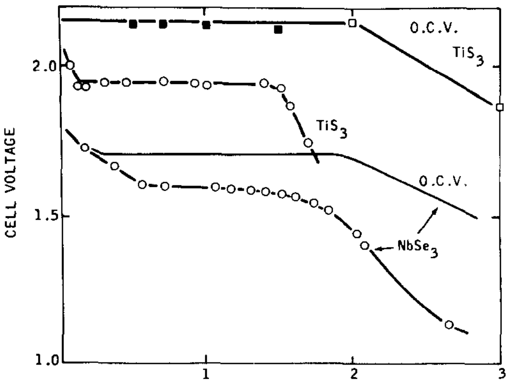

FIG. 6. Cell emfs for TiS_3 and $NbSe_3$ cells on open circuit and under a current drain of 2 mA/cm^2.

that this process is not reversible. On the other hand Li_3NbSe_3 is much more reversible. This can be associated with the environment about the metal; niobium is commonly found in trigonal prismatic coordination and so has a much lower tendency to distort its environment (*4*). In addition, the Se–Se bonds are midway in length between a single- and a no-bonding situation.

There is another important difference between the reactions of the di- and trichalcogenides. As shown in Fig. 7, after recharge, subsequent discharges occur at higher emfs than the initial discharge, suggestive of a permanent structural change. These structural changes may also explain the large voltage difference between the discharge and charge curves (about an order of magnitude higher than that found in Fig. 3 for Li/TiS_2); this is symptomatic of a nonintercalation reaction. This same behavior has been observed in $NiPS_3$, where the initial discharge is fairly constant at about 1.8 V (*20*), and subsequent discharges start out at over 2 V. $NiPS_3$ is a layered compound with a structure similar to that of TiS_2 but with nickel ions and P–P pairs occupying the titanium sites. $NiPS_3$ has been found to react with up to 3 $Li/NiPS_3$ (*20*), but there are octahedral sites for only 1.5 lithiums. In some cases a break in the emf composition curve has been observed at 1.5 (*21*), but this seems to be a function of the preparation technique. This may be a case similar to VSe_2, where in the end all the tetrahedral sites may be filled. The iron analog, $FePS_3$, is more complex due to a tendency toward nonstoichiometry of the iron. Another class of layered compounds that has been studied is FeOCl and its analogs; these will react with one lithium but are not easily rechargeable in lithium cells (*8*).

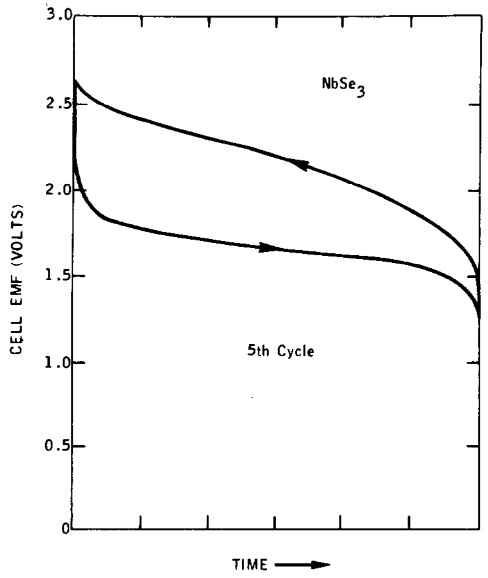

FIG. 7. Fifth cycle of a lithium/niobium triselenide cell at 2 mA/cm^2.

An extension of the trichalcogenides is VS_4, which occurs naturally as patronite. Here all the sulfurs are present as polysulfide. This compound has a fibrous structure made up of chains of VS_8 prisms; as prepared by sulfidation of V_5S_8, however, it frequently appears as hollow hexagonal pipes due to the rapid growth on the edges of the V_5S_8 platelets. This is shown in Fig. 8. This compound might be expected to react with at least four lithiums just to break the polysulfide bonds. However, both in electrochemical cells and using *n*-butyl lithium, less than two lithiums reacted per vanadium and these reactions were poorly reversible.

Several oxides have been investigated as cathodes in secondary cells and a number of these, e.g., V_2O_5, MoO_3, TiO_2, MnO_2, etc., incorporate lithium into their structures on reaction (*4, 8, 22*). Recently the rutile structure has been investigated because of the existence of vacant tunnels in the crystalline lattice. VO_2 was found to be reversible to lithium for $x < 0.3$ in Li_xVO_2 (*23*), and lithium was rapidly incorporated into TiO_2 (*22, 24, 25*). Recently a systematic survey (*26*) was made of the dioxides with the rutile structure, but the cell voltages were disappointingly low.

FIG. 8. VS_4 crystals grown by reaction of V_5S_8 with sulfur (×100 magnification).

Conclusion

Electrodes such as titanium disulfide which react with lithium by a continuous intercalation process show ideal secondary behavior. Here no structural changes occur apart from a small lattice expansion perpendicular to the basal planes. The trichalcogenides where significant structural changes occur on reaction are less reversible and are still incompletely understood at the present time.

Much effort is likely to be spent on conducting oxide materials in the next few years both to understand their insertion compounds and to find those that might be applicable for energy storage. Those that fulfill the following three criteria are the most likely candidates:

- structures that are layered or have accessible tunnel sites;
- have an accessible electronic band structure and high energy of formation; and
- contain transition metal ions in their higher oxidation states (*8*).

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