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METAL CHALCOGENIDES AS REVERSIBLE ELECTRODES

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Abstract - Certain transition metal chalcogenides are promising materials for use as cathodes in nonaqueous batteries involving the intercalation of alkali metals, notably lithium, into these layered compounds. The electrochemical behavior of these chalcogenides depends on various properties such as structure, stoichiometry, electrical conductivity, crystal morphology, etc. The influence of these properties and of the ultimate practical application of the battery on the selection of the cathode material is discussed. The battery properties of the chalcogenides are compared with those of other promising cathode materials, especially V_6O_{13}.

INTRODUCTION

In the early 1970's, stimulated by work on the superconducting properties of the layered transition metal dichalcogenides MX_2, Broadhead and Butherus [1,2] demonstrated the feasibility of using these layered materials (e.g., $NbSe_2$, TiS_2, etc.) as reversible cathodes in nonaqueous batteries. At that time, working with cells of the type $Li/Li^+/I_2\text{-}MX_2$, it was thought that the MX_2 served as an inert host material for intercalated electrochemically active species such as iodine. For this $Li/I_2\text{-}MX_2$ cell the reaction was postulated to be.

$$Li + \frac{1}{2} I_2 \text{ (in } MX_2) = LiI \qquad (1)$$

Later, however, Broadhead, Trumbore and Putvinski [3,4] showed that certain trichalcogenides, MX_3 (e.g., $NbSe_3$,etc.) behaved reversibly as cathodes in lithium cells without the presence of I_2. More recently, an MX_4 compound, $NbSe_{4.0-4.5}$, was shown by Murphy, Trumbore and Carides [5] to behave similarly.* Meanwhile, various workers, notably at Exxon [6], EIC [7], and Bell Laboratories [8], were showing that the actual cell reactions for Li/MX_y cells are of the type

$$nLi + MX_y = Li_nMX_y \qquad (2)$$

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* The existence of pure $NbSe_4$ now appears to be questionable while $NbSe_{4,5}$ corresponds to Nb_2Se_9 reported at this conference [A. Meerschaut, Paper No. II/6; also A. Kjekshus, private communication].

This general cell reaction represents in many cases the topotactic intercalation of Li into the layered MX_y with accompanying reduction of M^{4+} to M^{3+} and, for the higher chalcogenides, the cleavage of X-X bonds as illustrated in Fig. 1. The reader is referred to an extensive review article by

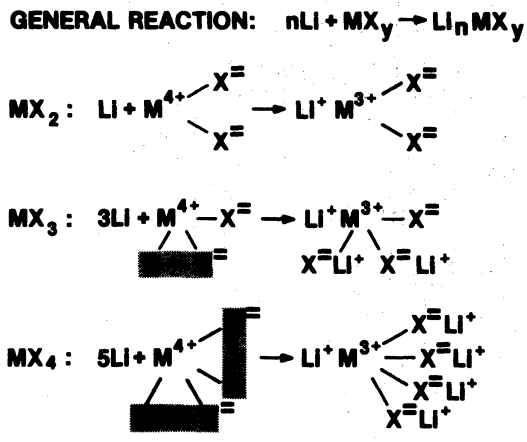

Fig. 1. Schematic illustration of the cell reactions for $LiMX_y$ cells indicating reduction of M^{4+} to M^{3+} and cleavage of X-X bonds in the higher chalcogenides.

Whittingham [9] for references to the very large body of work related to intercalation of various elements and compounds into MX_y as well as oxides and other host materials, with emphasis on MX_2 compounds. An earlier review by Murphy and Trumbore [10] dealing primarily with Li in MX_y compounds, with emphasis on MX_3 and $MX_{4-4.5}$, should also be helpful.

The key to the utilization of MX_y compounds as cathodes in practical rechargeable batteries, capable of many charge-discharge cycles, lies in the degree of "topotacticity" of reaction (2). In other words, the structural integrity of MX_y must be maintained on cycling lithium into (discharge) and out of (charge) the MX_y cathode material. We shall see that, unfortunately, reaction (2) is a deceptively simple representation of the cell reaction for a number of the more interesting MX_y compounds and that undesirable structural changes occur which detract greatly from the attractiveness of these particular MX_y compounds for use in batteries.

Another requirement for a useful cathode material is that the Li/MX_y couple provide a sufficiently high voltage. This is indeed the case, as shown in Fig. 2. Here the approximate range of reversible cell voltages is plotted for a number of Li/MX_y couples under low current or near-equilibrium conditions.

For comparison, Fig. 2 also includes values for a number of oxide systems including V_6O_{13}, which we shall consider later.

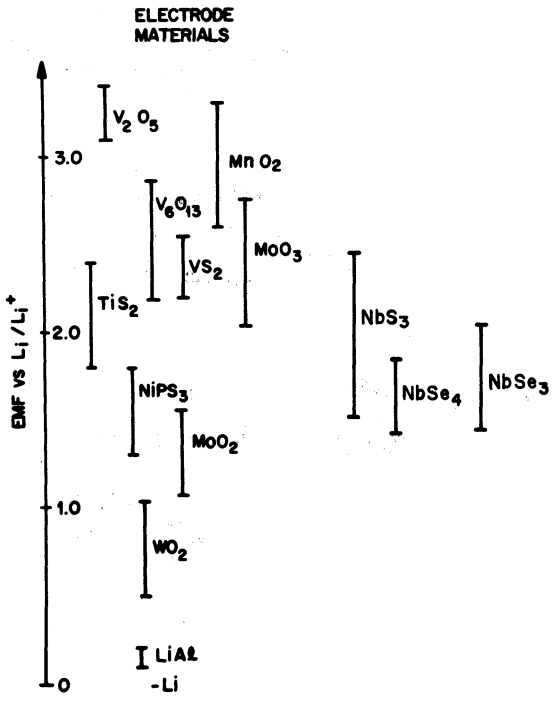

Fig. 2 Approximate voltage ranges of reversible operation for various Li/cathode couples.

In order to decide which of the MX_y compounds is the "best" cathode material for battery use, one has to consider the application for which the battery is intended. Although lithium batteries have been proposed for such heavy duty tasks as load leveling for electric utility companies and for electric vehicle propulsion [11], the first actual applications of lithium batteries are taking place at the other end of the power spectrum. Lithium primary (nonrechargeable) batteries with solid electrolytes and with nonaqueous electrolyte solutions are finding widespread application in cardiac pacemakers [12]. In addition, increasing numbers of lithium batteries are now being used in other low current (microamperes) applications involving hand calculators, watches, etc. One promising application for lithium rechargeable batteries of interest at Bell Laboratories is as reserve power sources for maintaining semiconductor memories on printed circuit boards during power outages. The performance demanded of the battery for these applications depends on the size and type of memory and illustrates the importance of proper battery voltage.

For example, certain memories require only 2 volts and relatively low currents of a few microamperes. Other memories require at least 3 volts and currents ranging as high as 0.1 to 1 mA or higher. For the former case, primary batteries of the type used in pacemakers are attractive candidates but for the latter, more demanding case, a rechargeable battery is mandated to meet cost and space requirements.

The selection of a cathode material for the memory applications can be illustrated with the help of Fig. 3, which shows the equilibrium discharge curves for a number of Li/MX_2 couples. Here we see that a single cell

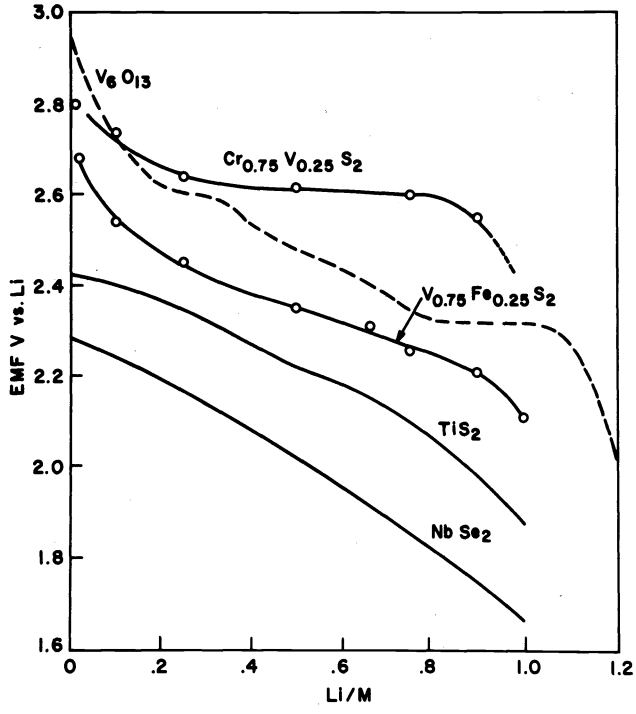

Fig. 3 Equilibrium (or low current) discharge curves for selected Li/MX_2 couples. Also included are results for Li/V_6O_{13}. Curves are from J. N. Carides (private communication).

$Li/NbSe_2$ battery would hold the 2 volt memory for only a fraction of its discharge capacity. A Li/TiS_2 single cell would be more suitable, while both $Li/Cr_{1-x}V_xS_2$ and $Li/Fe_{1-x}V_xS_2$ cell would maintain the memory over their entire discharge capacities. None of these couples would maintain the 3 volt memory with a single cell battery. Double cells, with twice the voltages shown in Fig. 3, would appear to qualify for all four MX_2 materials. However, the typical power supply voltage on a printed circuit board is 5 volts and a double cell of $Li/Cr_{3/4}V_{1/4}S_2$, with its plateau voltage of 5.2 volts, would discharge to 5 volts, well into the "knee" of the discharge curve and very little capacity would be left to maintain the 3 volt memory. On the other hand the $Fe_xV_{1-x}S_2$ battery would maintain most of its inherent capacity at 5.0 volts, illustrating the need for matching the cathode material to the desired application. (Alternate routes utilizing $Cr_{1-x}V_xS_2$ would be to use a Li-Al anode instead of pure lithium or to lower the chromium content, thus lowering the voltage plateau below 5.0 for a double cell.)

In the rest of this paper we shall consider the factors affecting the ability of the MX_y compounds to meet the cyclability, energy density and current requirements for practical lithium rechargeable batteries. The use of other alkali metals, particularly sodium, has also been considered but the results to date are less promising than the lithium results and, with one interesting exception, will not be treated here.

ENERGY DENSITY, STRUCTURAL AND CONDUCTIVITY CONSIDERATIONS

For memory maintenance and most other low current applications, the energy density per unit volume is of greater interest than the energy density per unit weight, which is more important for electric vehicle applications. In Table 1 the theoretical energy densities are listed for a number of Li/MX_y and certain other couples. These energy densities are based on the stoichiometric quantities of Li and MX_y and do not include the necessary evils of a real battery such as electrolyte solution, separator(s), container, current collectors, seals, etc. Attainment of 10-25% of the theoretical value is more or less typical in the rechargeable battery field. For comparison, two primary lithium battery systems are included in

Table 1, showing the achieved values in commercially available batteries. The achieved figure for Li/TiS_2 in Table 1 is based on Exxon's Model LTS-90 battery [13].

Table 1. Approximate Theoretical Energy Densities of Li Couples

Couple	Theoretical (WATT HOURS PER cm^3)	Achieved (WATT HOURS PER cm^3)
Li/TiS_2	1.1	0.1
Li/TiS_3	0.9	-
3 Li/TiS_3	1.9	-
3 Li/NbS_3	1.9	-
3 $Li/NbSe_3$	1.6	-
4 $Li/NbSe_4$	1.4	-
$Li/Fe_{1/4}V_{3/4}S_2$	1.4	-
$Li/Cr_{3/4}V_{1/4}S_2$	1.5	-
8 Li/V_6O_{13}	1.9	-
PRIMARY Li:		
$Li/SOCl_2$	2.4	0.9-1.2
Li/PbI_2PbS	1.4	0.5

The most "energetic" MX_y materials in Table 1 are TiS_3 and NbS_3 which, accommodating 3 lithiums per mole, have theoretical energy densities almost a factor of two higher than TiS_2, which can accommodate only one lithium. (Actually, as discussed later, some MX_2 can accommodate a second lithium but at a lower voltages.) To date, however, only TiS_2 has been used in a commercial rechargeable lithium battery [13]. TiS_3, the most economically attractive MX_y, suffers from the problem that only one of the three lithiums cycles reversibly. This has been attributed to an irreversible structural change upon incorporation of lithium which effectively ties up two lithiums [9,10,14]. At this time, it is not clear how cyclable NbS_3 is in a lithium cell. Although studies at EIC [7,14] indicate that the amount of lithium cycled in NbS_3 falls to a value less than one per NbS_3, the number remains near two lithiums for about 50 cycles and the further decay might have been due to lithium anode problems as discussed below.

A comparison of the structure of NbS_3 and $NbSe_3$ is revealing in connection with the role of the electrical conductivity in assessing a cathode material. There are Nb-Nb bonds in NbS_3 which localize the d-electrons from the niobium atoms; hence, NbS_3 is a semiconductor [15]. No such bonds are found in $NbSe_3$ [16] and the d-electrons are free to form a metallic conduction band. This, in turn, means that with $NbSe_3$ no conducting additives, such as graphite, are needed to decrease the cathode resistance and enhance current collection in the cathode structure. The semiconducting compounds such as NbS_3 required the addition of conducting diluents, thus resulting in a lower energy density and a reduction in the theoretical advantage over substances such as TiS_2. By properly controlling the time and temperature conditions, reaction of niobium and selenium may yield a composite structure consisting predominantly of the relatively high capacity but poorly conducting $NbSe_{4.0-4.5}$ enmeshed in a fibrous matrix of metallic $NbSe_3$ as shown in Fig. 4. This composite may be used directly as a cathode. Before turning away from this conductivity problem, it should

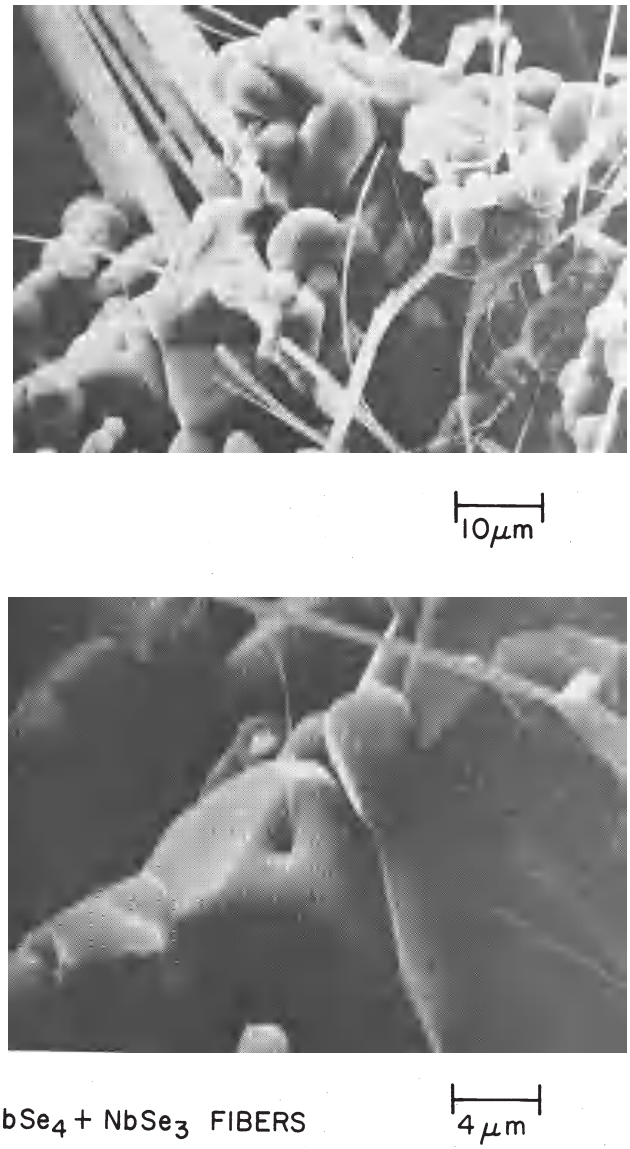

Fig. 4 SEM Photographs of a composite cathode of $NbSe_{4.0-4.5}$ in a matrix of fibrous $NbSe_3$.

be noted that the MX_2 compounds are generally good conductors and, as is well known, some are even superconductors at low temperatures. One should be cognizant of the fact that the conductivity of an MX_y compound may or may not change significantly upon incorporation of lithium as shown for $NbSe_3$ and TiS_3 in Table 2 [17]. Reduced conductivity at high Li concentrations in the metallic V_6O_{13} is also a problem [18].

Table 2. Pressed Pellet DC Resistivity of Lithiated $NbSe_3$ and TiS_3

	ρ(ohm-cm)		ρ(ohm-cm)
$NbSe_3$	3.4×10^{-3}	TiS_3	4
$LiNbSe_3$	10^{-1}	$LiTiS_3$	5
Li_2NbSe_3	4	Li_2TiS_3	4
Li_3NbSe_3	11	Li_3TiS_3	5

In the above discussion we have noted that structural or other changes taking place in certain MX_3 compounds during cell discharge (Li incorporation) can adversely affect their usefulness as cathode materials. In the case of $NbSe_3$, an apparently beneficial structural change occurs upon cycling in a cell. In Fig. 5 the first and second discharge curves are plotted for a $Li/NbSe_3$ cell. Note that the first discharge curve shows a very flat plateau

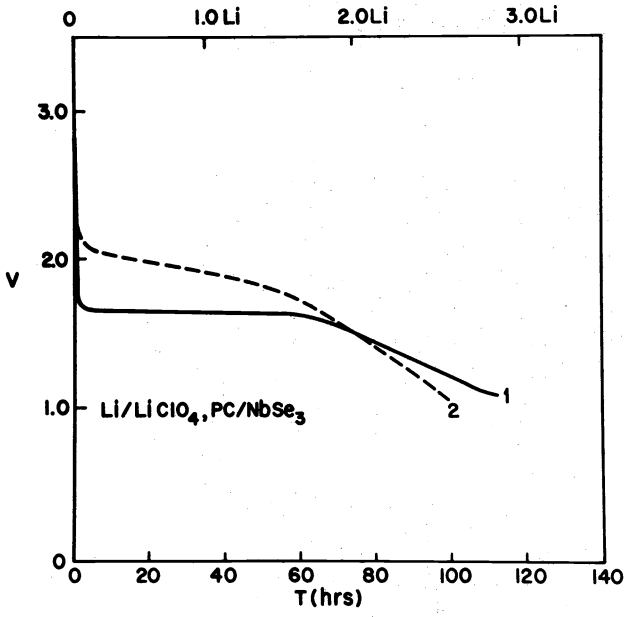

Fig. 5 First and second discharge curves at low current for $Li/NbSe_3$ cell; from Ref. 8.

at about 1.6 volts. This is the type of discharge curve one might expect if the lithium reacted to form a definite compound, such as Li_2NbSe_3, as contrasted with the monotonically decreasing voltage in the discharge curve for TiS_2 (Fig. 3). In the latter case, Li forms a continuous solid solution as x increases from 0 to 1 in Li_xTiS_2. In the $NbSe_3$ case, the lithiation (discharge) and delithiation (charge) of the "Li_3NbSe_3" apparently leaves behind a modified structure, based on the second discharge curve, most of which is at significantly higher voltages than the first discharge and resembles more closely the monotonic curves for Li/TiS_2. From a battery standpoint, this phenomenon makes the $NbSe_3$ much more attractive for the 3 volt memory applications, since by predischarging and charging a double cell $Li/NbSe_3$ battery, the voltage is raised from barely meeting the 3 volt cutoff requirement to an initial voltage of more than 4 volts.

Unfortunately, the nature of the change in $NbSe_3$ (and in NbS_3 as well) is presently unknown. The effect appears similar to that observed for TiS_3, in which succeeding discharges also occur at higher voltages than the initial discharge. However, the initial discharge curve for TiS_3 is not flat but relatively complex [10] (perhaps indicative of a mixed process of Li forming Li_2S and also intercalating in TiS_2?). The capacity for TiS_3 falls sharply to less than one lithium per TiS_3 whereas for $NbSe_3$, as shown in Fig. 6, the capacity after > 200 cycles (equivalent to > 100 deep "3Li" cycles) is still nearly two lithiums per $NbSe_3$ and 75%

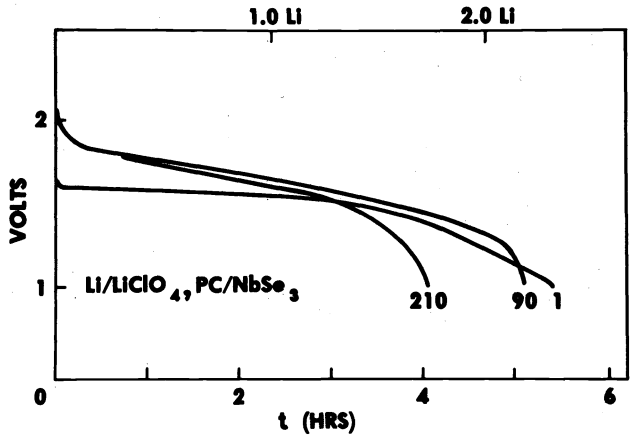

Fig. 6 Discharge behavior of $Li/NbSe_3$ cell. The lithium anode was renewed periodically because of anode failure (see later in text).

of the initial capacity. The discharge capacity of $Li/NbSe_4$ cells also decays rapidly on cycling and extensive lithiation results in the formation of some Li_2Se, as detected by x-ray measurements [5].

So far, we have considered primarily structural changes in MX_3 compounds. Of the MX_2 compounds, TiS_2 has received the most attention, enhanced by the appearance of Exxon's commercial $Li-Al/TiS_2$ battery, albeit of limited rechargeability (5 deep cycles). Another MX_2 compound which has received considerable attention recently is VS_2 and its alloys with Fe and Cr. Previously unknown in spite of efforts to prepare the compound, VS_2 was first synthesized by Murphy et al. [19] by treating the known compound $LiVS_2$ with a solution of iodine in acetonitrile to remove the Li, i.e.,

$$LiVS_2 + \frac{1}{2} I_2 \text{ (in acetonitrile)} = LiI + VS_2 \qquad (5)$$

The utilization of VS_2 in a Li/VS_2 cell was relatively low, however, due to another adverse structural problem on Li intercalation as illustrated by the phase diagram shown in Fig. 7 [20]. As the cell discharges and x increases in Li_xVS_2, new phases are formed which, for

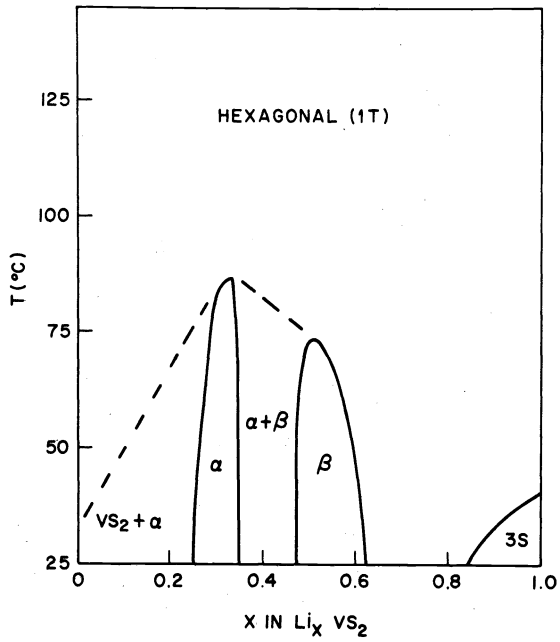

Fig. 7 Phase diagram for the $Li-VS_2$ system; from Ref. 20.

reasons not clear at this time, limit the performance of the cell. This inhibition can be overcome by going to temperatures above the multiphase region where the unwanted structures do not form. However, for lower temperature operation, substituting Fe or Cr for some of the vanadium in VS_2 was found to overcome or minimize the tendency of the structure to change. Furthermore, the voltages were quite attractive as discussed earlier (Fig. 3). Here we have a case in which the challenge of a detrimental structural transformation led to more promising battery materials; perhaps a similar approach might result in a modification of the properties of TiS_3.

CO-INTERCALATION OF MX_y: A NEW APPROACH?

It has been reported recently that a second lithium could be intercalated in certain MX_2 compounds including TiS_2, VS_2 and VSe_2 [21,22]. Unfortunately, these processes occur at voltages sufficiently low to be of little interest for practical Li/MX_2 cells. Also, there are some stability problems in certain cases and reversibility of both lithiums is not achieved. A novel approach has recently been taken by Basu and Worrell [23] who first intercalated a limited amount of sodium into TiS_2 to form $Na_{0.18}TiS_2$. This intercalation of sodium, which increases the lattice spacing in the layered compound, was then followed by the introduction of lithium in a Li/Na_xTiS_2 cell. The interesting observation is that 3 lithiums are incorporated at voltages that are attractive for battery use, as shown in Fig. 8, which

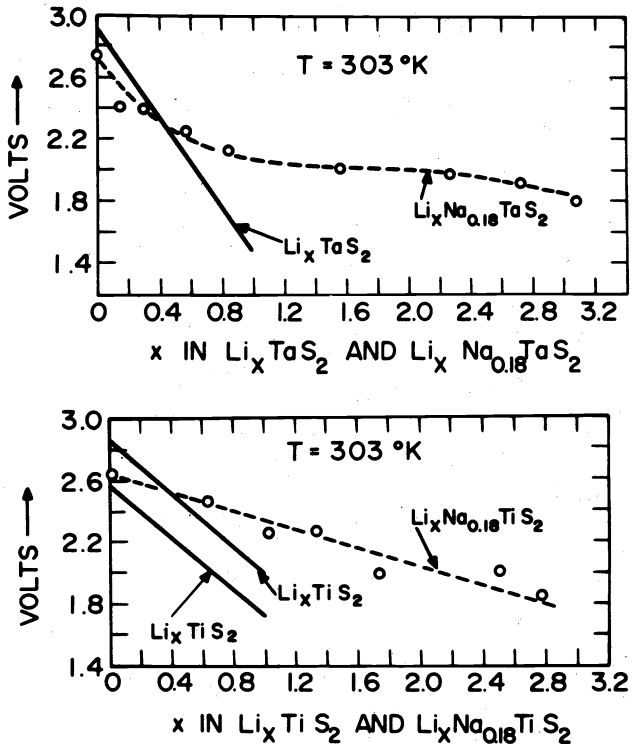

Fig. 8 (a) Variation of the open-circuit voltage as a function of the composition, x, of Li/Li_xTaS_2 and $Li/Li_xNa_{0.18}TaS_2$ cells. (b) Variation of the open-circuit voltage of Li/Li_xTiS_2 and $Li/Li_xNa_{0.18}TiS_2$ cells; from Ref. 23.

also shows similar results for TaS_2. This doubling or tripling of the capacity by co-intercalation could prove to be a very lucrative approach to improved cathode performance if it is shown that the Na_xMX_2 compounds or other pre-intercalated compounds hold up well under cycling in lithium batteries. If not, the pre-intercalated cathodes may still be of interest as cathodes in primary lithium batteries.

EFFECTS OF PARTICLE SIZE AND MORPHOLOGY

It is axiomatic in the battery field that smaller particle size (larger surface area) leads to higher rate (current) capability. For example, the importance of preparing TiS_2 in the form of fine particles has been demonstrated in connection with the Li/TiS_2 batteries [24]. The MX_2 compounds generally form as hexagonal platelets, as shown in Fig. 9 for $NbSe_2$. The diffusion of lithium into the gaps between the layers during cell discharge is very slow

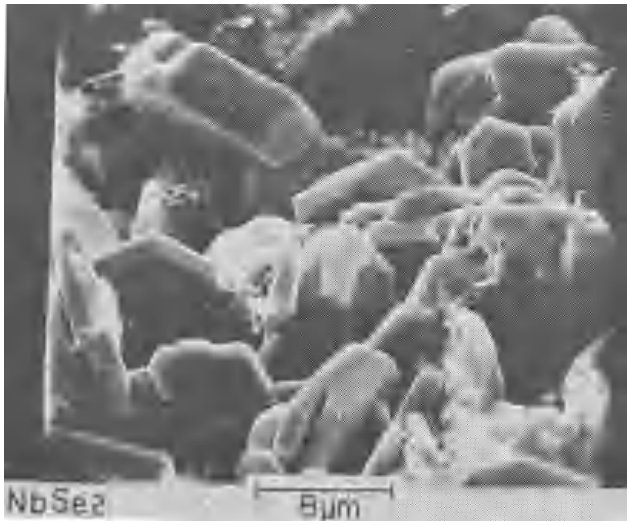

Fig. 9 SEM photograph of hexagonal platelets of $NbSe_2$.

perpendicular to the major faces but fast perpendicular to the edges of the crystals. On the other hand, for $NbSe_3$, whose fibrous morphology is shown in Fig. 10, the lithium can diffuse

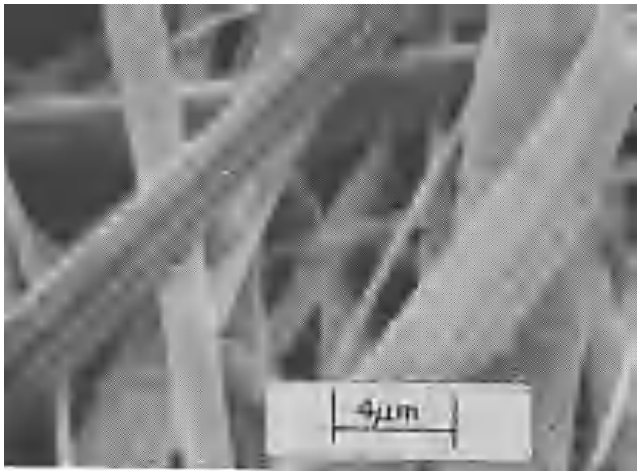

Fig. 10 SEM photograph of fibrous $NbSe_3$ cycled in the $Li/NbSe_3$ cell whose discharge behavior is shown in Fig. 6.

rapidly perpendicular to the major surfaces. All other things being equal, smaller particles of MX_2 are needed to attain the same current capability as MX_3 fibrous materials. An example of modifying growth procedures to attain smaller particles of TiS_2 is shown in Fig. 11. Here

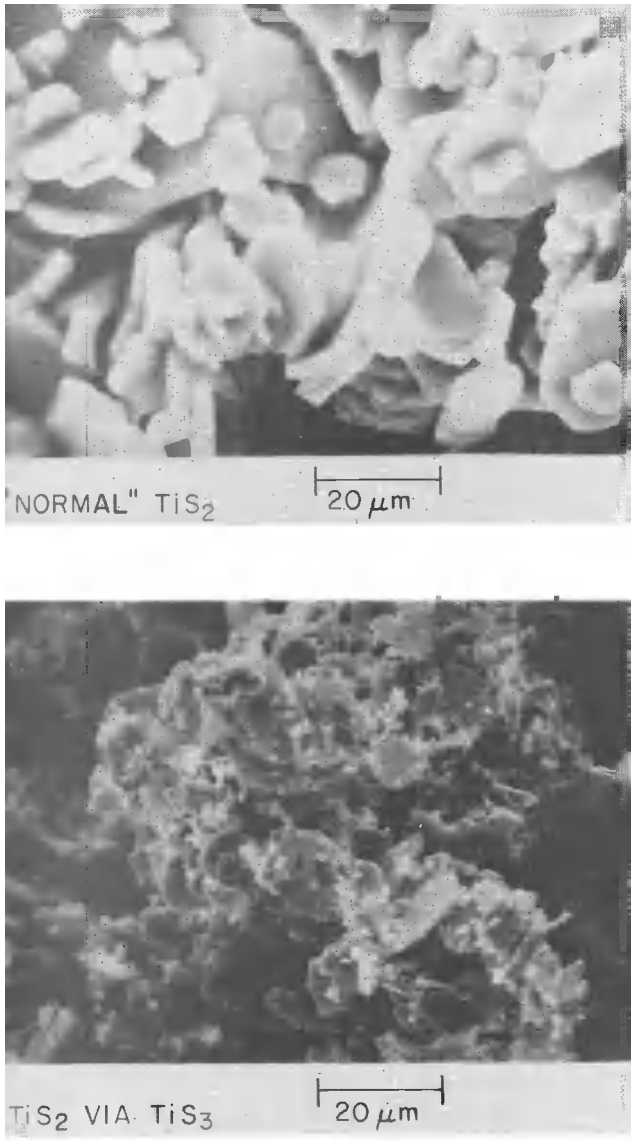

Fig. 11 SEM photographs showing modification of TiS_2 particle size by forming via TiS_3 fibers as compared with direct reaction ("normal" procedure) using same starting materials.

we compare the results of reacting titanium and sulfur stoichiometrically with a procedure of first making TiS_3 using the same starting materials, then decomposing to give TiS_2. The latter procedure is seen to yield appreciably smaller particles with correspondingly better cathode performance. Photographs of particles of various VS_2 compounds are shown in Fig. 12. These particles are comparable in size to the smaller TiS_2 particles without any special preparative procedures.

(presumably due to free iodine) and enhancement of a second "plateau" in the voltage range for Li-TiS_2 intercalation [25]. Although we now know that iodine is not needed in Li/MX_2 cells, there may be cases where a small amount of iodine would improve the performance of marginally pure cathode materials. A further possible benefit of iodine (or LiI) addition might be to "pin" the voltage at the Li/I_2 potential on overcharging a Li/MX_2cell. This could be an attractive characteristic in certain applications since the voltage of an overcharged Li/MX_y cell rises exponentially and, if unchecked, could result in decomposition of the electrolyte solution.

CHOICE OF ELECTROLYTE SOLUTION

The choice of the salt and solvent comprising the electrolyte solution is crucial for a number of reasons. First, the Li^+ ion may be solvated by the solvent to such a degree that both lithium and solvent may be incorporated into the layered MX_y [9]. This effect has been noted, for example, for $NbSe_3$-$NbSe_2$ "thin film" cathodes in cells employing $LiClO_4$-propylene carbonate solutions [8]. Such solvent incorporation can lead to extensive expansion of the cathode materials, even by a factor of two or so, leading to rupture of separators, rupture of bulging of containers, etc. Careful selection of electrolyte solution and MX_y may be necessary to minimize these effects and practical cells must be designed to accommodate any unavoidable expansion.

A second complication is the possibility of a reaction between the MX_y and the electrolyte solution. For example, when TiS_2 was placed in contact with solutions of $LiB(CH_3)_4$ in (dimethoxyethane)-dioxolane mixtures gas evolution was observed. Substitution of $LiB(C_6H_5)_4$ for $LiB(CH_3)_4$ resulted in no gas evolution under similar circumstances [26]. Lack of gas evolution does not necessarily indicate a lack of reaction in this case [27], but at least the products of the reaction do not lead to a potentially dangerous pressure buildup of gaseous products.

A third factor of importance when relatively high currents are needed for an application is the conductivity of the electrolyte solution. Unfortunately, one of the most frequently used solvents, propylene carbonate, with its advantages of a high dielectric constant (64), high boiling point (242°C) and low vapor pressure, suffers from a high viscosity which results in a significantly lower conductivity compared with the less viscous but more volatile solutions containing dioxolane, tetrahydrofuran, dimethoxyethane, etc.

Finally, two other very important factors, lithium anode rechargeability (cyclability) and safety are intimately related to choice of electrolyte solution. At present, these are the primary factors limiting the attainment of rechargeable lithium batteries. For a detailed discussion of recent progress in lithium cyclability and of the problems involved the reader is referred to a recent paper by Koch [28] in which a possible breakthrough toward a solution of the lithium cyclability problems is reported and references are given to earlier work.

NEW COMPETITION FOR MX_y

A discussion of rechargeable lithium battery cathode materials would not be complete without mention of a new and very promising alternative to the MX_y compounds. This material, V_6O_{13}, is not a layered material but a three-dimensional "framework" structure compound whose promising cathode properties have recently been reported by Murphy et al. [29]. The theoretical energy density, corresponding to 8 Li per V_6O_{13}, is quite attractive (Table 1) and the voltages are equally attractive for single cell or double cell NMOS memory applications as shown in Fig. 3. The morphologies of the material made by two techniques are shown in Fig. 13 and the smaller particle size material compares favorably with MX_y materials. The

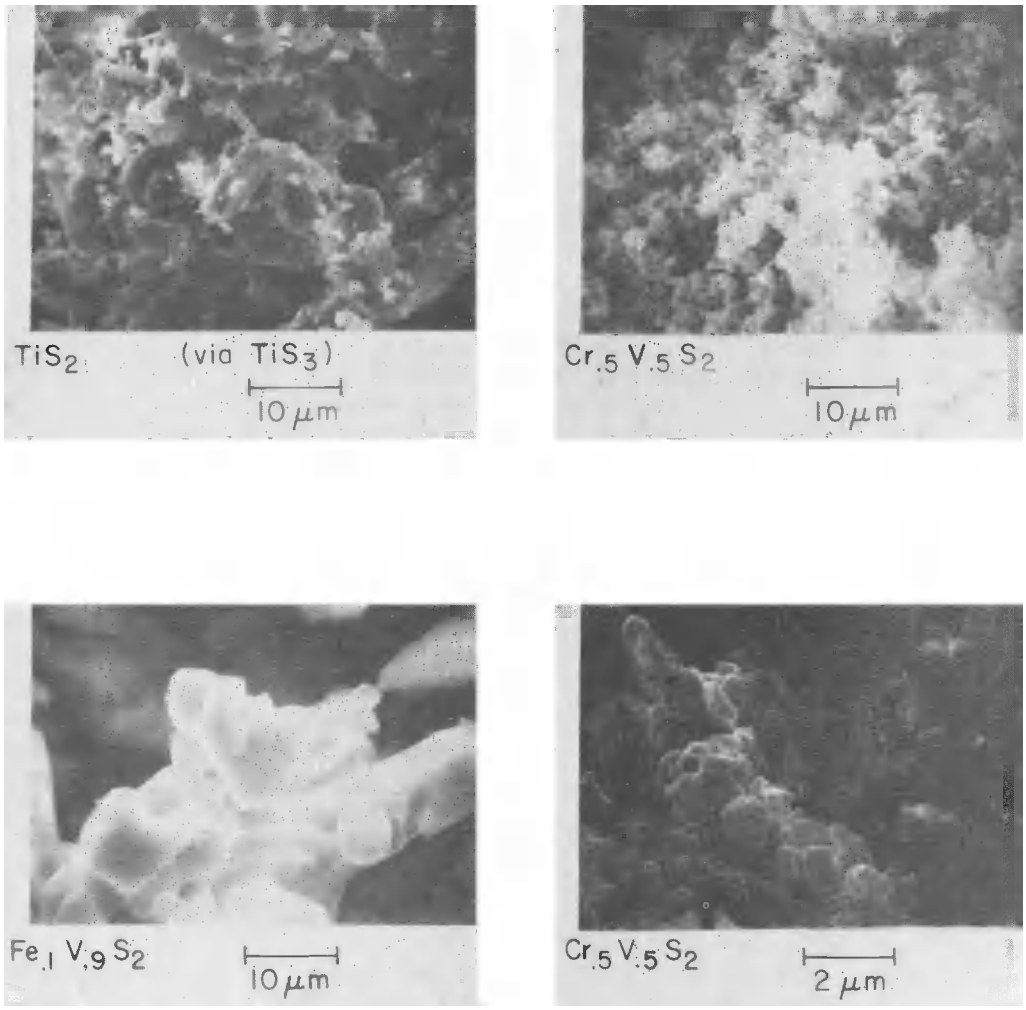

Fig. 12 SEM photographs showing morphologies of TiS_2 and various VS_2 compounds.

The crystal morphologies themselves can be altered significantly in certain cases. For example, by altering the growth conditions for $NbSe_{4.0-4.5}$, wither thin hexagonal platelets, needles or "chunky" polyhedra have been obtained [10]. Control of particle size and morphology could, especially in high rate batteries, mean the difference between acceptable and unacceptable battery performance.

STOICHIOMETRY EFFECTS

It is well known [9] that excess M in MX_2 compounds can reduce quite significantly the diffusion of Li in these layered compounds. Indeed, careful control of growth parameters is necessary to ensure that certain MX_2 compounds do not contain excess M. It has been postulated [5] that nonstoichiometric MX_2 compounds may have been responsible for the earlier erroneous conclusion [1,2] that iodine was intercalating in MX_2 and that MX_2 was an inert host material. Specifically, it was suggested that the iodine played the role of scavenger for either excess M and/or surface contaminants, thus clearing the way for lithium intercalation. Evidence in favor of this postulate lies in the elimination of cycling of a high voltage plateau

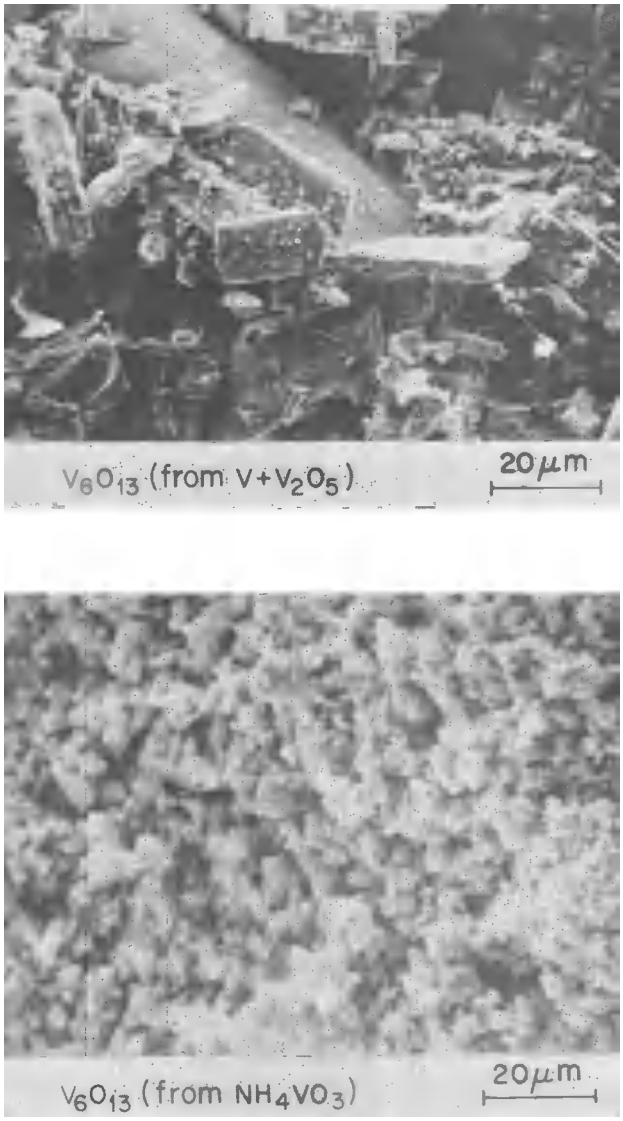

Fig. 13 SEM photographs showing morphologies of V_6O_{13} made by two different techniques. The larger particles were made by reacting V_2O_5 with vanadium metal while the smaller particles were made by the decomposition of NH_4VO_3 in argon.

preparative technique is particularly simple, involving heating of NH_4VO_3, the same material used to make V_2O_5. This ease of preparation, the relative insensitivity to moisture and good electrical conductivity (except at high Li incorporation) make V_6O_{13} an attractive material for cathode fabrication and high utilization of the active material. Furthermore, the cyclability of V_6O_{13} has been demonstrated in small test cells to be comparable to that of $NbSe_3$, the material we have studied most thoroughly at Bell Laboratories.

CONCLUSION

The ultimate test of the practicality of a Li/MX_y, Li/V_6O_{13} or any other rechargeable system is of course, its performance in a real battery, which may be subjected to extremes of temperature ranging from -40° to +70-80°C for certain applications. Much more work is needed on

the high temperature behavior where electrolyte stability, container corrosion, etc. come into play. Standards of safety in an era of increasing environmental concern must be established. However, the fact that hundreds of thousands of lithium primary batteries are now in use makes it seem inevitable that rechargeable Li/MX_y, or other rechargeable batteries containing cathode materials stimulated by MX_y research, will be common within the next years.

Concerning the MX_y compounds, there is a need for much more work on $Li-MX_y$ phase diagrams and structures. Even the binary M-X phase diagrams are not available for most of the systems of interest. The work of Mikkelsen [30] on P-T-X equilibria for the Ti-S system is an example of the type of data needed. The possibility exists that some of the MX_y compounds (e.g., TiS_3, $NbSe_3$?) may have been prepared with structures that are metastable at ambient temperatures. (Perhaps some of the structural changes on lithium incorporation represent a reversion to the stable structures?) A detailed study of the problem of fading capacity in Li/MX_y cells is also needed to separate out cathode problems (structure changes, reaction with electrolyte solution, fabrication problems, etc.) from lithium anode rechargeability problems.

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