

Vanadium Disulfide: Metal Substitution and Lithium Intercalation

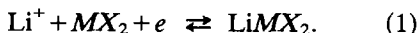
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The preparation and physical properties of the layered VS_2 , $M_xV_{1-y}S_2$ ($M = Fe$ or Cr), and their lithium intercalation adducts are described. These compounds were prepared by oxidative delithiation of $LiM_xV_{1-y}S_2$ with iodine. Crystallographic distortions present in Li_xVS_2 ($0.25 \leq x \leq 0.6$) are suppressed by Fe or Cr substitution for V. The electrochemical sluggishness of $Li/Li^+/VS_2$ cells is reduced by the substitution.

The two-dimensional Van der Waals bonded metal dichalcogenides have been the subject of intensive research in recent years. Of particular interest to a fundamental understanding of the electronic nature of matter is the discovery of charge density wave instabilities (CDW) (1, 2). At the same time these compounds are promising cathode materials for ambient-temperature secondary lithium batteries based on the reversible intercalation of lithium (3, 4):



Our interest in these and related areas led us to attempt to prepare VS_2 and CrS_2 , the only previously unreported disulfides of the Group IVB, VB, and VIB transition metals. We expected that emfs of Li/MX_2 cells would increase in the order $Ti < V < Cr$ based on reduction potentials of the corresponding M^{4+}/M^{3+} couples, leading to a corresponding increase in theoretical energy densities. In addition, VS_2 was expected to exhibit CDW behavior similar to that of VSe_2 (5).

Previous attempts to prepare VS_2 and CrS_2 by stoichiometric reactions at high temperature failed, the reaction with V

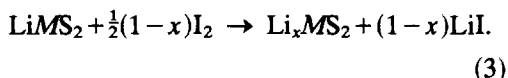
yielding V_5S_8 . Chianelli and Dines (6) recently reported the preparation of MS_2 compounds including VS_2 via the low-temperature metathesis reaction of MCl_4 and Li_2S . When prepared by this method, however, the MS_2 compounds are amorphous and not expected to share the fundamental properties of their two-dimensional analogs. Both V and Cr, however, readily form $LiMS_2$ ($M = V$ or Cr) compounds (7), isostructural with $LiTiS_2$, in which covalently bonded two-dimensional MS_2 layers are separated by lithium ions occupying octahedral sites between the MS_2 layers. Since such a compound would be the cathodic discharge product of a Li/MS_2 cell, we attempted to produce the MS_2 by charging cells of the type $Li/LiClO_4$, propylene carbonate (PC)/ $LiMS_2$ constructed in the discharged state. These attempts were not fully successful for reasons discussed later.

The value of the *n*-BuLi technique (8, 9, 10) in preparing lithiated compounds analogous to those obtained by cell discharge inspired us to also chemically mimic cell charging. Charging of the cell involves the oxidation half-reaction at the cathode [Eq. (1)] wherein lithium ions and electrons are

removed from the LiMX_2 . A reaction which might be expected to mimic charging utilizes water as an oxidizing agent:



However, this and other aqueous oxidation reagents have limitations which must be determined for each compound, such as concomitant hydrolysis of the metal sulfide, incomplete oxidation, the introduction of water into the Van der Waals gap coordination to lithium, and ion exchange of lithium by protons. We found that the I_2/I^- couple in polar nonaqueous solvents (e.g., acetonitrile) is free of the side reactions of aqueous reagents and effective in the delithiation reaction (11, 12):



This reagent readily affords the layered VS_2 from LiVS_2 , but is not a strong enough oxidant to yield CrS_2 from LiCrS_2 . Efforts to synthesize CrS_2 with the stronger oxidant bromine gave a substantial amount of chromium dissolution.

Lattice oxidation with lithium ion removal is part of a more general class of reactions which might be termed "oxidative deionation." With iodine, for example, other mobile ions present in an oxidizable lattice whose iodide is soluble should also be effectively removed from the lattice. We have found, for example, that Cu_2S and Cu_3P are readily converted to CuS and CuP , respectively, by iodine in acetonitrile. Steele (13) has reported that Cu may be electrochemically removed from bornite-type composition Cu_5FeS_4 , yielding a structure capable of reversible lithium incorporation. We have found that this Cu can readily be removed from bornite with iodine. We expect many new compounds will be prepared by low-temperature "oxidative deionation" of mobile ions such as Li, Na, K, Cu, or Ag. Attempts to prepare VS_2 with an

entirely different structure derived from the spinel, CuV_2S_4 , failed presumably due to Cu immobility.

The close structural similarity of VS_2 and LiVS_2 to TiS_2 and LiTiS_2 suggests that the electrochemistry of their Li/MS_2 couples would also be similar. However, VS_2 cells give significantly lower capacities, corresponding to less than 0.5 Li/V (12).

This limited capacity appears to be intimately related to distorted structures which occur at intermediate Li_xVS_2 ($0.25 \leq x \leq 0.6$) compositions (11). The phase diagram for this system is shown in Fig. 1. In the regions α and β , monoclinic distortions of the ideal hexagonal structure occur and two phase regions exist between α and β and between VS_2 and α . Indeed, Li/VS_2 cells operating at 85°C , in the single-phase region of Li_xVS_2 , show capacities near one Li per V.

Low mobility of Li^+ for some values of x , or slow nucleation of one of the phases, may be responsible for the electrochemical sluggishness. Silbernagel (14) has used ^7Li

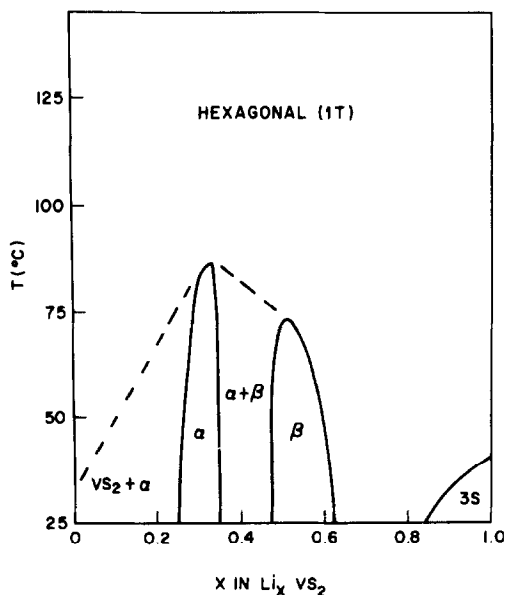


FIG. 1. Phase diagram for Li_xVS_2 as a function of lithium content, x (11).

nuclear spin-lattice relaxation rates as a measure of the microscopic hopping time for Li diffusion in similar compounds. An essentially frequency-independent relaxation rate implies a hopping time $\gg 100 \mu\text{sec}$ in LiVS₂ at 25°C (15, 16). For $x = 0.5$ and $x = 0.33$, initial results by Warren, et al. (16) indicate hopping times on the order of $10 \mu\text{sec}$. Transitions from the 1T phase to the distorted α and β phases reduce the Li⁺ mobility by only about a factor of 10. Thus if electrochemical sluggishness is caused by low Li⁺ mobility, this appears to occur as $x \rightarrow 1$ rather than in the α and β phases.

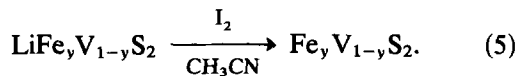
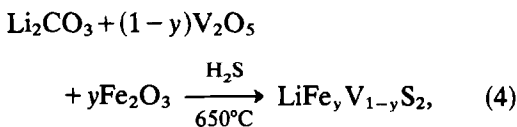
It has been noted recently that VSe₂ (9, 17, 18) and VS₂ (18) reversibly form Li₂VX₂ ($X = \text{S, Se}$) near 1 V vs Li/Li⁺. A similar formation of Li₂TiS₂ near 0.5 V followed by slow decomposition was proposed for TiS₂ (18). The vanadium systems show no evidence that phase nucleation limits their rate or capacity even though they are two phases between LiVX₂ and Li₂VX₂. The expansion of the VS₂ layer from LiVS₂ (hexagonal, $a = 3.381 \text{ \AA}$, $c = 6.139 \text{ \AA}$) to Li₂VS₂ (hexagonal, $a = 3.83 \text{ \AA}$, $c = 6.215 \text{ \AA}$) is much larger than between the α and β Li_xVS₂ and undistorted Li_xVS₂ compositions. These data and the ⁷Li NMR data suggest that phase nucleation rates are less important than the rate of lithium diffusion in limiting Li/VS₂ cell capacities.

We have attributed the existence of distorted Li_xVS₂ compositions to electronic instabilities within the VS₂ layers (11). Such instabilities may be due to CDW formation (especially for VS₂) or a Mott-like transition (especially for compositions near LiVS₂). Many two-dimensional metal chalcogenides including VSe₂ exhibit CDW, while a number of vanadium oxides show Mott-like transitions. Thompson (19) observed that the CDW "lock-in" temperature in different layered compounds increases with the crystallographic c/a ratio. Both VS₂ and LiVS₂ have relatively large c/a values of 1.786 and 1.816, respectively. The c/a ratio is larger

still at intermediate lithium compositions, and the region of highest c/a ratios (>1.85) corresponds to compositions exhibiting distorted structures ($0.25 < x < 0.6$).

From previous studies of metal substitution in layered chalcogenides, we knew that CDW transitions could be diminished or eliminated completely by such substitution (5). If the distortions in the Li_xVS₂ system could be suppressed, we would expect full capacity (1.0 Li/V) to be attainable in room-temperature Li/VS₂ cells. Studies in which Fe and Cr have been substituted for V in VS₂ indeed show improved capacity (12) (Fig. 2).

The compositions Fe_yV_{1-y}S₂ ($y \leq 0.5$) may be prepared (20) by a route analogous to that for VS₂:



The LiCr_yV_{1-y}S₂ ($0 \leq y \leq 1.0$) may be prepared (20) using Cr₂O₃ in Eq. (4). Only compositions with $y \leq 0.75$ may be delithiated via Eq. (5). The crystallographic c/a ratio decreases with increasing y in LiM_yV_{1-y}S₂ ($M = \text{Fe, Cr}$). For $y = 0$, $c/a = 1.816$, while with $M = \text{Fe}$ and $y = 0.5$, c/a decreases to 1.755, and for $M = \text{Cr}$ and $y = 0.75$, $c/a = 1.750$. These reduced c/a ratios and the disorder in the transition metal layer both tend to suppress the electronic instabilities. None of the compositions Li_xM_yV_{1-y}S₂ ($0 \leq x \leq 1$ and $y \geq 0.25$) show any evidence of phase transitions in magnetic susceptibility (4 to 360°K) or in DSC (215 to 573°K), showing that the phase transitions associated with Li_xVS₂ are eliminated, greatly broadened, or considerably weakened.

In addition to improved electrochemical reversibility of Fe- or Cr-substituted VS₂, the

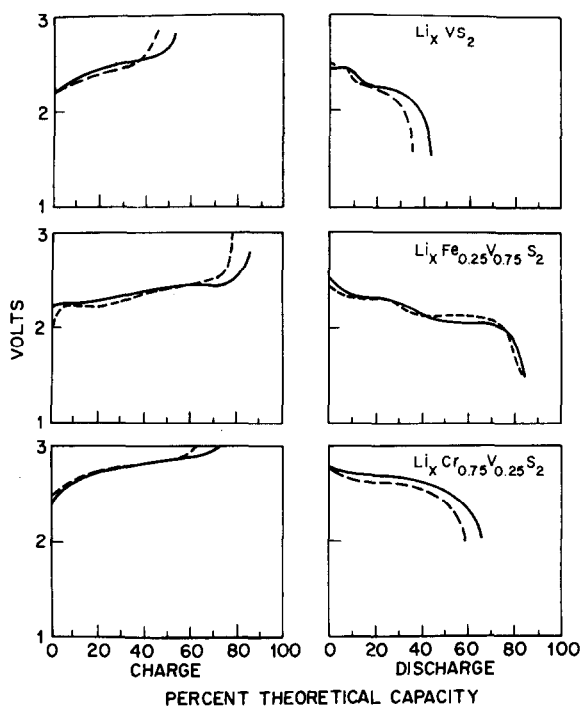


FIG. 2. Capacity of cells (12) based on VS_2 on first (—) and fifth (---) cycles. LiClO_4 (1 M) in PC was the electrolyte.

trends in cell emf are of interest. An initial hypothesis was that the emf would increase in the order $\text{Ti} < \text{V} < \text{Cr}$. Figure 3 shows open circuit emfs as a function of state of charge for several MX_2 . The emf of Fe-substituted VS_2 is virtually the same as for VS_2 itself and roughly 150–200 mV, greater than for TiS_2 . Substitution by Cr raises the cell emf so that at $\text{Cr}_{0.75}\text{V}_{0.25}\text{S}_2$ $E_{1/2}$ is 2.65 V, while for VS_2 $E_{1/2}$ is 2.30 V, and for TiS_2 it is 2.10 V. In addition to the higher emf, the voltage is more constant for Cr-containing cells as a function of state of charge; both properties may be desirable for specific applications. The failure of LiCrS_2 to undergo oxidative delithiation with iodine reflects the expected maximum potential expected for the Li/I_2 couple (2.85 V).

In the mixed transition metal compounds V/Fe or V/Cr we have used magnetic susceptibility and Mössbauer measurements to help determine the valence state of these

cations as a function of Li concentration (20). In the case of iron, the results show that the Fe is divalent for all Li concentrations so that it does not directly take part in the oxidation–reduction process. However the magnetic state of the Fe^{2+} depends on not only the lithium concentration but also on the Fe concentration itself. At low Fe concentration ($y \leq 0.1$), the Fe^{2+} remains low spin ($s = 0$), independent of the lithium concentration, but some of the vanadium develops a magnetic moment. At high Fe concentrations ($y \geq 0.25$), some of the Fe develops a magnetic moment when the Li concentration approaches 1.0.

When the V is replaced by Cr, the Cr is found to be nonmagnetic (20), consistent with the expected valence of Cr^{4+} . At full lithium intercalation the Cr develops a magnetic moment, consistent with the paramagnetic state of Cr^{3+} observed in LiCrS_2 . The change of valence of the Cr is

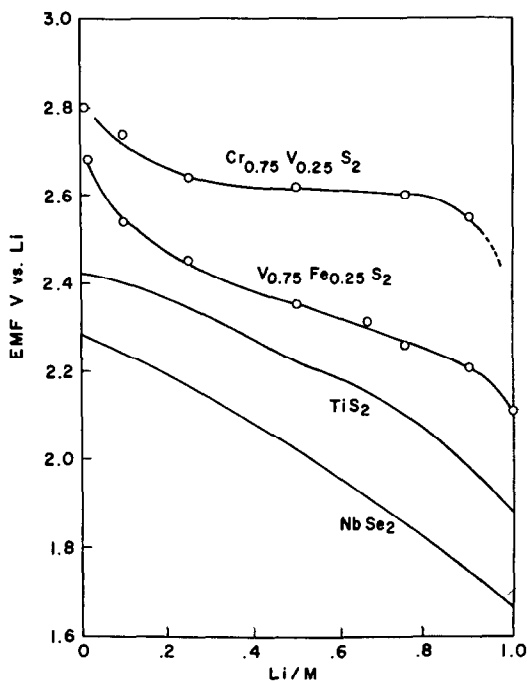


FIG. 3. Open circuit potentials for various Li/MX₂ cells. TiS₂ data from Ref. (21) and NbSe₂ data from Ref. (22).

consistent with the observation of increased cell potential with increased Cr substitution.

The results of the work presented here on the lithium VS₂-based systems illustrate several important points. First is the preparation of the previously unknown VS₂ and the promise of other new compounds prepared by "oxidative deionation." The importance of lattice distortions to reversible lithiation, and the suppression of the lattice distortions, has been demonstrated.

Acknowledgment

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