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Electrochemical Lithium Intercalation into Misfit Layer Sulfides

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Ternary sulfides of approximate formulas, $PbVS_3$, $PbTiS_3$, and $PbTi_2S_5$ and misfit layered structures were used as cathodes in lithium test cells. The discharge and OCV curves for $PbVS_3$ and $PbTiS_3$ were consistent with the concomitant occurrence of pristine and isostructural lithiated phases at low discharge depths, which led to a short quasi-plateau below 0.5 Li/formula unit, which was particularly outstanding for the vanadium compound. Further discharge resulted in progressive amorphization of the lithiation product in an extended plateau that was preserved at higher discharge depths in the case of vanadium. For $PbTi_2S_5$, the presence of consecutive 1-T related TiS_2 slabs in the structure allowed the formation of a 105-Å phase, which can be described as stage III, with a HLiHCHHCHHC stacking unit. The co-occurrence of this phase and pristine $PbTi_2S_5$ resulted in an initial plateau below 0.3 F. The X-ray diffraction data obtained between 0.3 and 0.8 F suggest the presence of stage III and stage I lithiated phases. Above 0.8 F, stage I and amorphous products are involved that give rise to an extended plateau in the discharge curve.

Introduction

Ternary chalcogenides of nominal composition $MM'X_3$ (real composition $(MX)_nM'X_2$; $1.08 < n < 1.23$; M = Pb, Sn, Bi, rare-earth metals, M′ = Ti, V, Nb, Ta, Cr, X = S, Se) have been paid special attention over the last two years because of their peculiar structures.[1-14] These compounds can be classified as composite layered crystals or misfit layer compounds. Their structure is described on the basis of alternate stacking of [MS] (C) and [$M'X_2$] (H) slabs along the *c* direction. Owing to the discrepant periodicities of the two sublattices, these materials tend to be incommensurate in one direction (the *a* axis).

A new series of misfit layered compounds of nominal composition MM'_2X_5 has also been reported.[1,15-18] Only the crystal structures of $(PbS)_{1.12}(NbS_2)_2$[16] and $(PbS)_{1.18}(TiS_2)_2$ have been determined so far.[18] In these systems, each [MS] slab is separated by two [$M'S_2$] layers that give rise to a stacking sequence ...HHCHHC..., which differs from the ...HCHC... sequence found for the $MM'X_3$ composition.

The structurally flexible matrix system of these compounds and the high mobility of guest cations surrounded by readily polarizable chalcogenide anions prompted us to study their properties as hosts for the intercalation of electron-donating species. The results obtained by chemical lithiation with *n*-butyllithium showed the reaction to take place topochemically and guest ions to induce a marked distortion of the [MX] slabs in contrast to [$M'X_2$] layers, which only underwent small changes.[19,20] We also found that compounds with a nominal stoichiometry 1:2:5 intercalate larger amounts of lithium per transition-metal atom than those of 1:1:3 composition. Moreover, the exposure of lithiated product $Li_xPbTi_2S_5$ to water gives rise to monolayer and bilayer hydration processes of the intercalated ions.[21] This behavior was ascribed to the occurrence of a [$M'X_2$] double sandwich for the ternary sulfide.

An alternative method for inducing an electron/ion reaction such as that described above is via an electrochemical reduction process. In fact, electrochemical techniques not only make convenient means of synthesizing intercalation compounds, but also allow the evaluation of thermodynamic and kinetic reaction properties.[22] Also, as the amount of guest ion involved in the process can be controlled more accurately than that inserted via chemical reduction, detection and characterization of the metastable phases are occasionally easier. The phase diagram of Li_xNbSe_2 ($0 < x \le 1$) is an elegant example of this behavior. The interpretation of chemical lithiation results led to the assumption that Li_xNbSe_2 occurs as a single phase for all *x* values between 0 and 1.[23] However, ex-

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perimental evidence for the occurrence of staging phenomena in the Li_xNbSe_2 system at room temperature has been found by using $Li/NbSe_2$ electrochemical cells.[24] Very recently, the electrochemical lithium intercalation into $PbNb_2S_5$ has been reported.[25] A continuous solid solution "$Li_xPbNb_2S_5$" was found with the same structure as parent compound $PbNb_2S_5$ but with an expansion of the unit cell along the *c* axis.

In this work we report the electrochemical intercalation of Li^+ into misfit layer compounds $PbTiS_3$, $PbVS_3$, and $PbTi_2S_5$, in order to obtain further information on the occurrence of partially lithiated ordered phases. Remarkable differences in reactivity have been observed between the two types of stoichiometry, which have been interpreted in relation to the structural features of both series of compounds.

Experimental Section

Samples of approximate composition $PbVS_3$, $PbTiS_3$, and $PbTi_2S_5$ were prepared by direct synthesis from their elements, as described elsewhere.[7,14,19] The metal elements and sulfur were supplied by Strem Chemicals and Merck, respectively. Phase purity and the structure of the pristine and lithiated phases were checked by X-ray powder diffractometry (XPD) using a Siemens D500 diffractometer furnished with Cu Kα radiation and a graphite monochromator. Electron diffraction patterns obtained on a JEOL 200 CX apparatus were used to confirm the misfit layered structure of the compounds.

Lithium ribbon (Strem Chem. 99.95%) and cooper powder (Merck 99.7%) were used as anode material and substrate, respectively. A 1 M $LiClO_4$–PC solution was required as electrolyte. $LiClO_4 \cdot 3H_2O$ (Merck) was dehydrated by vacuum melting at 300 °C for a few hours, and the organic solvent was purified by vacuum fractional distillation, the intermediate fraction being collected and stored in a drybox (M. Braun) under an Ar atmosphere.

The electrochemical cell was prepared in the drybox by placing a clean lithium disk, two glass fiber separator disks soaked with the electrolyte solution, and a pellet of the cathodic material concerned into a Teflon container with two stainless steel terminals. The pellet of cathodic material was made by compressing the powdered sample at about 3 tons on an inert metallic support (Cu). Each pellet contained 80 mg of sample and was 13 mm in diameter.

Galvanostatic discharge measurements were performed at various current densities and a fixed cutoff voltage by using an AMEL 549 potentiostat-galvanostat. Data acquisition was carried out with a DAS-8 PGA/PC system. The average lithium composition of the cathode material was calculated from the amount of electron charge transferred to the active material, on the assumption that no current flow was due to side reactions. X-ray diffraction characterization of these compounds at various depths of discharge called for a plastic fiber to cover the sample in order to avoid undesirable reactions with air during the recording. To obtain steady-state open-circuit voltage (OCV) values, measurements were carried out as the galvanostatic discharge at a current density of 50 μA cm^{-2} but with periodic halting of the discharge in order to allow for equilibration, which was assumed to be reached when the potential changed by less than 2 mV.h^{-1}.

Results and Discussion

The potential/charge transfer diagrams for the insertion of alkali Li^+ ions into host cathode chalcogenides are shown in Figure 1. They were recorded under galvanostatic conditions at current densities from 100 to 500 μA cm^{-2}. Quasi-equilibrium open-circuit voltage data were also obtained by stepwise discharge at a constant current. As is well-known, sloping portions in the discharge curves are

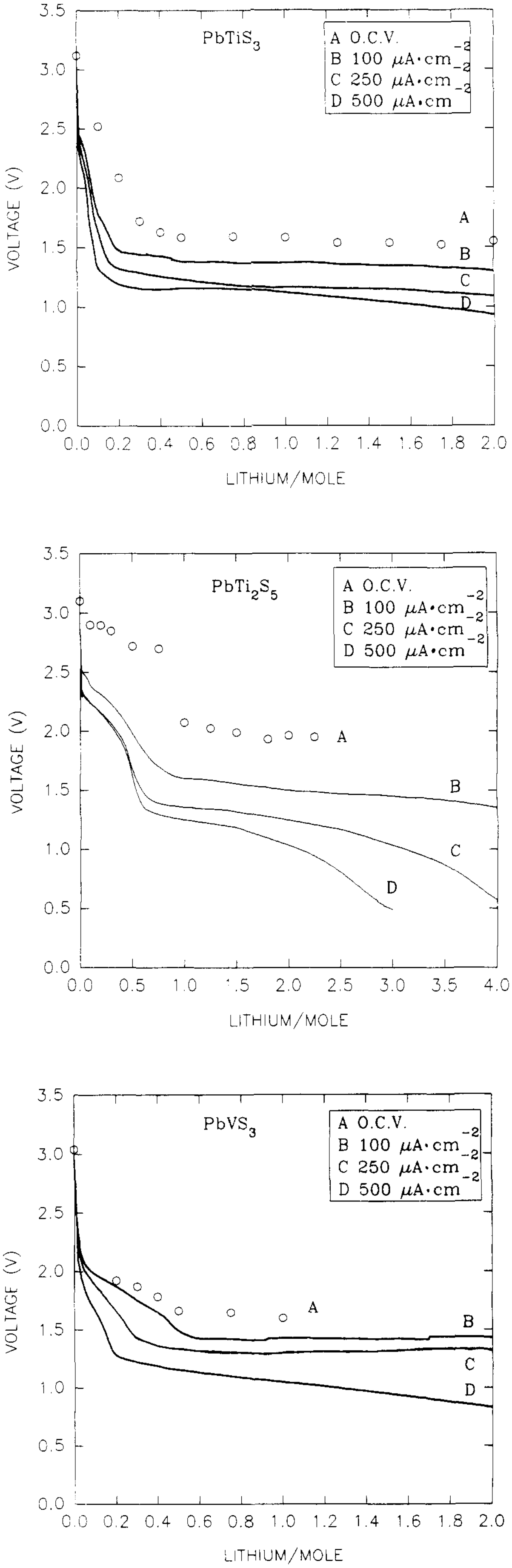

Figure 1. Discharge curves (continuous line) and OCV data (O) for (a, top) $PbTiS_3$, (b, middle) $PbVS_3$, and (c, bottom) $PbTi_2S_5$.

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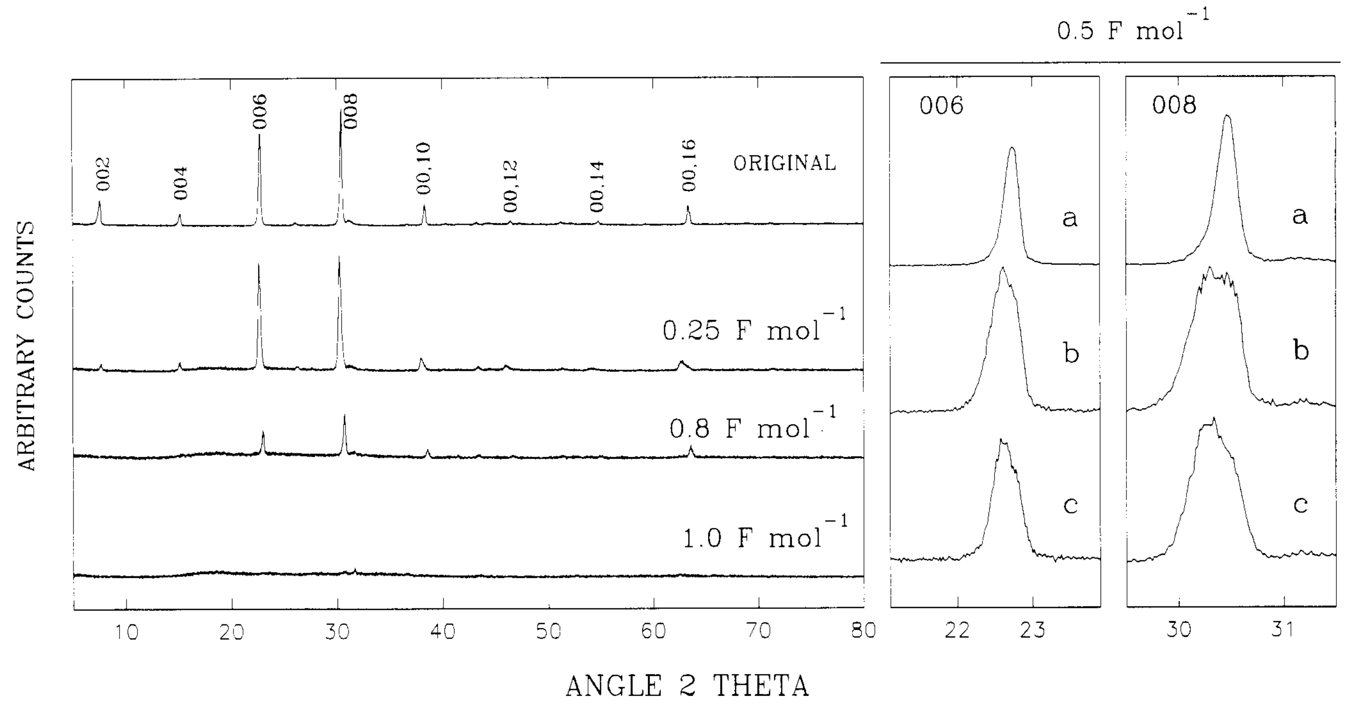

Figure 2. X-ray powder diffraction data of pristine and electrochemically lithiated products at different depths of discharge of $PbTiS_3$. Right: details of the 006 and 008 lines for (a) pristine sample, (b) and (c) discharged at 0.5 F mol^{-1}, as-prepared (b) and after equilibrium (c).

ascribed to the presence of single-phase cathode material while constant-voltage regions are thermodynamically equivalent to multiphase system.[26]

An initial OCV of 3.2 V was recorded for lithium versus $PbTiS_3$. Qualitatively, the discharge curve can be divided in two regions (Figure 1a). The first region shows a significant, continuous decrease in the potential with the degree of insertion, x. In the case of the OCV curve, this region spreads over mole concentrations of lithium of approximately $x \simeq 1$ (where x is the mole fraction of inserted species), and the voltage reaches a value about 1.5 V. For higher degree of intercalation the voltage is relatively independent of x.

The electrochemical behavior of the $PbTi_2S_5$ system is significantly different from that of the compound with the 1:1:3 stoichiometry (Figure 1b). First, the cell discharge capacity is much higher. Thus, while the discharge curve of the $PbTiS_3$ system recorded at 100 μA cm^{-2} drops to 1.5 V for a degree of intercalation of 0.3 Li^+, such a voltage value is obtained at 2.0 Li^+ ions for $PbTi_2S_5$. Moreover, the OCV discharge curve is characterized by several distinct plateaus of varying length above a lower limit of 1.7 V. Two-phase regions occurred over the ranges $0.1 < x < 0.3$, $0.5 < x < 0.8$, and $1 < x < 2$. This rather complicated profile can be rationalized in terms of different energy sites and is supported by the related X-ray diffraction data discussed below. On the other hand, the discharge curves are markedly influenced by the current density, which suggests that the electrochemical behavior is controlled either by a slow diffusion of Li^+ ions into the host or by the formation of multiphase systems as reflected in the OCV curve. At increasingly higher currents, the length of plateau is reduced and the voltage decreases below 1 V. Under this condition the electrolyte may become thermodynamically unstable. Thus an electrolyte breakdown can occur and smooth voltage decrease for large values of x can take place.

When the misfit compound $PbVS_3$ was discharged at various current densities in solutions containing 1 M $LiClO_4$/propylene carbonate, the discharge curves showed an intermediate behavior between those described for $PbTiS_3$ and $PbTi_2S_5$. As shown in Figure 1c, the decrease in the potential was more gradual than that recorded for $PbTiS_3$. Thus, for identical Faradaic yield and current densities, this cell provides higher potential values. The OCV curve deserves further comments. For lithium contents less than 0.3, the curve shows a gradual decrease in potential due to the slow kinetics at ambient temperature that makes obscure the two-phase region so that the width of this region cannot be determined accurately enough.

It can be seen that concentration polarization in the initial potential dropping of $PbTi_2S_5$ is larger than that in the following constant-potential region and the polarization of this system is larger than those for $PbTiS_3$ and $PbVS_3$. This decrease in concentration during discharge might be caused by the delay of Li^+ ion diffusion in the sulfide electrode.[27]

Finally, a sharp, continuous decrease in the voltage is also observed at the beginning of the discharge process, as frequently reported for other systems. Such behavior has been ascribed to the occurrence of a dilute gas phase with a homogeneous distribution of the guest ions within the host structure.[28] Some authors[29] have questioned this explanation due to the low temperature of the intercalation process that makes difficult a homogeneous distribution in the complete volume of the pellet. An alternative interpretation has been proposed in terms of nonequilibrium states in the initial region of the reaction. The X-ray diffraction studies discussed below agree with this explanation.

Figures 2–4 show the X-ray diffraction patterns changes with progressive reduction of $PbTiS_3$, $PbVS_3$, and $PbTi_2S_5$,

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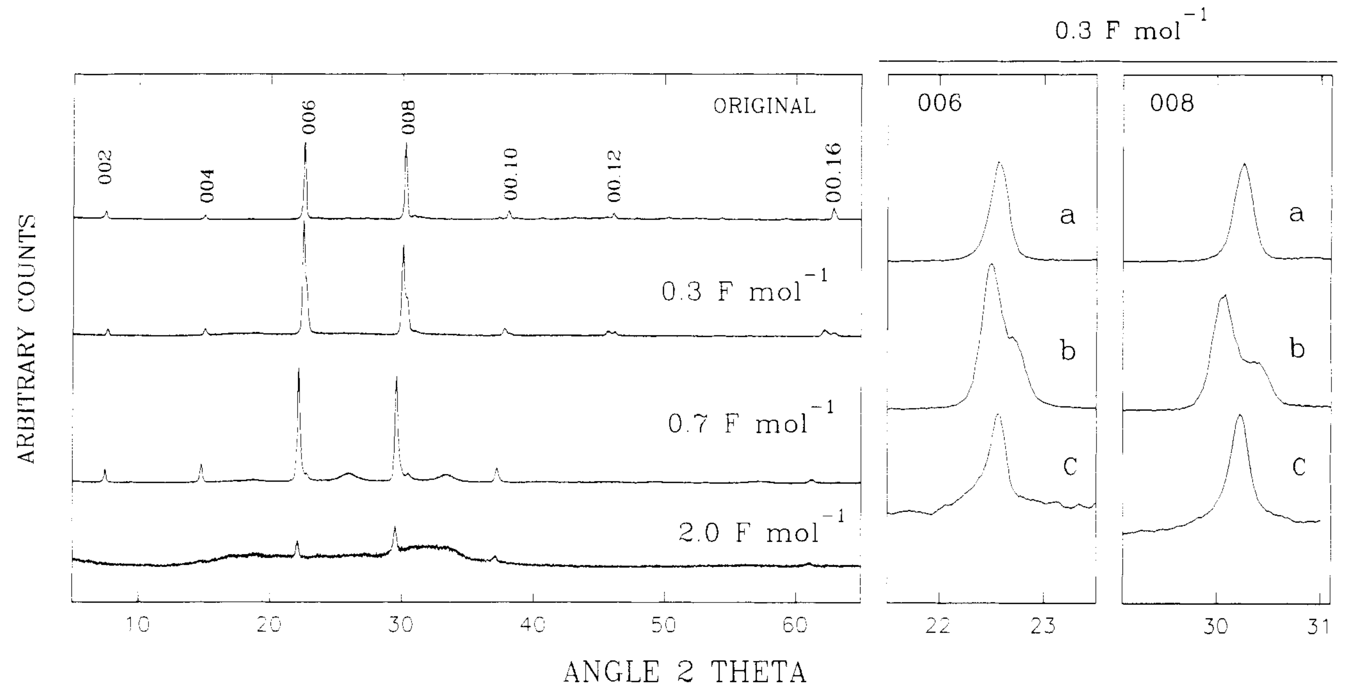

Figure 3. X-ray powder diffraction data of pristine and electrochemically lithiated products at different depths of discharge and $PbVS_3$. Right: details of the 006 and 008 lines for (a) pristine sample (b) and (c) discharged at 0.3 F mol^{-1}, as-prepared (b) and after equilibrium (c).

respectively. The different depths of discharge are also given in the figures. For $PbTiS_3$ and $PbVS_3$ compounds at $x = 0.25$ and 0.3, the X-ray diffraction patterns showed double lines in the positions where multiple-order reflections of the basal spacings would be expected (see the details of selected reflections in Figures 2b and 3b). This was specially outstanding for $PbVS_3$ (Figure 3b). The first set of lines is consistent with the presence of unlithiated phases, while the second leads to the *c* parameters given in Table I, which are significantly larger than those of the pristine phases. This behavior can be attributed to the co-occurrence of both unlithiated and lithiated phases, the contrast with the gradual conversion observed in chemically lithiated systems.[19] This two-phase mechanism, which is similar to those reported for some thermal decomposition reactions,[30] probably arises from the distortions induced by lithium intercalation in these systems, which do not allow the entire particle to be intercalated. It seems likely that for a low level of discharge, a partially intercalated platelet consists of a caplike cover of lithiated phase surrounding a central unlithiated core. Thus, the particles may collapse in partially lithiated domains, thereby hindering uniform distribution of lithium in the initial particles. In chemically lithiated samples, the prolonged treatment in *n*-butyllithium solutions under continuous stirring probably allows the redistribution of lithium in the different domains formed at the first steps of lithiation. To check this assumption, the XRD patterns of the electrochemically lithiated solids were recorded after maintaining the samples for 3 days in an inert atmosphere (Figures 2c and 3c). A single phase with an intermediate *c* parameter was detected, which implies lithium redistribution, leading to a single-phase product.

For the samples prepared by interrupting the discharge curves at $x = 0.80$ ($PbTiS_3$) and 0.70 ($PbVS_3$) in the extended quasi-plateau at about 1.5 V, the XPD data show an apparent single-phase product with a *c* parameter higher than pristine phases (see Table I). However, the intensity of these reflections decreases markedly for Li contents higher than 0.5, thus indicating a gradual amorphization of the lithiated phase, which is consistent

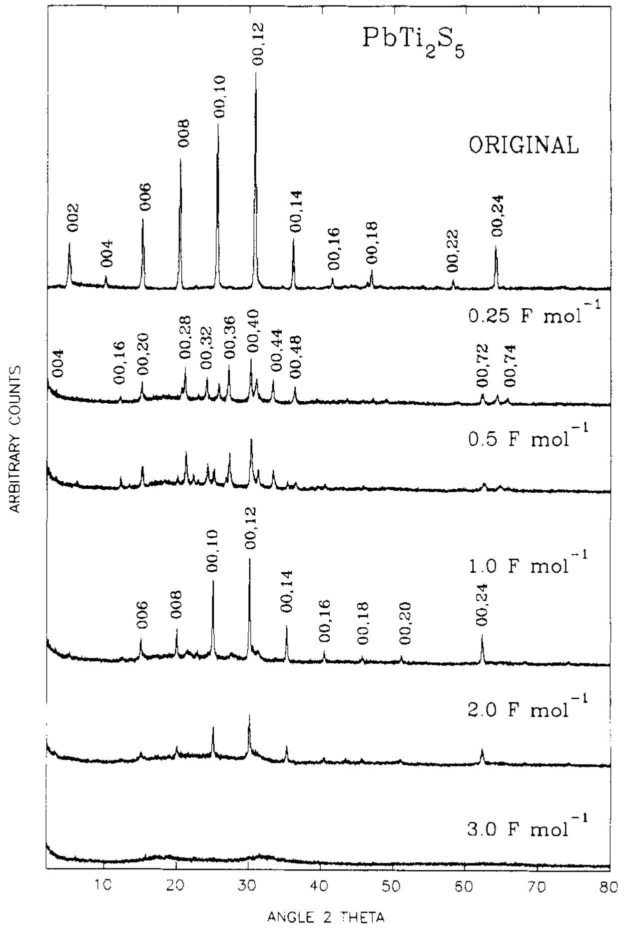

Figure 4. X-ray powder diffraction data of pristine and electrochemically lithiated products at different depths of discharge of $PbTi_2S_5$. Miller indices of pristine $PbTi_2S_5$, stage III (0.25 F) and stage I (1.0 F).

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Table I. Unit Cell *c* (Å) Dimensions of Electrochemically Lithiated Products

$PbTiS_3$			$PbVS_3$			$PbTi_2S_5$		
D	*L*	*H*	*D*	*L*	*H*	*D*	*L*	*H*
0.00	23.74 (9)		0.00	23.92 (8)		0.00	34.90 (1)	
0.25	23.77 (7)	23.89 (7)	0.30	23.89 (9)	23.99 (9)	0.25	34.90 (1)	105.46 (5)
0.50	23.72 (7)	23.86 (7)	0.70		24.28 (9)	0.50	104.98 (5)	35.29 (8)
0.80		23.89 (8)				0.75	106.41 (3)	35.54 (3)
						1.00		35.49 (5)

[a] *D*: Depth of discharge (F/mol). *L*: Lower lithium content phase. *H*: Higher lithium content phase.

with the chemical behavior.[19] Thus the plateau can be ascribed to the coexistence of the lithiated crystalline and amorphous solids. For $x \cong 1.0$ ($PbTiS_3$) and 2.0 ($PbVS_3$), the XPD data (Figures 2 and 3) are consistent with the high degree of amorphization leading to low-intensity broadened 00*l* profiles and a broad band. No extra lines ascribable to crystalline reduction products as lead, vanadium, or titanium were observed.

For $PbTi_2S_5$, the XPD patterns of samples prepared by interrupting the discharge curve are shown in Figure 4. For $x = 0.25$, in the first plateau of the OCV curve, the occurrence of low-angle reflections not observed in the original misfit or chemically lithiated samples with lithium contents higher than 0.6 was observed. These include a set of six multiple-order reflections of a phase with a *c* parameter close to 105 Å. This set could in principle be ascribed to a possible co-intercalation of the electrolyte solvent PC with lithium, as the layer spacing is found to increase from 6 to 17.8 Å in $LiTiS_2$ on electrolyte co-intercalation.[36] However, this co-intercalation is known to be irreversible, i.e., the co-intercalated PC cannot be removed electrochemically. In our case, further discharge off the test batteries from $x = 0.25$ F/mol removed the 105 Å phase. In addition, $Li_xPbTi_2S_5$ phases obtained by chemical intercalation using *n*-butyllithium were immersed in PC for extended periods and no intercalation was detected.

On the other hand, the 105-Å phase can be interpreted as a stage III lithiated phase in which every third HH interlayer region is occupied by lithium ions. This leads to the repeating unit HLiHCHHCHHC (Figure 5), as lithium insertion is more favorable in the van der Waals gap that separates two consecutive H slabs in the structure. The occurrence of staging in lithium intercalated dichalcogenides has been ascribed to the distortions induced in the lattice,[24,26] while the coordination of intercalated lithium is assumed to remain octahedral, in contrast with larger cations such as Na^+, K^+, and Rb^+,[31] and NH_4^+,[32] where trigonal prismatic coordination has been found. If the same pattern is applied to the misfit layer sulfides, then the Li ions should tend to occupy the octahedral sites defined by the consecutive H slabs. The fact that staging was not observed in $PbVS_3$ or $PbTiS_3$ is in agreement with the above description.

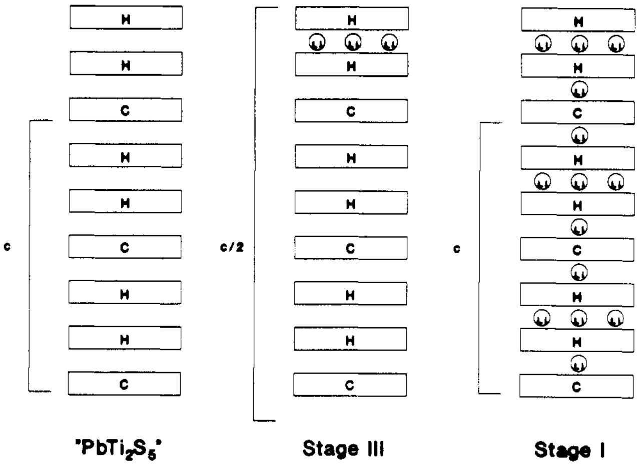

Figure 5. Scheme of the lithiation stages in $PbTi_2S_5$.

On the other hand, if the above interpretation is accepted, then the third-order reflection of the 105-Å basal spacing gives the average spacing of the slabs of stage III. This value is ca. 35 Å, which is slightly larger than that observed in the pristine misfit phase. Besides, no reflections were found that could imply the presence of stage II. Thus, the coexistence of pristine and stage III phases may account for the first plateau in the OCV curve. If the cell is discharged further to an equilibrium voltage below 2.7 V and corresponding to the second plateau of the OCV curve (see Figure 1b), the XRD pattern of the sample obtained for a degree of intercalation $x = 0.5$ shows the occurrence of a new set of multiple-order reflections together with that assigned to a stage III lithiated phase (Figure 4). The *c*-axis dimension obtained from this new set of reflections was 35.3 Å, similar to that found in the intercalates obtained by chemical methods.[19] Thus, this result is consistent with the formation of a stage I lithiated phase, in which every van der Waals gap contains equal concentration of lithium. This phase is stable from $x = 0.5$ to at least $x = 1$ and coexists with stage III lithiated phase over a composition range of $x = 0.5$–0.7, region in which a plateau is observed in the OCV curve. It should be noted that there is not an easy mechanism of conversion from stage III to stage I, as that proposed by Daumas and Hérold for the stage II–stage I conversion.[33] Thus this transformation probably requires a lithium redistribution that may lead to an extended region of coexistence of both phases. Finally, the third plateau is related to the gradual amorphization of stage I, as previously described for the 1:1:3 phases.

As mentioned above, electrochemical lithium intercalation into misfit layer compounds has been performed so far in "$PbNb_2S_5$".[25] The galvanostatic intermittent discharge curve has been interpreted according to a model in which Li is randomly distributed over the accessible sites in the host, except near $x = 0.25$ and $x = 0.50$, where ordered structures may occur. From a geometrical point of view, this compound has a similar structure with identical stacking sequence of C and H slabs to that found in "$PbTi_2S_5$" but with different geometrical coordination for the transition metal. Whereas Nb atoms are coordinated by six sulfur atoms located at the vertices of a slightly distorted trigonal prism, TiS_2 sandwiches have a distorted CdI_2-type structure. Thus, it seems that not only geometrical factors control the mechanism of the intercalation process, as suggested by Auriel et al.,[25] but also the electronic structure of the lattice plays an active role in the

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intercalation inducing structural changes in the host.

On the other hand, if the unit-cell parameters of the electrochemically stage I lithiated 1:1:3 and 1:2:5 phases are compared, a marked expansion of the 1:2:5 series is observed, whereas the lithiation process hardly affects the interlayer spacing of 1:1:3 phases. This effect has already been described in the chemically lithiation of misfit layer chalcogenides where single phase stage I products are obtained. The explanation given by Rouxel[31] to the enhanced expansion found in lithiated TiS_2 can be taken analogously for $PbTi_2S_5$.

The stability of the three phases upon lithium electrochemical intercalation can be summarized as follows: compounds with a 1:1:3 nominal stoichiometry are less prone to intercalate lithium than 1:2:5 phases and become amorphous very readily upon lithiation, independently of the constituent elements. Further subtle differences are found in the discharge behaviour of $(PbS)_{1.18}TiS_2$ and $(PbS)_{1.12}VS_2$ cathodes. These systems have similar structures in which the transition metal ions have a distorted octahedral coordination. Thus, a similar band structure may be supposed. However, measurements of the electrical transport properties of single crystals have been reported for $(PbS)_{1.18}TiS_2$[34] and $(PbS)_{1.12}VS_2$.[7] Whereas the former compound showed metallic conductivity, a semiconducting behavior was found for the vanadium misfit compound. These electronic differences might also affect the thermodynamics of the intercalation process reflected in the fine differences shown by the discharge curves.

On the other hand, the differences in the structure may give new light on the different behavior of 1:1:3 and 1:2:5 phases. Thus, for $PbVS_3$ and $PbTiS_3$ it is sensible to assume that the holes where lithium ions occur are located between PbS and $M'S_2$, where repulsions between Li and Pb ions protruding from the sulfur layers may induce an enhanced lattice distortion. This electronic hindrance is apparently absent in the true van der Waals gap between TiS_2 slabs with vacant interlayer octahedral and tetrahedral holes defined by the packing of chalcogen atoms. The fulfillment of the octahedral sites could be associated with the discontinuous change of voltage observed in the OCV curve, Figure 1b, from 2.7 to 2.1 V around $x = 1$. The location of the remaining Li at the end of the discharge curve is uncertain. Similar problems for lithium location shows the phase Li_2TiS_2 obtained by electrochemical lithium intercalation and whose XRD pattern can be indexed in the same symmetry than $LiTiS_2$.[35] However, multiple-site ion occupancy has been suggested to account for the high lithium contents of some systems, as VSe_2.[36] The other accomodation alternative would be between MX (C) and $M'X_2$ (H) layers. If this is so, then it is difficult to understand the behaviour of the $MM'X_3$ series the degree of lithium intercalation of which is rather low.

Conclusions

We have reported evidence that electrochemical lithium intercalation into misfit layer sulfides occurs via different mechanisms depending on the stoichiometry of the host phase. Whereas Li_xPbTiS_3 and Li_xPbVS_3 have basically the same structure as the pristine misfit phases, several regions of coexisting phases has been observed for $Li_xPbTi_2S_5$ in the $0 < x < 1$ range. For $x = 0.3$, a stage III compound is observed with every third interlayer gap of the HH type containing intercalated lithium. For $x = 1$, $Li_xPbTi_2S_5$ is a stage I compound in which the host lattice has the same structure as pure $PbTi_2S_5$. For intermediate compositions, there is a mixture of coexisting stage III and stage I phases. The origin of this complexity in the phase diagram is attributed to the stacking sequence of MS and $M'S_2$ slabs along the *c* axis. In fact, the misfit layer compound $PbTi_2S_5$ is built of alternately a double layer PbS and two TiS_2 sandwiches separated by a van der Waals gap. Within this gap, octahedral and tetrahedral sites are available for intercalation. In contrast, both misfit layer compounds $PbTiS_3$ and $PbVS_3$ are characterized by a regular $-MS-M'S_2-MS-M'S_2-$ stacking sequence along the *c* axis. Such stacking sequence prevents the existence of van der Waals gaps with equivalent energy sites to those found in the 1:2:5 series.

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Registry No. $PbVS_3$, 37356-17-5; $PbTiS_3$, 12066-65-8; $PbTi_2S_5$, 131576-85-7; Li, 7439-93-2; Cu, 7440-50-8; $LiClO_4$, 7791-03-9; $Li_{0-2}PbTiS_3$, 143075-94-9; $Li_{0-4}PbTi_2S_5$, 143075-93-8; $Li_{0-2}PbVS_3$, 143075-92-7; propylene carbonate, 108-32-7.

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