

## Insertion/extraction of lithium and sodium in transition metal oxides and chalcogenides\*

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**Abstract.** Lithium and sodium can be reversibly inserted into a variety of transition metal oxide and chalcogenide hosts at low temperatures. The reaction is essentially topochemical involving electron-transfer and accompanying diffusionless transformation of the anion array in many cases. Alkali metal insertion/extraction reactions provide new routes for the synthesis of novel solids exhibiting unusual structure and properties. It appears that while the structure of the insertion compound is determined by the host structure and the size of the alkali metal ion, the extent of insertion/extraction is decided by the redox characteristics and electronic conductivity of the host.

**Keywords.** Insertion/extraction reactions; intercalation of lithium and sodium; transition metal oxides and chalcogenides.

### 1. Introduction

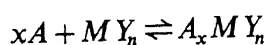
An area of considerable current interest in solid state chemistry concerns reversible insertion of mobile atomic or molecular guest species into crystalline host solids (Whittingham and Jacobson 1982). A wide variety of solids possessing chain, layered or three dimensional (framework) structures has been investigated in insertion reactions (Schöllhorn 1984). Among a large number of guest species that has been investigated, insertion/extraction of lithium and, to a lesser extent, sodium has acquired importance in recent years, because they offer attractive solid-solution systems that could be of use as positive electrode materials in high energy-density solid state batteries or electrochromic displays (Murphy and Christian 1979; Whittingham 1978). A particularly attractive aspect of such reactions both from the scientific and the technical viewpoint is that insertion/extraction of alkali metal atoms, which is accompanied by electron/ion transfer, occurs reversibly around ambient temperatures with minimal structural reorganisation of the host (*topochemical reaction*). Besides their possible use in solid state batteries, investigation of insertion/extraction reactions of lithium and sodium has opened up new vistas of solid state chemistry hitherto unexplored. Thus alkali metal insertion/extraction in metal oxides and chalcogenides at ambient temperatures has provided 'soft' routes for the synthesis of new materials which cannot possibly be synthesized otherwise. The reaction has revealed the occurrence of novel topotactic transformations of the host structure with amazing ease and rapidity. The reaction can also result in remarkable changes in the electronic properties of the host material. In this paper an attempt is made to present an overview of lithium and sodium

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intercalation in transition metal oxides and chalcogenides, bringing out their importance in preparative and structural solid state chemistry.

## 2. Alkali metal insertion/extraction in metal oxides

Although reversible topotactic insertion of lithium was demonstrated first in  $\text{TiS}_2$  (Whittingham 1976) while attempting to develop suitable electrode materials for nonaqueous batteries, attention soon shifted to oxide host materials because oxides possess more rigid frameworks and can offer higher cell voltages than sulphides. In order for a insertion reaction



to be useful as a battery cathode system offering a high cell voltage, the free energy change of the reaction should be a large negative value. Large negative free energy changes are expected when  $A$  is a small electropositive atom,  $M$  is in its highest formal oxidation state and  $Y$  is small and electronegative. Thus, to obtain a high cell voltage in a solid state battery, lithium is preferable to sodium and metal oxides are preferable to metal sulphides as host materials.

Among a large number of metal oxides with layered or three dimensional structures wherein lithium and sodium intercalation has been investigated, we restrict our attention to the  $\text{ReO}_3$  and related crystallographic shear phases, rutile-related oxides and layered oxides derived from the rocksalt structure.

$\text{ReO}_3$  possesses the same octahedral framework as the cubic perovskite, the cubooctahedral site being vacant (figure 1).  $\text{WO}_3$  adopts a distorted  $\text{ReO}_3$  framework. On lithium intercalation, the monoclinic structure of  $\text{WO}_3$  is rendered more symmetric, becoming tetragonal and then cubic at the limiting composition  $\text{Li}_{2/3}\text{WO}_3$ . A neutron diffraction study revealed that  $\text{Li}_{0.36}\text{WO}_3$  adopts a superstructure of  $\text{ReO}_3$  ( $a = 7.446 \text{ \AA}$ ) wherein lithium occupies distorted perovskite type cavities with a four-fold rectangular oxygen coordination (Wiseman and Dickens 1976). The recently discovered hexagonal form of  $\text{WO}_3$  (figure 1) possessing large empty channels readily intercalates lithium and other alkali metals (Cheng *et al* 1981). Electrochemical intercalation gave the upper phase limits of  $\text{Li}_{1.6}\text{WO}_3$ ,  $\text{Na}_{2/3}\text{WO}_3$  and  $\text{K}_{1/6}\text{WO}_3$  (Schlasche and Schöllhorn 1982). It is suspected that lithium in hexagonal  $\text{Li}_{1.6}\text{WO}_3$  occupies multiple sites in the hexagonal as well as the smaller triangular channels. Cubic  $\text{ReO}_3$  incorporates lithium readily yielding three phases:  $\text{Li}_x\text{ReO}_3$ ,  $0 \leq x \leq 0.35$  (cubic),  $x = 1.0$  and  $1.8 \leq x \leq 2.0$  (hexagonal) (Murphy *et al* 1981). Lithium insertion in  $\text{ReO}_3$  is accompanied by an interesting structural transformation from the  $\text{ReO}_3$  to the  $\text{LiNbO}_3$  structure. A neutron diffraction study of  $\text{LiReO}_3$  and  $\text{Li}_2\text{ReO}_3$  (Cava *et al* 1982) has revealed that both the phases crystallize in a hexagonal  $\text{LiNbO}_3$ -type structure wherein lithium is octahedrally coordinated. The structural transformation accompanying lithium insertion renders the material unsuitable for cathodes because it gives rise to a large activation energy and consequent decrease in the reaction rate.

Attempts have been made to retain the advantages of the  $\text{ReO}_3$  structure and avoid structural transformation during lithium insertion by working with *crystallographic shear* (cs) phases as hosts. A number of oxides derived from the  $\text{ReO}_3$  structure through cs is known (Anderson 1972). One of the simplest oxides possessing  $\text{ReO}_3$ -related cs structure is  $\text{V}_6\text{O}_{13}$ . Its structure (figure 2) can be thought of as resulting from a (3,2)

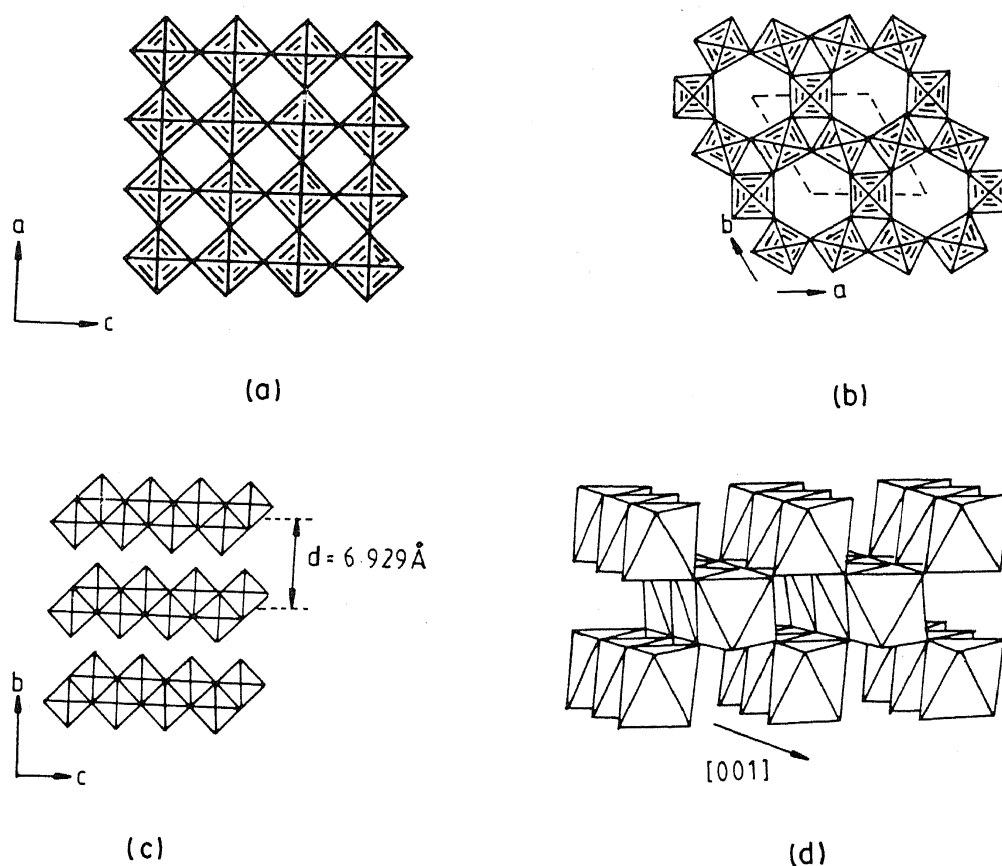


Figure 1. Structures of (a)  $\text{ReO}_3$  (b) hexagonal  $\text{WO}_3$  (c)  $\text{MoO}_3$  and (d) rutile.

shear of the cubic  $\text{ReO}_3$  structure.  $\text{V}_2\text{O}_5$  and  $\text{VO}_2(\text{B})$  can also be regarded as derived from  $\text{ReO}_3$  (figure 2). All the three oxides of vanadium incorporate lithium readily at room temperature, but none take up sodium (Murphy and Christian 1979). Lithium insertion results in uniaxial expansion of the perovskite-like cavity. The extent of lithium incorporation seems to be determined primarily by the strength of bonding in the direction of expansion. Among the three oxides of vanadium,  $\text{V}_6\text{O}_{13}$  taking up as many as eight lithium atoms per formula unit (four at room temperature and six at 320 K) has been found to be good cathode material for battery application (Murphy *et al* 1979). The insertion is entirely reversible since the parent oxide can be recovered by oxidative delithiation using 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ). The metal-insulator transition at 147 K in  $\text{V}_6\text{O}_{13}$  is destroyed by insertion of a few atom percent of lithium. The structure of  $\text{Li}_8\text{V}_6\text{O}_{13}$  has not been determined.  $\text{FeV}_3\text{O}_8$  which possesses the  $\text{VO}_2(\text{B})$  structure takes up to two lithium atoms. A neutron diffraction study of  $\text{Li}_2\text{FeV}_3\text{O}_8$  (Cava *et al* 1981) has shown that lithium ions occupy two of the four square pyramidal sites available within the tetracapped cubooctahedral cavity in the host structure. In  $\text{Li}_8\text{V}_6\text{O}_{13}$ , lithium ions may be located at similar sites.

The investigations with vanadium oxides have shown that cs structures unlike  $\text{ReO}_3$  are quite stable towards lithium insertion but contain fewer sites for lithium as compared to the  $\text{ReO}_3$  structure. Cava and coworkers (1983a, b) have recently investigated block structures of the Wadsley-Roth type where large chunks of  $\text{ReO}_3$  structure are present. An example of such a block structure phase is  $\text{V}_{2.5}\text{W}_{0.5}\text{O}_7$  which

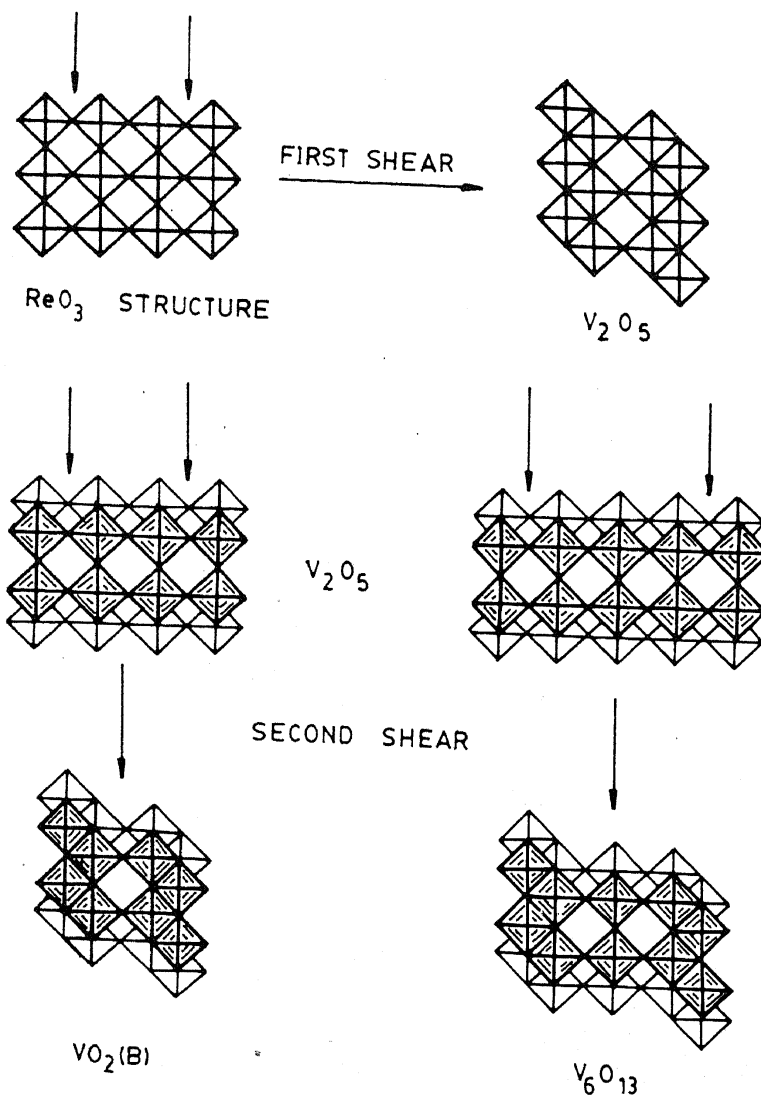


Figure 2. Structures of vanadium oxides derived from the ReO<sub>3</sub> structure through crystallographic shear (after Greenblatt *et al* 1982).

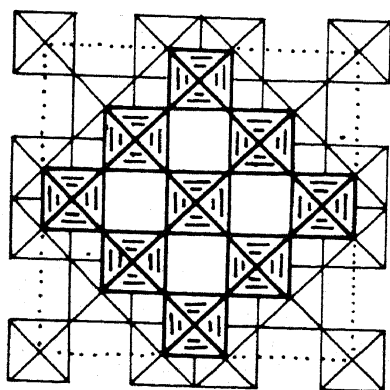


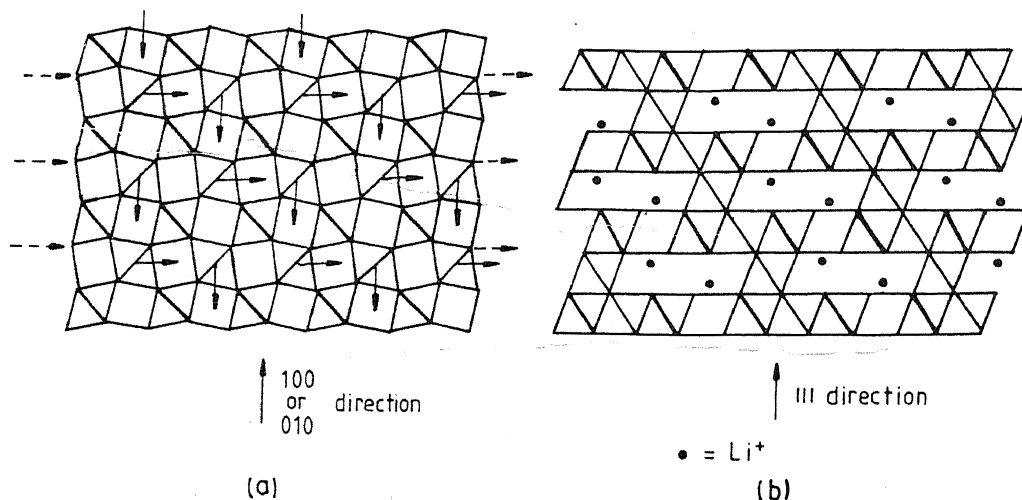
Figure 3. [001] projection of the idealised  $3 \times 3 \times \infty$  block structure. Shaded octahedra are at level  $\frac{1}{2}c$  from the level of unshaded octahedra (after Cava *et al* 1983a).

adopts a  $3 \times 3 \times \infty$  structure (figure 3). The structure consists of  $\text{ReO}_3$ -like blocks of  $3 \times 3$  octahedral dimension extending infinitely in one direction; the blocks are shared with adjacent ones through edges. Among the several block structure phases investigated, compounds of the  $M_3O_7$  stoichiometry such as  $\text{V}_{2.5}\text{W}_{0.5}\text{O}_7$ ,  $\text{V}_{2.8}\text{W}_{0.2}\text{O}_7$  and  $\text{V}_{2.5}\text{Mo}_{0.3}\text{W}_{0.2}\text{O}_7$  display a good combination of structural stability and an adequate number of interstitial sites for lithium insertion.

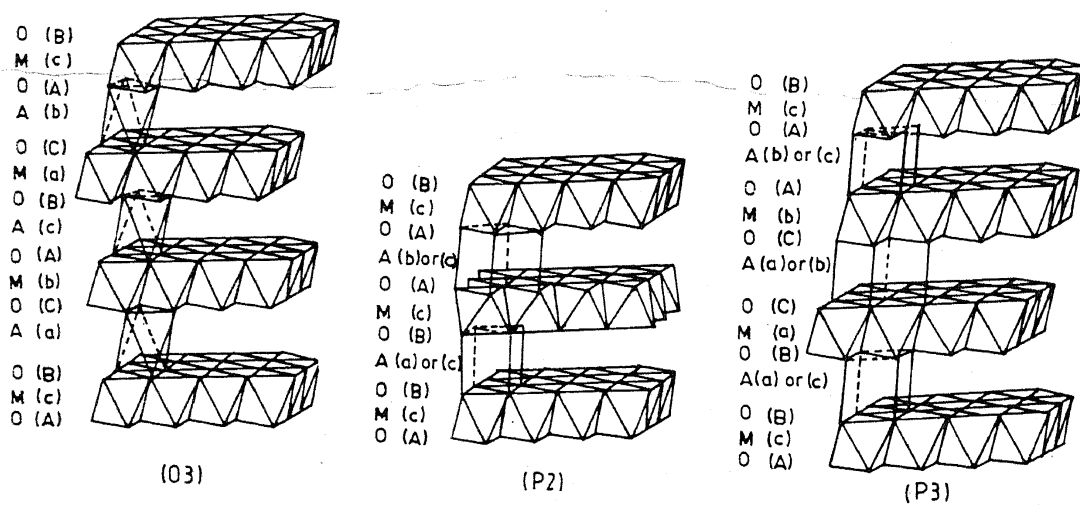
Unlike  $\text{ReO}_3$  and  $\text{WO}_3$ ,  $\text{MoO}_3$  has a layered structure (figure 1) formed by edge and corner sharing of  $\text{MoO}_6$  octahedra. The layers are separated by a van der Waals gap. Accordingly,  $\text{MoO}_3$  intercalates a wide variety of atoms and molecules including lithium (Schöllhorn 1982; Dickens and Reynolds 1982). Chemical and electrochemical insertion of lithium in  $\text{MoO}_3$  proceeds topotactically yielding a single phase  $\text{Li}_x\text{MoO}_3$  for  $0.2 < x < 0.5$ .  $\text{Mo}_{18}\text{O}_{52}$  which has a shear structure closely related to  $\text{MoO}_3$  exhibits a similar reactivity. Lower valence molybdenum oxides  $\text{Mo}_4\text{O}_{11}$ ,  $\text{Mo}_8\text{O}_{23}$  and  $\text{Mo}_9\text{O}_{26}$  which possess shear structures related to  $\text{ReO}_3$  (Kihlberg 1963) can also take up lithium reversibly (Besenhard and Schöllhorn 1976).

Lithium insertion in transition metal dioxides possessing rutile related structures has been investigated by Murphy *et al* (1978). The rutile structure (figure 1) which consists of infinite chains of edge-shared  $\text{MO}_6$  octahedra which are cross-linked through corners provides vacant channels along [001] of the tetragonal cell. The channels contain both octahedral and tetrahedral sites where lithium can be incorporated. Among the several rutile-type oxides investigated, considerable lithium insertion occurs only with the dioxides of Cr, Mn, Mo, W, Ru, Os and Ir. The results seem to indicate the importance of both the unit cell volume and the electronic conductivity of the host material in determining the extent of lithium insertion. Metallic conductivity in the host facilitates lithium insertion by screening the coulomb repulsion between  $\text{Li}^+$  ions. A plot of room temperature resistivity versus unit cell volume reveals that both low resistivity and a large cell volume ( $> 60 \text{ \AA}^3$ ) favour topochemical insertion of lithium. More importantly, lithium insertion in metallic conducting  $\text{MoO}_2$ ,  $\text{RuO}_2$  and  $\text{IrO}_2$  is accompanied by a structural transformation from the rutile to an ordered NiAs structure, as revealed by power neutron diffraction study of  $\text{LiMoO}_2$ ,  $\text{Li}_{0.9}\text{RuO}_2$  and  $\text{Li}_{0.9}\text{IrO}_2$  (Cox *et al* 1982; Davidson and Greedan 1984). Compared to the host structure, the insertion compounds are greatly expanded along [100] and [010] and contracted along [001]. The unit cell of  $\text{Li}_{0.9}\text{RuO}_2$  is orthorhombic ( $a_0 = 5.062$ ,  $b_0 = 4.967$  and  $c_0 = 2.771 \text{ \AA}$ ) and is related to the hexagonal cell of NiAs as follows:  $a_H \simeq c_0 \simeq \sqrt{3} b_0$ ;  $c_H \simeq a_0$ . The structures of both  $\text{LiMoO}_2$  and  $\text{Li}_{0.9}\text{RuO}_2$  can be regarded as a new type of NiAs superstructure in which cations are ordered at the octahedral sites in the basal planes. Lithiation of  $\beta\text{-MnO}_2$  with *n*-butyl lithium to give  $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$  results in a rutile-spinel transformation (Goodenough *et al* 1984). A mechanism which involves a cooperative redistribution of cations followed by a diffusionless readjustment of the anion array has been suggested for the rutile-spinel transformation (figure 4).

Lithium insertion/extraction has been investigated in several oxides of the ordered rocksalt structure type containing cubic close packed anion array. Oxides of the formula  $\text{LiMO}_2$  ( $M = \text{V, Cr, Co, Ni}$ ) crystallize in a layered ( $\alpha\text{-NaFeO}_2$ ) ( $O3$ ) structure (figure 5) in which Li and  $M$  atoms occupy octahedral sites in alternate (111) cation planes in the cubic close packed anion array. Mizushima *et al* (1980) have shown that lithium can be extracted electrochemically from  $\text{LiCoO}_2$  yielding  $\text{Li}_x\text{CoO}_2$  ( $0 < x < 1$ ) wherein the layer structure is retained. We have shown that lithium can be



**Figure 4.** Mechanism for the rutile-spinel transformation. Cation occupied octahedra are shown. In (a) rutile structure, solid arrows indicate cation displacements and dotted arrows, the direction of shear required for the transformation to the spinel structure (b) (after Goodenough *et al* 1984).



**Figure 5.** Packing of  $MO_6$  octahedra in  $A_xMO_2$  oxides. O3 structure corresponds to the ordered rocksalt structure of  $\alpha$ - $NaFeO_2$  (after Delmas *et al* 1982b).

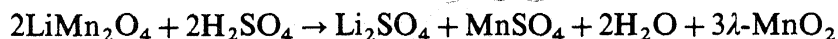
extracted chemically at room temperature from the isostructural  $LiVO_2$  using  $Br_2$  in  $CHCl_3$  as the oxidative delithiating agent (Vidyasagar and Gopalakrishnan 1982).  $Li_xVO_2$  retain the cubic close packed anion array, but not the layered structure, upto  $x \sim 0.2$ . Nearly complete removal of lithium destroys the lattice yielding x-ray amorphous  $VO_2$  which transforms to monoclinic  $VO_2$  at high temperatures. Further investigation of  $Li_xVO_2$  system (de Picciotto *et al* 1984) has revealed the existence of two phases in the system: phase I for  $0.7 < x < 1.0$  which retains the parent structure of  $LiVO_2$  and phase II for  $0.1 < x < 0.3$  which adopts a near-cubic structure wherein approximately one-third of vanadium migrates to vacant lithium sites; part of vanadium is suspected to be present as  $V^{5+}$  at the tetrahedral sites.

Lithium insertion/extraction reactions in various forms of  $\text{TiO}_2$  have been investigated (Murphy *et al* 1983). While rutile and brookite take up only small quantities of lithium (1–2 atom %), anatase yields a maximum composition of  $\text{Li}_{0.7}\text{TiO}_2$  on reaction with *n*-butyl lithium. The composition  $\text{Li}_{0.5}\text{TiO}_2$  transforms irreversibly around 770 K to  $\text{LiTi}_2\text{O}_4$  spinel, thus affording a neat method for the synthesis of this superconducting oxide (Murphy *et al* 1982).  $\text{Li}_{0.5}\text{VO}_2$  undergoes a similar transformation yielding  $\text{LiV}_2\text{O}_4$  spinel (de Picciotto and Thackeray 1985).  $\text{LiTi}_2\text{O}_4$  can be inserted with additional lithium to give spinel-like  $\text{Li}_2\text{Ti}_2\text{O}_4$  which transforms irreversibly to a disordered rocksalt structure at high temperatures.  $\text{LiTi}_2\text{O}_4$  spinel can be oxidatively delithiated using  $\text{I}_2$  in  $\text{CH}_3\text{CN}$  to yield a limiting composition  $\text{Li}_{0.1}\text{TiO}_2$  which is similar to  $\text{Li}_x\text{VO}_2$  possessing a defect rocksalt structure. Lithium can also be inserted into the metastable  $\text{TiO}_2(\text{B})$  giving  $\text{Li}_{0.75}\text{TiO}_2(\text{B})$ ; the structure of the latter is believed to be similar to that of  $\text{Li}_2\text{FeV}_3\text{O}_8$  in which lithium occupies square pyramidal sites (Cava *et al* 1981, 1984).

$\alpha$  and  $\beta$ - $\text{Li}_2\text{MoO}_3$  crystallizing in ordered rocksalt structures (Dickens and Reynolds 1982) can be oxidatively delithiated using  $\text{Br}_2$  in  $\text{CHCl}_3$ .  $\text{Li}_{2-x}\text{MoO}_3$  phases retain the cubic close packed anion array until lithium removal is nearly complete (Vasudeva Bhat and Gopalakrishnan 1985a). Reversible insertion of lithium and sodium has been reported in  $\text{Fe}_2(\text{MoO}_4)_3$  possessing a three dimensional (NASICON) framework structure (Nadiri *et al* 1984). It is not clear whether iron or molybdenum is reduced by alkali metal insertion in this compound.  $\text{LiFeSnO}_4$  polymorphs crystallizing in the ramsdellite structure intercalates one atom of lithium corresponding to reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  (Greenblatt *et al* 1985).

Lithium insertion/extraction reactions in manganese oxides have been extensively investigated by Goodenough *et al* (1984). Lithiation of  $\text{Mn}_3\text{O}_4$  (hausmanite) to give  $\text{LiMn}_3\text{O}_4$  suppresses the cooperative Jahn-Teller distortion of the host and this is consistent with the formulation of the phase as  $(\text{Li}^+ \text{Mn}^{2+})_t (\text{Mn}^{3+} \text{Mn}^{2+})_o \text{O}_4$ . On the other hand, lithiation of  $\text{LiMn}_2\text{O}_4$  spinel to give  $\text{Li}_2\text{Mn}_2\text{O}_4$  distorts the structure to tetragonal symmetry indicating that manganese is trivalent in the latter. Further lithiation of  $\text{Li}_2\text{Mn}_2\text{O}_4$  yields a new phase  $\text{Li}_{2-x}\text{MnO}_2$  in which most of the manganese is reduced to  $\text{Mn}^{2+}$ . The new phase is trigonal adopting the  $\text{Li}_2\text{VSe}_2$  structure consisting of hexagonal close packed anions;  $\text{Mn}^{2+}$  ions occupy alternate octahedral-site basal planes and  $\text{Li}^+$  ions the tetrahedral sites of the other basal planes (David *et al* 1983).

An interesting case of topochemical delithiation is that of  $\text{LiMn}_2\text{O}_4$  which occurs on treatment with aqueous  $\text{H}_2\text{SO}_4$  (Hunter 1981). The product was considered to be a new form of manganese dioxide,  $\lambda$ - $\text{MnO}_2$ , which retained the spinel framework of the parent. Delithiation of  $\text{LiMn}_2\text{O}_4$  to give  $\lambda$ - $\text{MnO}_2$  depends on two properties: (i) room temperature mobility of  $\text{Li}^+$  in the  $\text{Mn}_2\text{O}_4$  spinel framework and (ii) surface disproportionation of  $\text{Mn}^{3+}$ . The overall reaction could be



Subsequent work (Thackeray *et al* 1984; Mosbah *et al* 1983) has shown that Hunter's  $\lambda$ - $\text{MnO}_2$  is indeed  $\text{Li}_{0.02}\text{MnO}_2$ . Presence of residual lithium is revealed by neutron diffraction. Electrochemical delithiation of  $\text{LiMn}_2\text{O}_4$  proceeds easily upto  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ ; lithium ions in this phase are ordered to give a new superstructure.

Lithium insertion in  $\text{Fe}_3\text{O}_4$  and  $\alpha$ - $\text{Fe}_2\text{O}_3$  has been investigated (Thackeray *et al* 1982). The crystal structure of  $\text{Li}_{1.5}\text{Fe}_3\text{O}_4$  shows that the  $\text{Fe}_2\text{O}_4$  subarray of the spinel

structure remains intact. Lithiation of  $\alpha\text{-Fe}_2\text{O}_3$  results in a transformation of the anion array from the hexagonal to cubic close packing. A significant finding of these investigations of lithium insertion in manganese and iron oxides is that three-dimensional diffusion of  $\text{Li}^+$  occurs at room temperature in close packed oxide lattices; insertion/extraction of lithium is often accompanied by diffusionless transformations of the anion array between cubic close packing to hexagonal close packing (or tetragonal close packing, as in the rutile structure).

Insertion/extraction of sodium in oxides has been studied less extensively. The smaller electronegativity and larger mass render sodium (and other alkali metals) less attractive for battery applications. Structurally, insertion/extraction of sodium and potassium in oxides and chalcogenides shows interesting features that are different from the case of lithium insertion (Hagemuller 1983). Unlike lithium, sodium and potassium can occupy trigonal prismatic sites in  $A_xMX_2$  layered phases especially when  $x$  is small and  $M$  is in a high oxidation state. Insertion/extraction of sodium in close packed oxides results in subtle phase transitions by lateral gliding of oxide layers giving new metastable phases. Electrochemical extraction of sodium from  $\text{NaMO}_2$  ( $M = \text{Ti, Cr, Co, Ni}$ ) has been investigated (Delmas *et al* 1982b; Maazaz *et al* 1983). All these oxides crystallize in the  $\alpha\text{-NaFeO}_2(O3)$  structure (figure 5). Electrochemical insertion/extraction of sodium on  $\text{Na}_x\text{CoO}_2$  leads to reversible structural transformations between  $O3$  and  $P3$  structures (figure 6). Of the four phases that are known in the  $\text{Na}_x\text{CoO}_2$  system,  $P2$  phase is never obtained by electrochemical extraction of sodium from  $\text{NaCoO}_2$ . A  $O3\text{-}P3$  transformation would involve mere gliding of anion sheets, while a  $O3(P3)\text{-}P2$  transformation would require the  $\text{Co-O}$  bond breaking as well.  $O3\text{-}P3$  transformations in  $\text{Na}_x\text{MO}_2$  have been reported by Miyazaki *et al* (1982, 1983). These workers have found that deintercalation of lithium and sodium from oxides is primarily determined by the oxidation potential of the  $M$  cation. Sodium can be extracted partially from  $\text{NaMO}_2$  ( $M = \text{Cr, Co, Ni}$ ), but lithium cannot be removed from  $\text{LiCrO}_2$  and  $\text{LiCoO}_2$  using chemical oxidants such as  $\text{Br}_2$  and  $\text{I}_2$ . Mendiboure *et al* (1985) have investigated electrochemical insertion and extraction of sodium in  $\text{Na}_x\text{MnO}_2$  phases. During intercalation, the  $P2$  structure of  $\text{Na}_{0.7}\text{MnO}_2$  is retained in the range  $0.45 \leq x \leq 0.85$ , while  $\alpha\text{-NaMnO}_2$  shows two reversible structural transitions. The Jahn-Teller effect associated with  $\text{Mn}^{3+}$  results in electron localization which in turn tends to trap  $\text{Na}^+$  ions.

An interesting aspect of complex oxides containing lithium and sodium is that they undergo facile ion-exchange in aqueous or molten salt media (England *et al* 1983). The exchange is topotactic and in some cases accompanied by novel structural transformations. Ion-exchange reactions offer another low temperature route for the synthesis of metastable phases (Gopalakrishnan 1984). Thus  $\alpha\text{-LiCrO}_2$  and  $\alpha\text{-LiFeO}_2$  with  $O3$  structure can be synthesized from their sodium analogues by ion-exchange in molten lithium nitrate. Similarly ion-exchange of  $\alpha\text{-LiMO}_2$  ( $M = \text{Cr, Fe, Co, Rh}$ ) with molten salts of  $\text{Cu, Ag}$  or  $\text{Pd}$  yields new phases with delafossite structure. Exchange of sodium in  $\text{Na}_{0.7}\text{CoO}_2$  ( $P2$ ) with lithium chloride in methanol yields a new modification ( $O2$ ) of  $\text{LiCoO}_2$  possessing the anion layer sequence  $ABCBA$ . The new modification is metastable and transforms to the stable  $O3$  structure around 490 K (Delmas 1982a). The  $P2\text{-}O2$  transformation involves gliding of anion layers similar to the  $P3\text{-}O3$  transformations of  $\text{NaMO}_2$  ( $M = \text{Co, Ni}$ ).

$\text{LiNbO}_3$  and  $\text{LiTaO}_3$  undergo facile ion-exchange in hot aqueous acids to give  $\text{HNbO}_3$  and  $\text{HTaO}_3$  (Rice and Jackel 1982). The exchange is accompanied by a



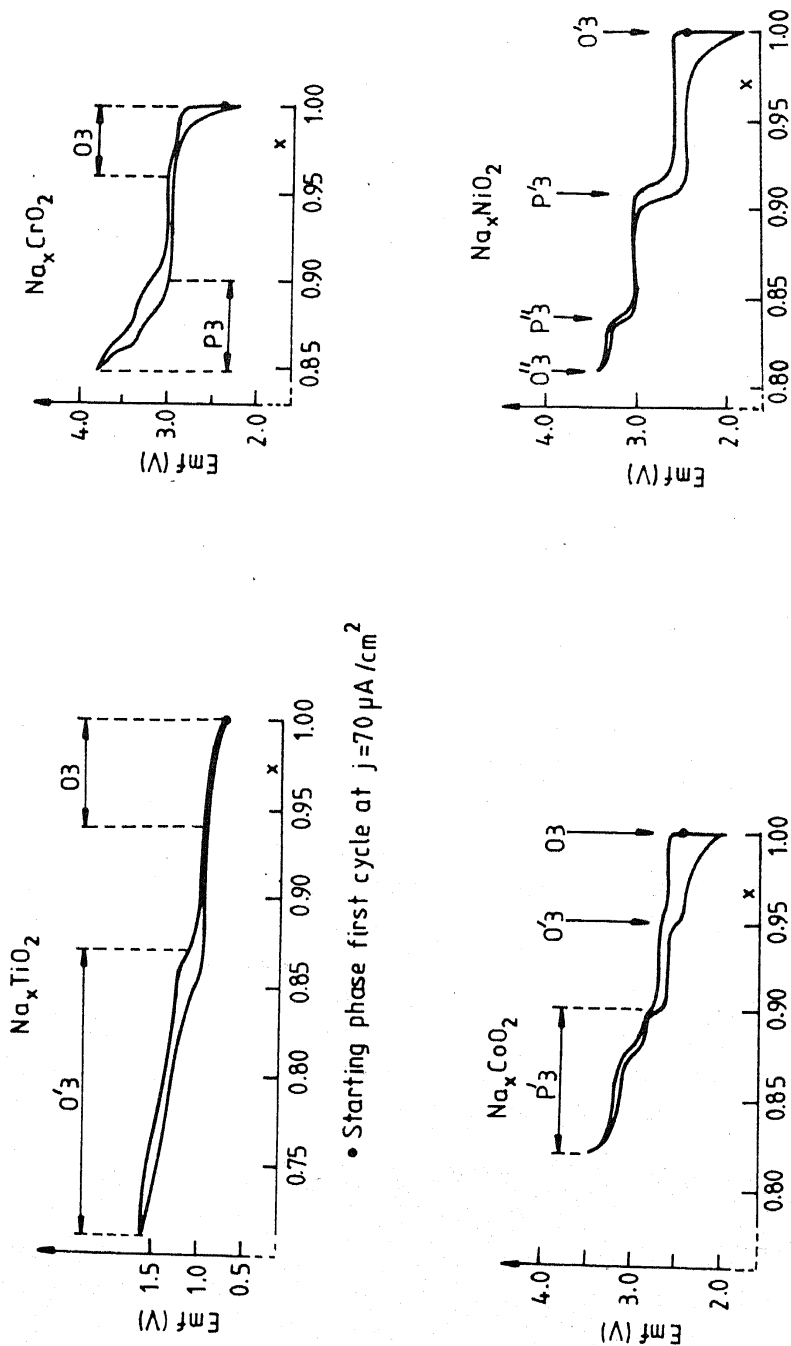


Figure 6. Electromotive force (Emf) versus composition curves for  $\text{Na}_x\text{MO}_2$  ( $M = \text{Ti, Cr, Co, Ni}$ ) oxides. Emf is measured in a cell using  $\text{NaMO}_2$  cathode, sodium anode and  $\text{NaClO}_4$  in propylene carbonate as electrolyte (after Delmas *et al* 1982b).

topotactic transformation of the rhombohedral  $\text{LiNbO}_3$  structure to the cubic  $\text{ReO}_3$  structure. Protons exist as OH groups in the protonated phases and hence they are indeed oxyhydroxides,  $\text{NbO}_2(\text{OH})$  and  $\text{TaO}_2(\text{OH})$  possessing the  $\text{ReO}_3$  structure. The transformation involves a mechanism which is the reverse of that accompanying lithium insertion in  $\text{ReO}_3$ ; the  $\text{NbO}_3$  octahedral network is twisted by  $\sim 60^\circ$  about the hexagonal  $c$  axis. During this, no bonds are broken; the rotation merely rearranges the HCP anion array of the  $\text{LiNbO}_3$  structure to the  $3/4$  CCP array of the  $\text{ReO}_3$  structure.

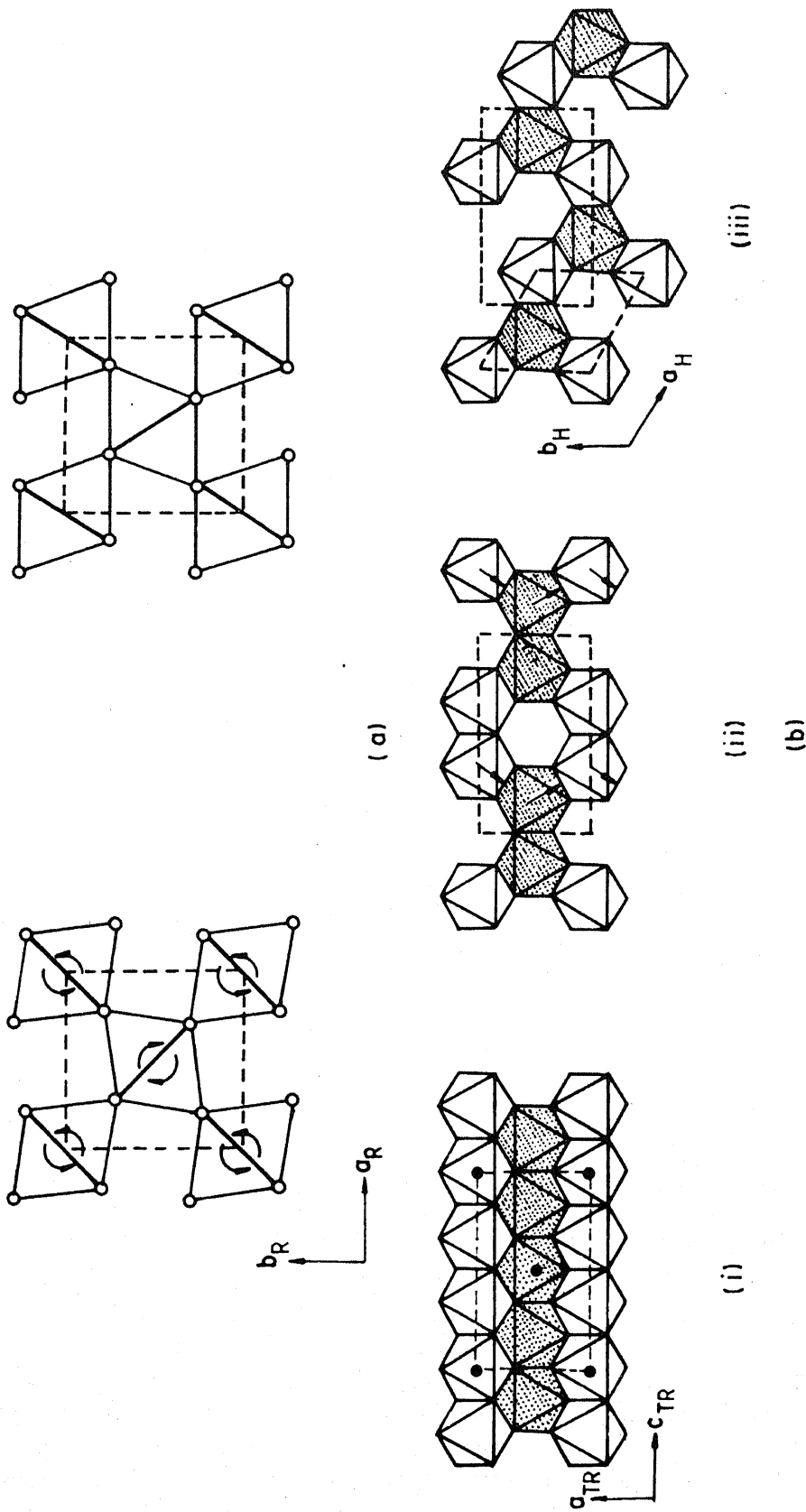
Trirutile  $\text{LiNbWO}_6$  and  $\text{LiTaWO}_6$  undergo similar exchange in hot aqueous acids to give  $\text{HNbWO}_6$  and  $\text{HTaWO}_6$  (Vasudeva Bhat and Gopalakrishnan 1985b). The exchange is accompanied by a structural transformation from the rutile structure to the  $\text{ReO}_3$  structure. A plausible mechanism (figure 7) would involve transformation of the tetragonal close packed anion array of the rutile structure to the HCP array followed by cation rearrangement to give a  $\text{LiNbO}_3$ -like framework. The latter would then transform to the  $\text{ReO}_3$  structure by a mechanism similar to the  $\text{LiNbO}_3$ - $\text{HNbO}_3$  transformation. These findings reveal that not only facile exchange of lithium from close packed oxide lattices can be achieved at low temperatures but also that the exchange is often accompanied by subtle topotactic transformations of the anion subarray. Such facile, often reversible, rearrangements of the anion array would imply not only that the energy differences between different anion packings are much smaller than the cohesive energies but also that exchange or extraction/insertion of mobile cations provides the required energy and pathways for such transformations to occur. The energetics and mechanism of structural transitions accompanying insertion/extraction and exchange of alkali metals in transition metal oxides deserve further investigation.

### 3. Alkali metal insertion/extraction in metal chalcogenides

Insertion/extraction of alkali metals in a variety of transition metal chalcogenides possessing framework, layered and chain structures has been investigated extensively (Rouxel 1979; Whittingham 1978). Intercalation in layered dichalcogenides of transition metals of group IVB (Ti, Zr, Hf), VB (V, Nb, Ta) and VIB (Cr, Mo, W) has attracted particular attention for several reasons. By insertion/extraction, it is possible to change the density of states of cation  $d$ -levels thus altering the electrical and magnetic properties of the host. Insertion/extraction results in structural transformations (polytypic and intrapolytypic) accompanied by change of coordination of alkali metals and 'staging'.

The primary motivation for extensive investigation of these materials is the mixed conduction behaviour of  $A_xMX_2$  phases which render them useful as electrode materials for solid state batteries, the prototype example of such a system being  $\text{Li}_x\text{TiS}_2$ . The subject has been excellently reviewed in the literature (Whittingham 1978; Rouxel 1979; Subba Rao and Shafer 1979). We shall restrict ourselves to some of the recent developments in this area with particular emphasis on preparative and structural aspects.

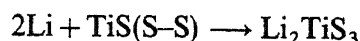
Extraction of alkali metals from ternary transition metal chalcogenides has enabled synthesis of new binary chalcogenides. Thus,  $\text{VS}_2$  and  $\text{CrSe}_2$  which cannot be prepared by high temperature methods have been synthesized from  $A_x\text{VS}_2$  and  $A_x\text{CrSe}_2$  by chemical or electrochemical extraction of alkali metals (Murphy *et al* 1977a, b; van



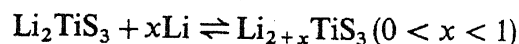
**Figure 7.** (a) Transformation of tetragonal close packed anion array of the rutile structure to hexagonal close packed (HCP) array by rotation of the occupied octahedra. (b) Transformation of  $\text{NbWO}_6$  framework in  $\text{LiNbWO}_6$  (trirutile) to  $\text{NbO}_3$  framework of  $\text{LiNbO}_3$  structure. The oxygen array is idealised to HCP. Only occupied octahedra are shown. Shaded and unshaded octahedra are at different levels. (i)  $\text{LiNbWO}_6$  trirutile. Li-occupied octahedra are shown with a filled circle. (ii)  $\text{NbWO}_6$  network after removal of lithium. Arrows indicate direction of cation displacement. (iii)  $\text{NbWO}_6$  network after cation rearrangement. This network is similar to  $\text{NbO}_3$  network in  $\text{LiNbO}_3$  (after Vasudeva Bhat and Gopalakrishnan 1985b).

Bruggen *et al* 1980). A new form of  $\text{FeS}_2$  possessing the layered  $\text{CdI}_2$  structure has been synthesized by electrochemical extraction of lithium from  $\text{Li}_2\text{FeS}_2$  (Dugast *et al* 1981). The Chevrel phase cluster sulphide  $\text{Mo}_6\text{S}_8$  can be easily prepared by extracting lithium from  $\text{Li}_x\text{Mo}_6\text{S}_8$  by treatment with dilute  $\text{HCl}$  (Behlok *et al* 1982). It is significant that treatment with dilute acid removes lithium from  $\text{Li}_x\text{Mo}_6\text{S}_8$ . Ion exchange and oxidative extraction of alkali metals have enabled the synthesis of pseudo one-dimensional ternary molybdenum chalcogenides,  $A_{2-x}\text{Mo}_6\text{X}_6$  ( $A$  = alkali metal;  $X$  = Se, Te) (Tarascon *et al* 1984). A new orthorhombic form of  $\text{WS}_2$  containing octahedrally coordinated tungsten has been synthesized by oxidative extraction of alkali metal from  $A_x\text{WS}_2$  ( $A$  = Na, K) (Schöllhorn *et al* 1984). Unlike hexagonal  $\text{WS}_2$ , the new modification of  $\text{WS}_2$  exhibits metallic behaviour.  $\text{KFeS}_2$  and related sulphides possessing infinite chains of edge-shared  $\text{FeS}_4$  tetrahedra can be inserted with lithium (Jacobson *et al* 1979b). Lithium insertion in  $\text{KFeS}_2$  is accompanied by a structural transformation and reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ .  $\text{LiKFeS}_2$  adopts a tetragonal layered structure which is related to  $\text{CuTe}$  (Jacobson and McCandlish 1979).

The trichalcogenides  $\text{MX}_3$  possessing chain structures intercalate lithium but the reaction is not entirely reversible unlike the dichalcogenides. In  $\text{TiS}_3$  for example insertion of first two lithium atoms, which is irreversible, breaks the S-S bonds:



Insertion of the third lithium appears to be more like the case of  $\text{TiS}_2$ .



Amorphous trichalcogenides of molybdenum and tungsten intercalate considerable quantities of lithium and sodium reversibly (Jacobson *et al* 1979a; Murugesan and Gopalakrishnan 1982). Recent investigations have shown marked differences between the insertion behaviour of amorphous and crystalline  $\text{MoS}_3$ ,  $\text{WS}_3$ ,  $\text{V}_2\text{S}_5$ ,  $\text{MoS}_2$  and  $\text{TiS}_2$ , the amorphous materials exhibiting high discharge capacities when used as electrode material (Whittingham *et al* 1980).

#### 4. Concluding remarks

We have presented an overview of insertion/extraction of lithium and sodium in transition metal oxide and chalcogenide hosts. Insertion/extraction which occurs at ambient temperatures is essentially a topochemical reaction, often accompanying diffusionless transformations of the anion array resulting in stabilization of new metastable phases. Insertion/extraction of alkali metals into transition metal compounds is a redox process involving electron transfer and is facilitated by good electronic conductivity of the host. It appears that while the structure of the insertion compound is largely determined by the host structure and the size of alkali metal ion, the extent of insertion/extraction is governed by the redox characteristics of the transition metal ion and the electronic conductivity of the host. Ternary oxides containing lithium undergo facile proton exchange in aqueous acids to yield new metal oxyhydroxides.

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