

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

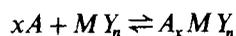
An area of considerable current interest in solid state chemistry concerns reversible insertion of mobile atomic or molecular guest species into crystalline host solids (Whittingham and Jacobson 1982). A wide variety of solids possessing chain, layered or three dimensional (framework) structures has 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 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 an 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 ReO_3 and related crystallographic shear phases, rutile-related oxides and layered oxides derived from the rocksalt structure.

ReO_3 possesses the same octahedral framework as the cubic perovskite, the cubooctahedral site being vacant (figure 1). WO_3 adopts a distorted ReO_3 framework. On lithium intercalation, the monoclinic structure of 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 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 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 ReO_3 incorporates lithium readily yielding three phases: Li_xReO_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 ReO_3 is accompanied by an interesting structural transformation from the ReO_3 to the LiNbO_3 structure. A neutron diffraction study of LiReO_3 and Li_2ReO_3 (Cava *et al* 1982) has revealed that both the phases crystallize in a hexagonal 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 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 ReO_3 structure through cs is known (Anderson 1972). One of the simplest oxides possessing ReO_3 -related cs structure is V_6O_{13} . Its structure (figure 2) can be thought of as resulting from a (3, 2)

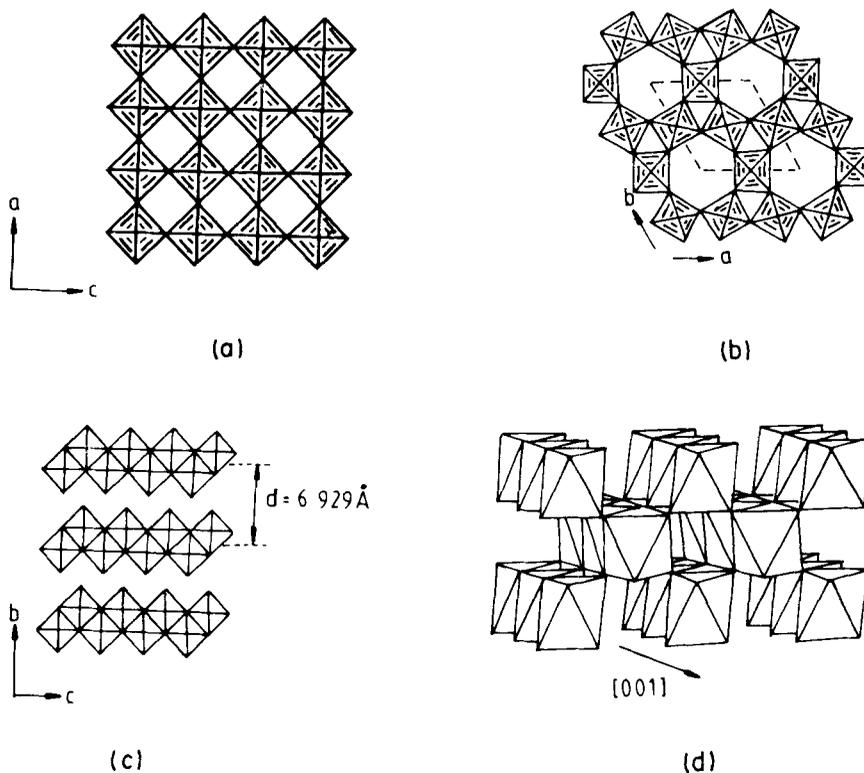


Figure 1. Structures of (a) ReO_3 (b) hexagonal WO_3 (c) MoO_3 and (d) rutile.

shear of the cubic ReO_3 structure. V_2O_5 and $\text{VO}_2(\text{B})$ can also be regarded as derived from 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, V_6O_{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 V_6O_{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. FeV_3O_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 ReO_3 are quite stable towards lithium insertion but contain fewer sites for lithium as compared to the ReO_3 structure. Cava and coworkers (1983a,b) have recently investigated block structures of the Wadsley-Roth type where large chunks of 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

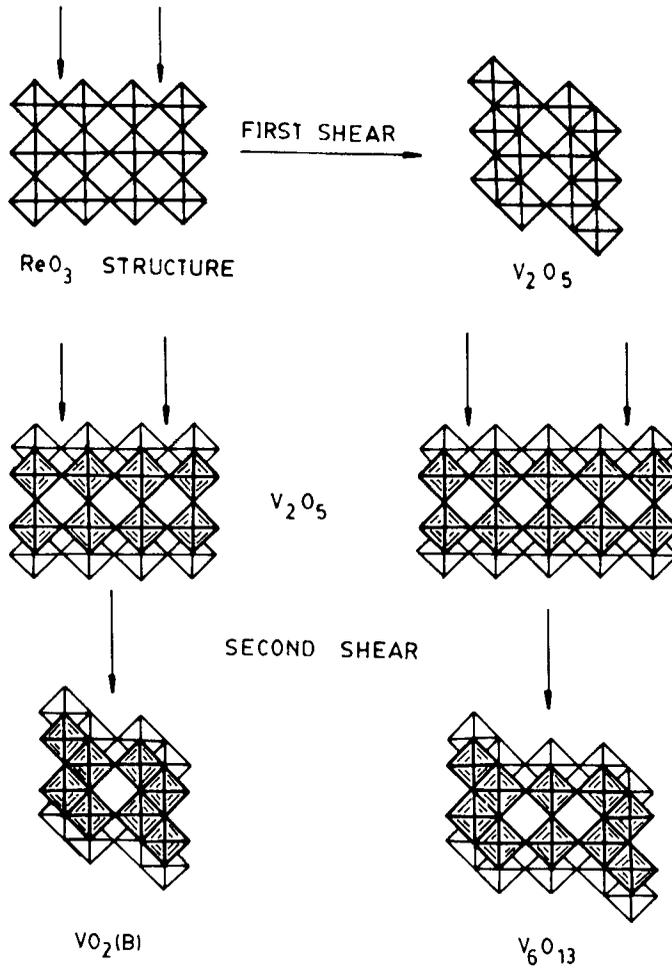


Figure 2. Structures of vanadium oxides derived from the ReO_3 structure through crystallographic shear (after Greenblatt *et al* 1982).

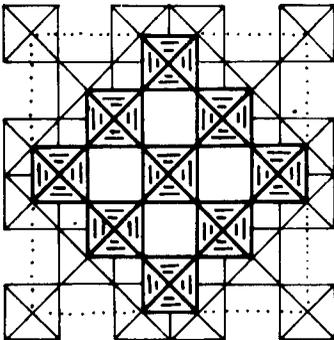


Figure 3. [001] projection of the idealised $3 \times 3 \times \infty$ block structure. Shaded octahedra are at level $\frac{1}{2}c$ from the level of unshaded octahedra (after Cava *et al* 1983a).

adopts a $3 \times 3 \times \infty$ structure (figure 3). The structure consists of ReO_3 -like blocks of 3×3 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 ReO_3 and WO_3 , MoO_3 has a layered structure (figure 1) formed by edge and corner sharing of MoO_6 octahedra. The layers are separated by a van der Waals gap. Accordingly, 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 MoO_3 proceeds topotactically yielding a single phase Li_xMoO_3 for $0.2 < x < 0.5$. $\text{Mo}_{18}\text{O}_{52}$ which has a shear structure closely related to MoO_3 exhibits a similar reactivity. Lower valence molybdenum oxides Mo_4O_{11} , Mo_8O_{23} and Mo_9O_{26} which possess shear structures related to ReO_3 (Kihlborg 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 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 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 MoO_2 , RuO_2 and IrO_2 is accompanied by a structural transformation from the rutile to an ordered NiAs structure, as revealed by power neutron diffraction study of 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 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 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 LiCoO_2 yielding Li_xCoO_2 ($0 < x < 1$) wherein the layer structure is retained. We have shown that lithium can be

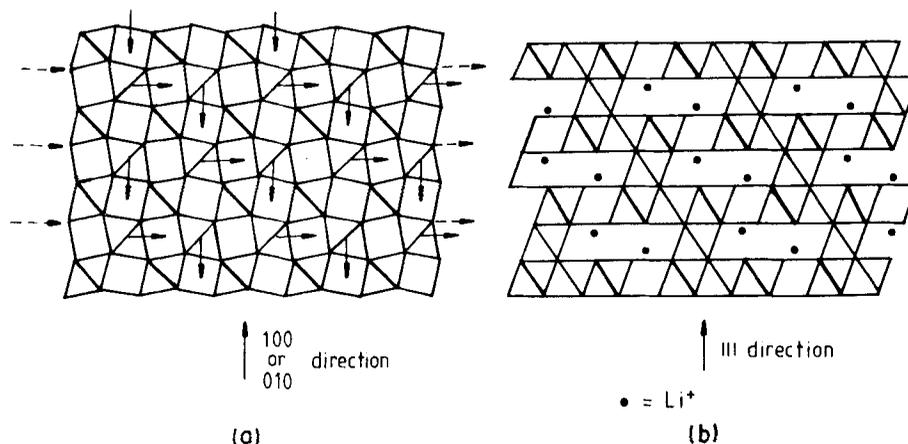


Figure 4. Mechanism for the rutile-spinel transformation. Cation occupied octahedra are shown. In (a) rutile structure, solid arrows indicate cation displacements and dotted arrows, the direction of shear required for the transformation to the spinel structure (b) (after Goodenough *et al* 1984).

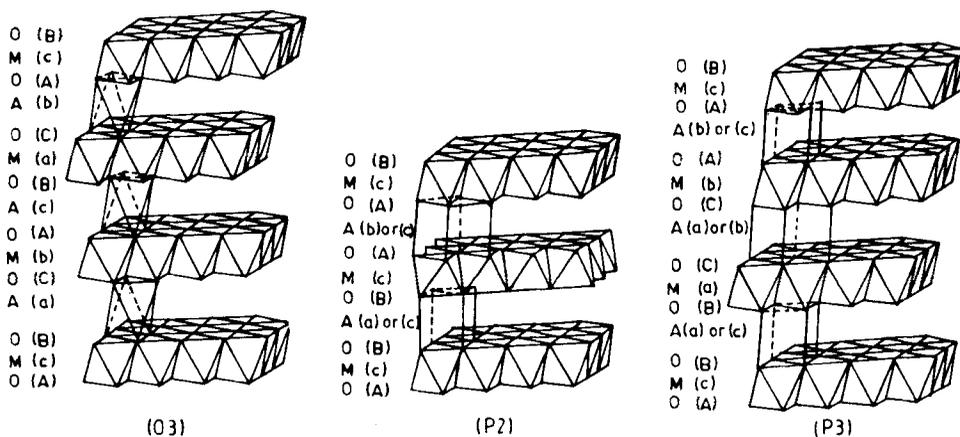


Figure 5. Packing of MO_6 octahedra in A_xMO_2 oxides. O3 structure corresponds to the ordered rocksalt structure of α - $NaFeO_2$ (after Delmas *et al* 1982b).

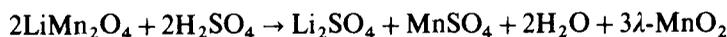
extracted chemically at room temperature from the isostructural $LiVO_2$ using Br_2 in $CHCl_3$ as the oxidative delithiating agent (Vidyasagar and Gopalakrishnan 1982). Li_xVO_2 retain the cubic close packed anion array, but not the layered structure, upto $x \sim 0.2$. Nearly complete removal of lithium 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 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 LiTi_2O_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 LiV_2O_4 spinel (de Picciotto and Thackeray 1985). LiTi_2O_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. LiTi_2O_4 spinel can be oxidatively delithiated using I_2 in CH_3CN to yield a limiting composition $\text{Li}_{0.1}\text{TiO}_2$ which is similar to Li_xVO_2 possessing a defect rocksalt structure. Lithium can also be inserted into the metastable TiO_2 (B) giving $\text{Li}_{0.75}\text{TiO}_2$ (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).

α and β - Li_2MoO_3 crystallizing in ordered rocksalt structures (Dickens and Reynolds 1982) can be oxidatively delithiated using Br_2 in 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. LiFeSnO_4 polymorphs crystallizing in the ramsdellite structure intercalates one atom of lithium corresponding to reduction of Fe^{3+} to Fe^{2+} (Greenblatt *et al* 1985).

Lithium insertion/extraction reactions in manganese oxides have been extensively investigated by Goodenough *et al* (1984). Lithiation of Mn_3O_4 (hausmanite) to give LiMn_3O_4 suppresses the cooperative Jahn-Teller distortion of the host and this is consistent with the formulation of the phase as $(\text{Li}^+ \text{Mn}^{2+})_i (\text{Mn}^{3+} \text{Mn}^{2+})_o \text{O}_4$. On the other hand, lithiation of LiMn_2O_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 Mn^{2+} . The new phase is trigonal adopting the Li_2VSe_2 structure consisting of hexagonal close packed anions; Mn^{2+} ions occupy alternate octahedral-site basal planes and Li^+ ions the tetrahedral sites of the other basal planes (David *et al* 1983).

An interesting case of topochemical delithiation is that of LiMn_2O_4 which occurs on treatment with aqueous H_2SO_4 (Hunter 1981). The product was considered to be a new form of manganese dioxide, λ - MnO_2 , which retained the spinel framework of the parent. Delithiation of LiMn_2O_4 to give λ - MnO_2 depends on two properties: (i) room temperature mobility of Li^+ in the Mn_2O_4 spinel framework and (ii) surface disproportionation of Mn^{3+} . The overall reaction could be



Subsequent work (Thackeray *et al* 1984; Mosbah *et al* 1983) has shown that Hunter's λ - MnO_2 is indeed $\text{Li}_{0.02}\text{MnO}_2$. Presence of residual lithium is revealed by neutron diffraction. Electrochemical delithiation of LiMn_2O_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.

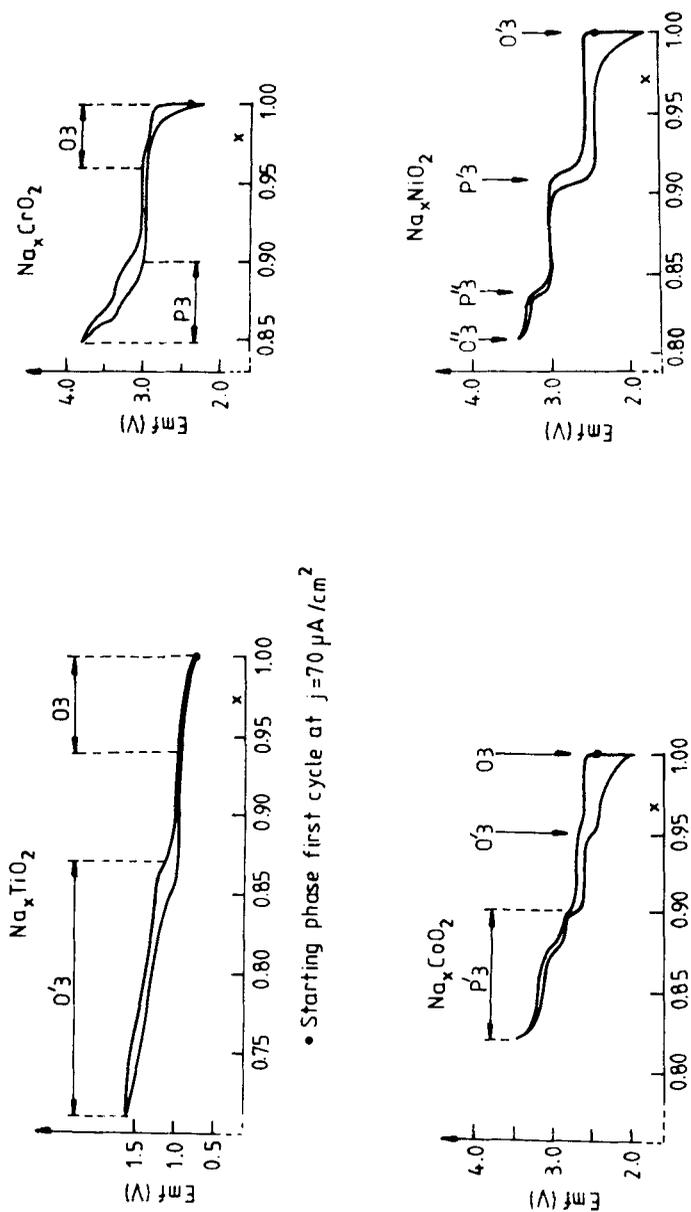
Lithium insertion in Fe_3O_4 and α - Fe_2O_3 has been investigated (Thackeray *et al* 1982). The crystal structure of $\text{Li}_{1.5}\text{Fe}_3\text{O}_4$ shows that the Fe_2O_4 subarray of the spinel

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 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 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 Na_xCoO_2 leads to reversible structural transformations between $O3$ and $P3$ structures (figure 6). Of the four phases that are known in the Na_xCoO_2 system, $P2$ phase is never obtained by electrochemical extraction of sodium from NaCoO_2 . A $O3\text{-}P3$ transformation would involve mere gliding of anion sheets, while a $O3(P3)\text{-}P2$ transformation would require the Co-O bond breaking as well. $O3\text{-}P3$ transformations in Na_xMO_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 NaMO_2 ($M = \text{Cr, Co, Ni}$), but lithium cannot be removed from LiCrO_2 and LiCoO_2 using chemical oxidants such as Br_2 and I_2 . Mendiboure *et al* (1985) have investigated electrochemical insertion and extraction of sodium in Na_xMnO_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 Mn^{3+} results in electron localization which in turn tends to trap 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 Cu, Ag or 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 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 NaMO_2 ($M = \text{Co, Ni}$).

LiNbO_3 and LiTaO_3 undergo facile ion-exchange in hot aqueous acids to give HNbO_3 and HTaO_3 (Rice and Jackel 1982). The exchange is accompanied by a



• Starting phase first cycle at $j = 70 \mu\text{A}/\text{cm}^2$

Figure 6. Electromotive force (Emf) versus composition curves for Na_xMO_2 ($M = \text{Ti, Cr, Co, Ni}$) oxides. Emf is measured in a cell using NaMO_2 cathode, sodium anode and NaClO_4 in propylene carbonate as electrolyte (after Delmas *et al* 1982b).

topotactic transformation of the rhombohedral LiNbO_3 structure to the cubic 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 ReO_3 structure. The transformation involves a mechanism which is the reverse of that accompanying lithium insertion in ReO_3 ; the 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 LiNbO_3 structure to the $3/4$ CCP array of the ReO_3 structure.

Trirutile LiNbWO_6 and LiTaWO_6 undergo similar exchange in hot aqueous acids to give HNbWO_6 and HTaWO_6 (Vasudeva Bhat and Gopalakrishnan 1985b). The exchange is accompanied by a structural transformation from the rutile structure to the 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 LiNbO_3 -like framework. The latter would then transform to the ReO_3 structure by a mechanism similar to the LiNbO_3 - 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 Li_xTiS_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, VS_2 and 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

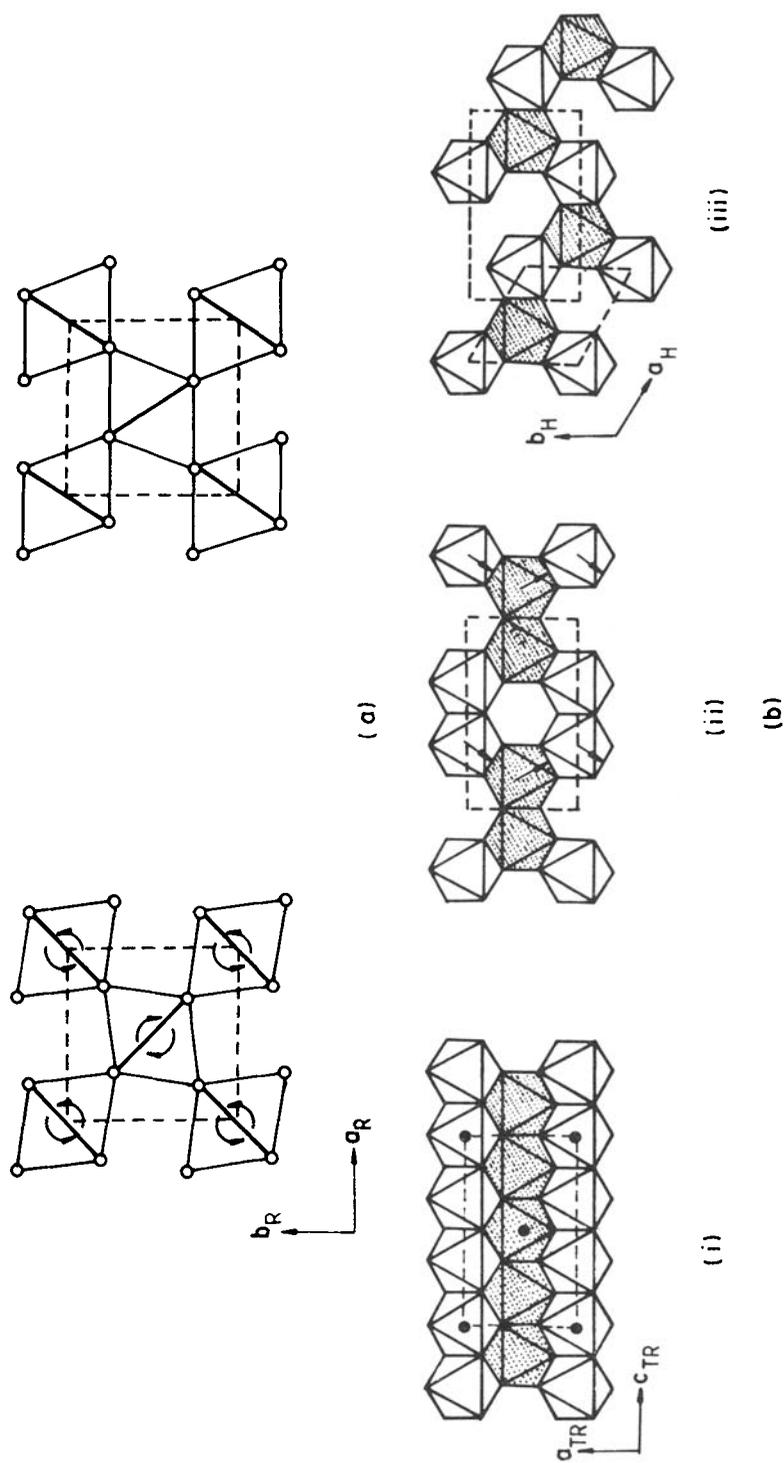
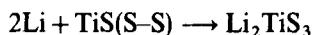


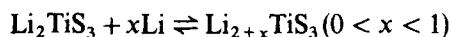
Figure 7. (a) Transformation of tetragonal close packed anion array of the rutile structure to hexagonal close packed (HCP) array by rotation of the occupied octahedra. (b) Transformation of NbWO_6 framework in LiNbWO_6 (trirutile) to NbO_3 framework of LiNbO_3 structure. The oxygen array is idealised to HCP. Only occupied octahedra are shown. Shaded and unshaded octahedra are at different levels. (i) LiNbWO_6 trirutile. Li-occupied octahedra are shown with a filled circle. (ii) NbWO_6 network after removal of lithium. Arrows indicate direction of cation displacement. (iii) NbWO_6 network after cation rearrangement. This network is similar to NbO_3 network in LiNbO_3 (after Vasudeva Bhat and Gopalakrishnan 1985b).

Bruggen *et al* 1980). A new form of FeS_2 possessing the layered CdI_2 structure has been synthesized by electrochemical extraction of lithium from Li_2FeS_2 (Dugast *et al* 1981). The Chevrel phase cluster sulphide Mo_6S_8 can be easily prepared by extracting lithium from $\text{Li}_x\text{Mo}_6\text{S}_8$ by treatment with dilute 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 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 WS_2 , the new modification of WS_2 exhibits metallic behaviour. KFeS_2 and related sulphides possessing infinite chains of edge-shared FeS_4 tetrahedra can be inserted with lithium (Jacobson *et al* 1979b). Lithium insertion in KFeS_2 is accompanied by a structural transformation and reduction of Fe^{3+} to Fe^{2+} . LiKFeS_2 adopts a tetragonal layered structure which is related to CuTe (Jacobson and McCandlish 1979).

The trichalcogenides MX_3 possessing chain structures intercalate lithium but the reaction is not entirely reversible unlike the dichalcogenides. In 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 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 MoS_3 , WS_3 , V_2S_5 , MoS_2 and 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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