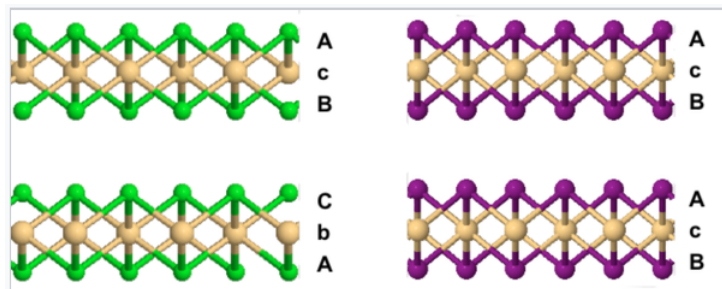


## 8.5: Layered Structures and Intercalation Reactions

**Layered structures** are characterized by strong (and typically covalent) bonding between atoms in two dimensions and weaker bonding in the third. A broad range of compounds including metal halides, oxides, sulfides, selenides, borides, nitrides, carbides, and allotropes of some pure elements (B, C, P, As) exist in layered forms. Structurally, the simplest of these structures (for example binary metal halides and sulfides) can be described as having some fraction of the octahedral and/or tetrahedral sites are filled in the fcc and hcp lattices. For example, the  $\text{CdCl}_2$  structure is formed by filling all the octahedral sites in alternate layers of the fcc lattice, and the  $\text{CdI}_2$  structure is the relative of this structure in the hcp lattice.

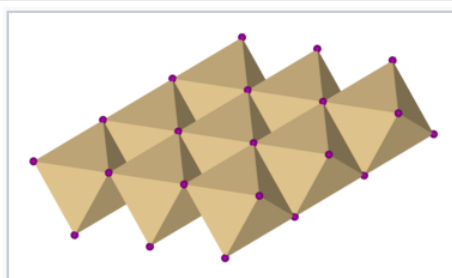
In the  **$\text{CdCl}_2$  structure**, the stacking sequence of anion layers is ABCABC...

In the  **$\text{CdI}_2$  structure**, the anion stacking sequence is ABAB..., and all the cations are eclipsed along the stacking axis.



Comparison of the  $\text{CdCl}_2$  (left) and  $\text{CdI}_2$  (right) crystal structures

These are examples of **6-3 structures**, because the cations are coordinated by an octahedron of six anions, and the anions are coordinated by three cations to make a trigonal pyramid (like  $\text{NH}_3$ ). Another way to describe these structures is to say that the  $\text{MX}_6$  octahedra each share six edges in the  $\text{MX}_2$  sheets.



Polyhedral drawing of one layer of the  $\text{CdCl}_2$  or  $\text{CdI}_2$  structure showing edge-sharing  $\text{MX}_6$  octahedra

Because these structures place the packing atoms (the anions) in direct van der Waals contact, they are most stable for relatively **covalent** compounds. Otherwise, the electrostatic repulsion between contacting anions would destabilize the structure energetically. More ionic  $\text{MX}_2$  compounds tend to adopt the fluorite ( $\text{CaF}_2$ ) or rutile ( $\text{TiO}_2$ ) structures, which are not layered.

Despite the fact that these two structure types are the same at the level of nearest and next-nearest neighbor ions, the  $\text{CdI}_2$  structure is much more common than the  $\text{CdCl}_2$  structure.

### **$\text{CdCl}_2$ structure:**

$\text{MCl}_2$  (M = Mg, Mn, Fe, Co, Ni, Zn, Cd)

$\text{NiBr}_2$ ,  $\text{NiI}_2$ ,  $\text{ZnBr}_2$ ,  $\text{ZnI}_2$

### **$\text{CdI}_2$ structure:**

$\text{MCl}_2$  (M = Ti, V)

$\text{MBr}_2$  (M = Mg, Fe, Co, Cd)

$\text{MI}_2$  (M = Mg, Ca, Ti, V, Mn, Fe, Co, Cd, Ge, Pb, Th)

$M(OH)_2$  ( $M = Mg, Ca, Mn, Fe, Co, Ni, Cd$ )

$MS_2$  ( $M = Ti, Zr, Sn, Ta, Pt$ )

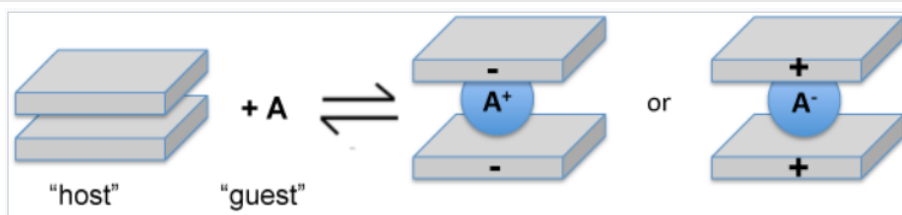
$MSe_2$  ( $M = Ti, Zr, Sn, V, Pt$ )

$MTe_2$  ( $M = Ti, Co, Ni, Rh, Pd, Pt$ )

Physically, layered compounds are **soft** and **slippery**, because the layer planes slide past each other easily. For example, graphite,  $MoS_2$ , and talc (a silicate) are layered compounds that are used widely as **lubricants** and lubricant additives.

An important reaction of layered compounds is **intercalation**. In intercalation reactions, guest molecules and ions enter the galleries that separate the sheets, usually with expansion of the lattice along the stacking axis. This reaction is typically reversible if it does not perturb the bonding within the sheets. Often the **driving force for intercalation is a redox reaction**, i.e., electron transfer between the host and guest. For example, lithium metal reacts with  $TiS_2$ ,  $MoS_2$ , and graphite to produce  $LiTiS_2$ ,  $Li_xMoS_2$  ( $x < 1$ ), and  $LiC_6$ . In these compounds, lithium is ionized to  $Li^+$  and the sheets are negatively charged. Oxidizing agents such as  $Br_2$ ,  $FeCl_3$ , and  $AsF_5$  also react with graphite. In the resulting intercalation compounds, the sheets are positively charged and the intercalated species are anionic.

Intercalation reactions are especially important for electrochemical energy storage in **secondary batteries**, such as **lithium ion** batteries, **nickel-metal hydride** batteries, and **nickel-cadmium** batteries. The reversible nature of the intercalation reaction allows the electrodes to be charged and discharged up to several thousand times without losing their mechanical integrity. In lithium ion batteries, the negative electrode material is typically graphite, which is intercalated by lithium to make  $LiC_6$ . Several different oxides and phosphates containing redox active transition metal ions ( $Mn, Fe, Co, Ni$ ) are used as the positive electrode materials.



Oxidative or reductive intercalation involves the placement of anions or cations between sheets.

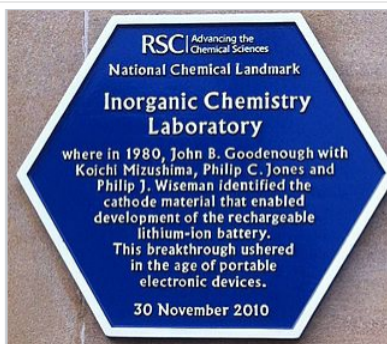
Lithium ion batteries based on  $CoO_2$  were first described in 1980<sup>[1]</sup> by John B. Goodenough's research group at Oxford. In batteries based on  $CoO_2$ , which has the  $CdI_2$  structure, the positive electrode half-reaction is:



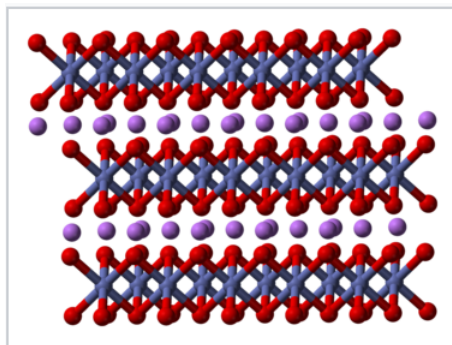
The negative electrode half reaction is:



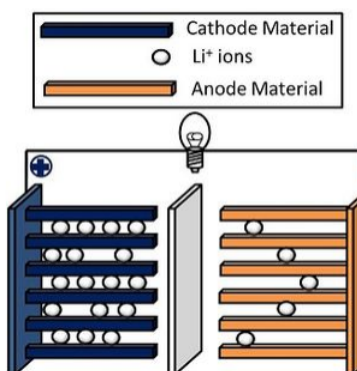
The battery is fully charged when the positive electrode is in the  $CoO_2$  form and the negative electrode is in the  $LiC_6$  form. Discharge involves the motion of  $Li^+$  ions through the electrolyte, forming  $Li_xCoO_2$  and graphite at the two electrodes.



Blue plaque erected by the Royal Society of Chemistry commemorating the development of cathode materials for the lithium-ion battery



Crystal structure of  $\text{LiCoO}_2$ <sup>[2]</sup>



The lithium ion battery is a "rocking chair" battery, so named because charging and discharging involve moving  $\text{Li}^+$  ions from one side to the other.  $\text{CoO}_2$  is one example of a positive electrode material that has been used in lithium ion batteries. It has a high energy density, but batteries based on  $\text{CoO}_2$  have poor thermal stability. Safer materials include lithium iron phosphate ( $\text{LiFePO}_4$ ), and  $\text{LiMO}_2$  ( $M$  = a mixture of Co, Mn, and Ni). These batteries are used widely in laptop computers, portable electronics, cellular telephones, cordless tools, and electric and hybrid vehicles.

A similar intercalation reaction occurs in nickel-cadmium batteries and nickel-metal hydride batteries, except in this case the reaction involves the movement of protons in and out of the  $\text{Ni}(\text{OH})_2$  lattice, which has the  $\text{CdI}_2$  structure:



There are many layered compounds that cannot be intercalated by redox reactions, typically because some other stable product is formed. For example, the reaction of layered  $\text{CdI}_2$  with Li produces  $\text{LiI}$  ( $\text{NaCl}$  structure) and Cd metal.

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