CH5715
Energy Conversion and Storage

Part 2: Ionic Conduction, Electrochemistry, Batteries and Other Applications

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Aims:

To introduce students to the principals and applications of ionic conductors, electrochemistry and batteries

For lecture notes: http://koruk.wp.st-andrews.ac.uk

Summary

L1-3 Wks 6-7 Conductivity in ionic solids, Crystalline Conductors, Polymer Electrolytes

L4-5 Wk 8 Lithium Ion Batteries, Electrodes Intercalation

L6-7 Wk 9 Electrochemical Reactions and Impedance Spectroscopy

L8-9 Wk 10 Other Applications High Temperature Batteries, Oxygen Transport Membranes

Tutorial Friday Wk 10 25th April

What is Electrochemistry?

Electrolytes	Interfaces	Electrodes
1. Molten salts e.g. NaCl		
2. Ceramic electrolytes e.g. Na β alumina		Metals e.g. Pt, Ag, Hg
3. Solution electrolytes e.g. $AgNO_3$ in H_2O	⟺	Semiconductors e.g. Si, GaAs
4. Polymer electrolytes e.g. poly(ethylene oxide): $NaClO_4$ $(CH_2\text{-}CH_2\text{-}O)_n:NaClO_4$		

Solution Electrolytes

salt + solvent → solution

-ve ΔG

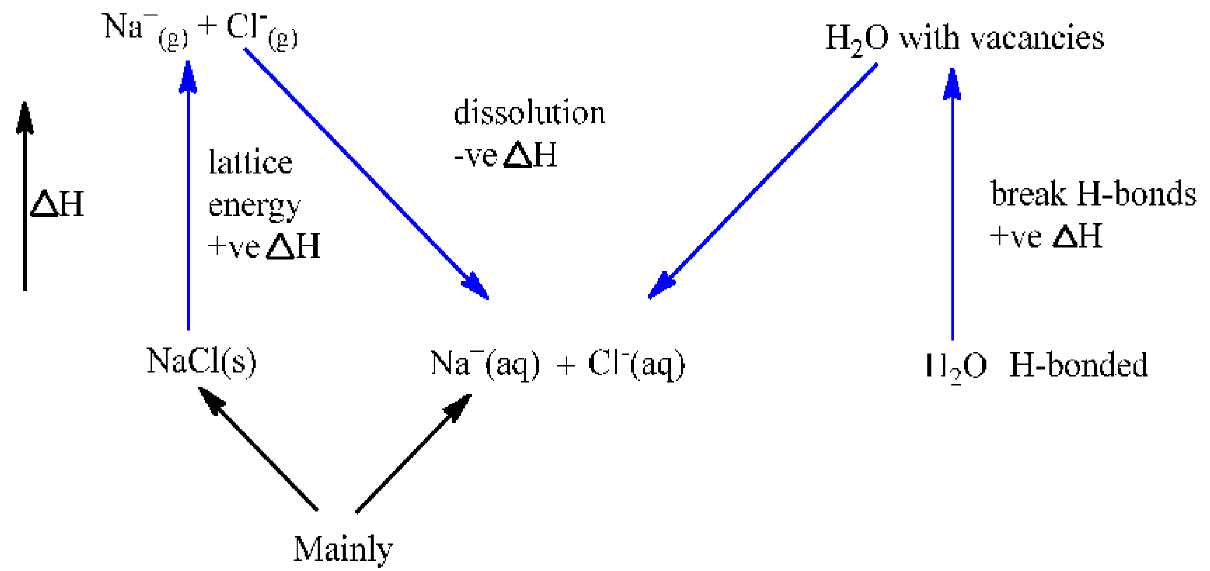
$\Delta G = \Delta H - T\Delta S$

ΔS of salt increases ΔS of solvent decreases

Overall ΔS positive but still small

Dissolution depends on enthalpy changes

NaCl does not dissolve in hexane



IONIC CONDUCTORS

- Defects in solids
- Ionic migration in solids
- Fast ion conductors
- Examples of Solid Electrolytes

Applications of Solid Electrolytes

- Na/S batteries
- Li batteries
- Mixed conduction – Oxygen Transport Membranes
- Insertion chemistry - electrodes
- Solid oxide fuel cells

How do ions move in solid electrolytes?

General requirements

1. Mobile ions must partially occupy a set of energetically equivalent or near equivalent sites.

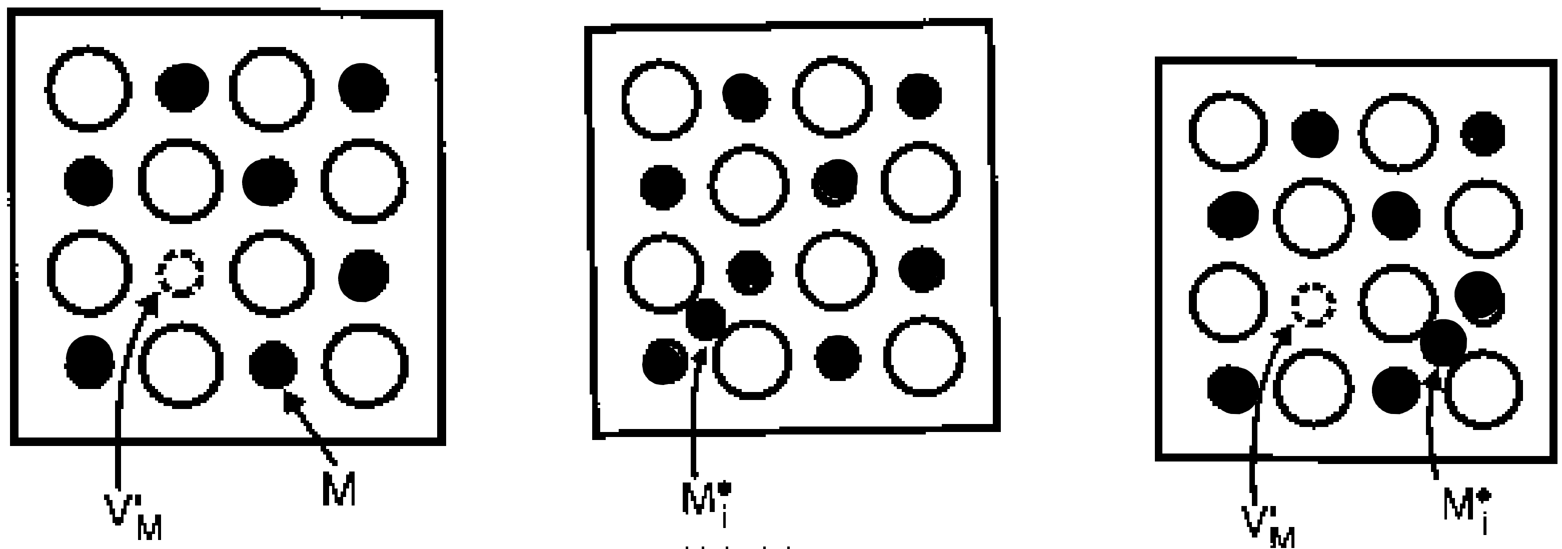
2. The sites must be interconnected by continuous pathways.

1. **Partial occupancy**

A perfect crystal of NaCl would not support ionic conductivity. Schottky defects → a few Na^+ and Cl^- vacancies → ions can move.

Solid electrolytes are good conductors - contain many ions and many vacancies i.e. occupancies of 10% to 90%.

Point defects and cation migration



(a) Vacancies (vacant lattice site) [Schottky defect is V'_M plus $V^{\bullet}_X$]

(b) Interstitials (atom on an interstitial site)

Frenkel defects (vacancy plus interstitials)

Intrinsic Conductivity

$$K = \frac{[V_{Na}][V_{Cl}]}{[Na^{+}][Cl^{-}]} \approx \frac{N_V^2}{N^2}$$

E_f = Energy of formation for V_{Na} and V_{Cl}

$$\mathrm{K} = C\exp(-E_f / kT)$$

$$\therefore N_V = N\sqrt{C\exp(-E_f / kT)}$$

$$= C\exp(-E_f / 2kT)$$

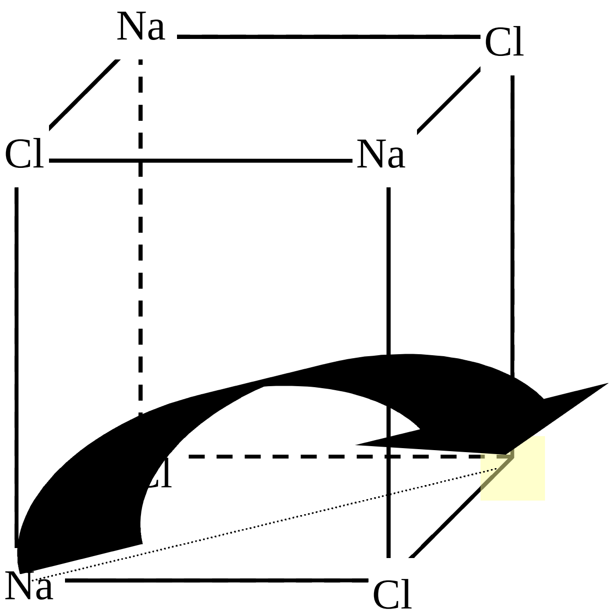
Extrinsic conductivity

Aliovalent doping

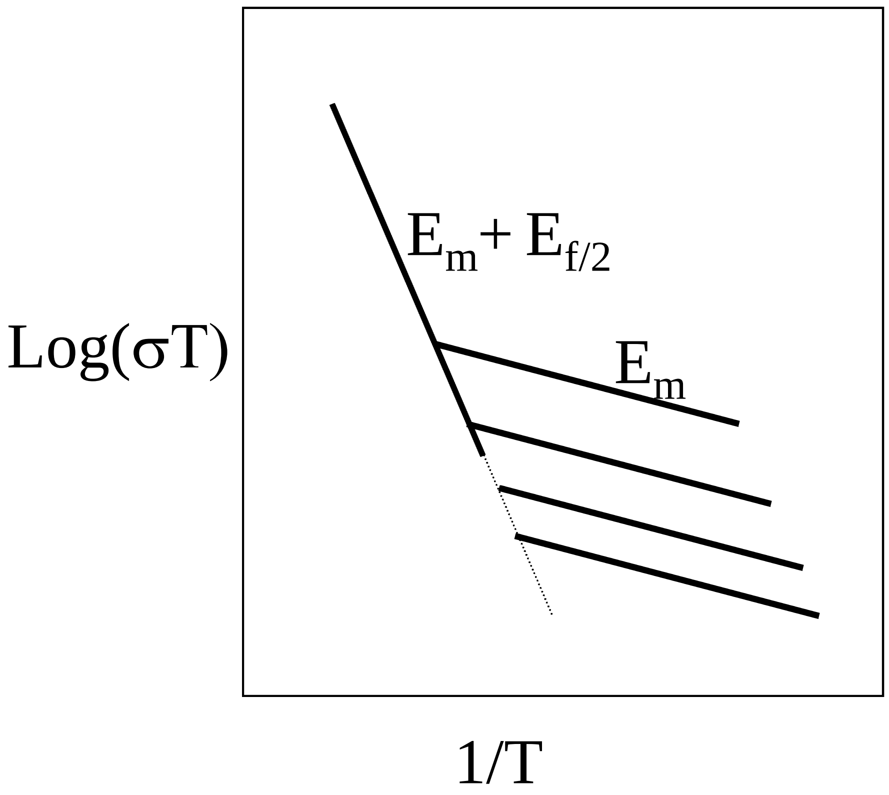
eg **NaCl** $2\ Na^{+} \rightarrow Cd^{2+} + V_{Na}^{-}$

ZrO_2 $2\ Zr^{4+} \rightarrow 2\ Y^{3+} + V_{O}^{2+}$

CaF_2 $Ca^{2+} \rightarrow Y^{3+} + F_{I}^{-}$

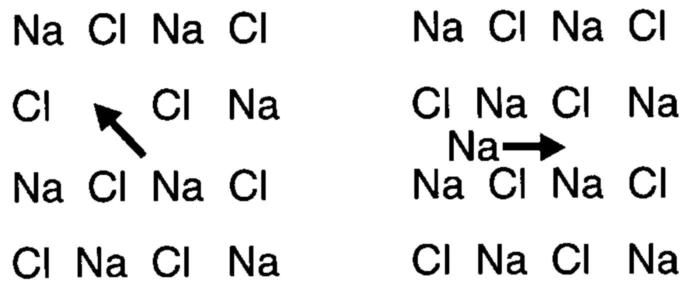


Jump mechanism in 3d space



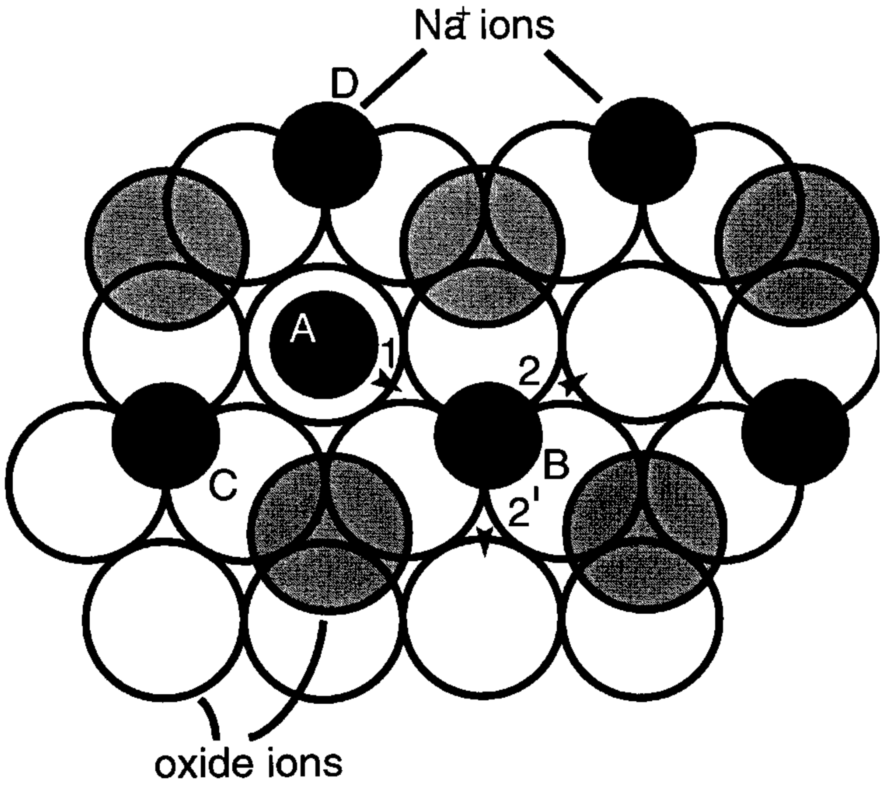
Influence of dopants on conductivity behaviour in NaCl

Vacancy and Interstitial Conduction Mechanisms



(a) (b)

Interstitialcy mechanism



Ionic Migration/Ionic Conductivity

Ionic Conductivity (Scm^{-1})

Ionic crystals < 10^{-13} - 10^{-4}

Solid Electrolytes 10^{-4} - 10

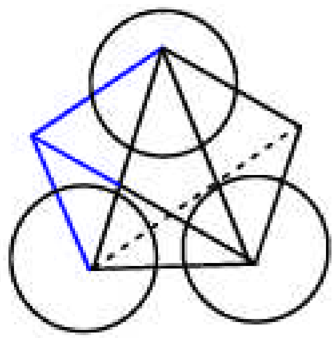
Strong liquid electrolytes 10^{-3} - 10^{1}

$$\sigma = ne\mu$$

$\mu = f(T)$ Nernst Einstein relation $\mu = qD/kT$.

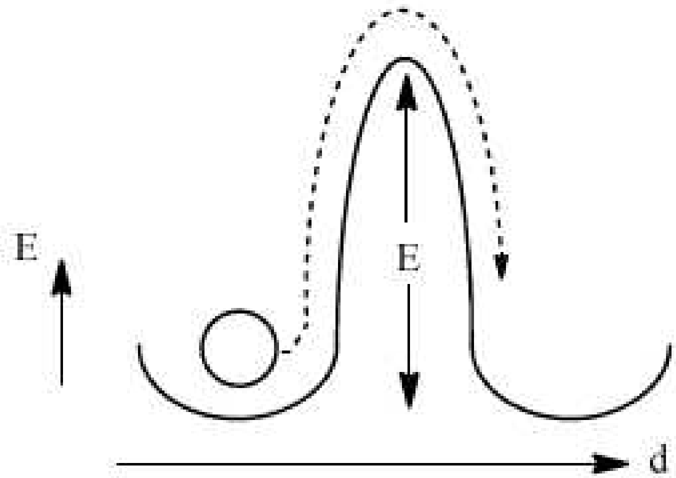
2. Pathways

e.g. move between two tetrahedral sites



through a narrow bottleneck.

Potential Energy Profile



ion vibrates in its site, $\nu^{\circ} = 10^{13}\ s^{-1}$

Boltzman distribution of energies

Each second a proportion, ν, of the 10^{13} vibrations (ν°) will have enough energy to escape the site (i.e. $\geq$ E)

ν = no. of successful jumps

hopping mechanism

μ s function of (v,d)

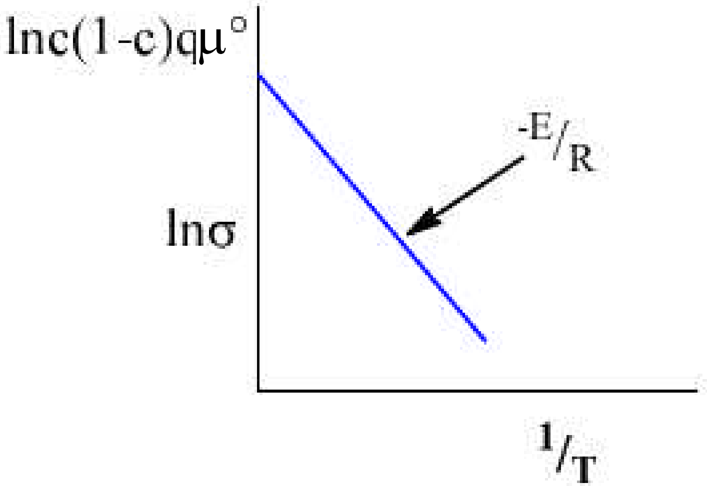
where μ - mobility of the ion
d - jump distance between sites

$\mu = \mu^\circ \exp(^{-E}/_{RT})$

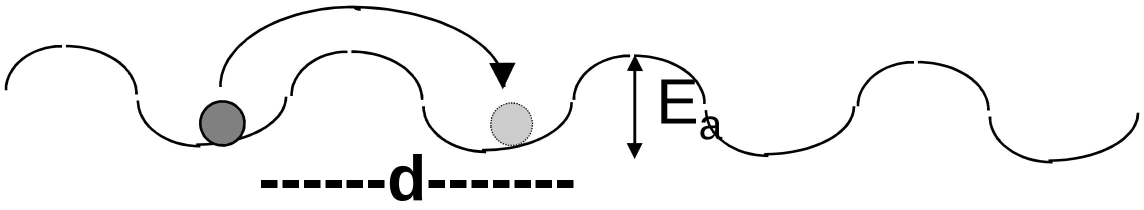
$\sigma = c(1-c)qu^\circ \exp(^{-E}/_{RT})$

c- concentration

q - charge



Ionic hopping model



Arrhenius equation

$$\sigma T \quad = A\exp(-E_a / kT)$$

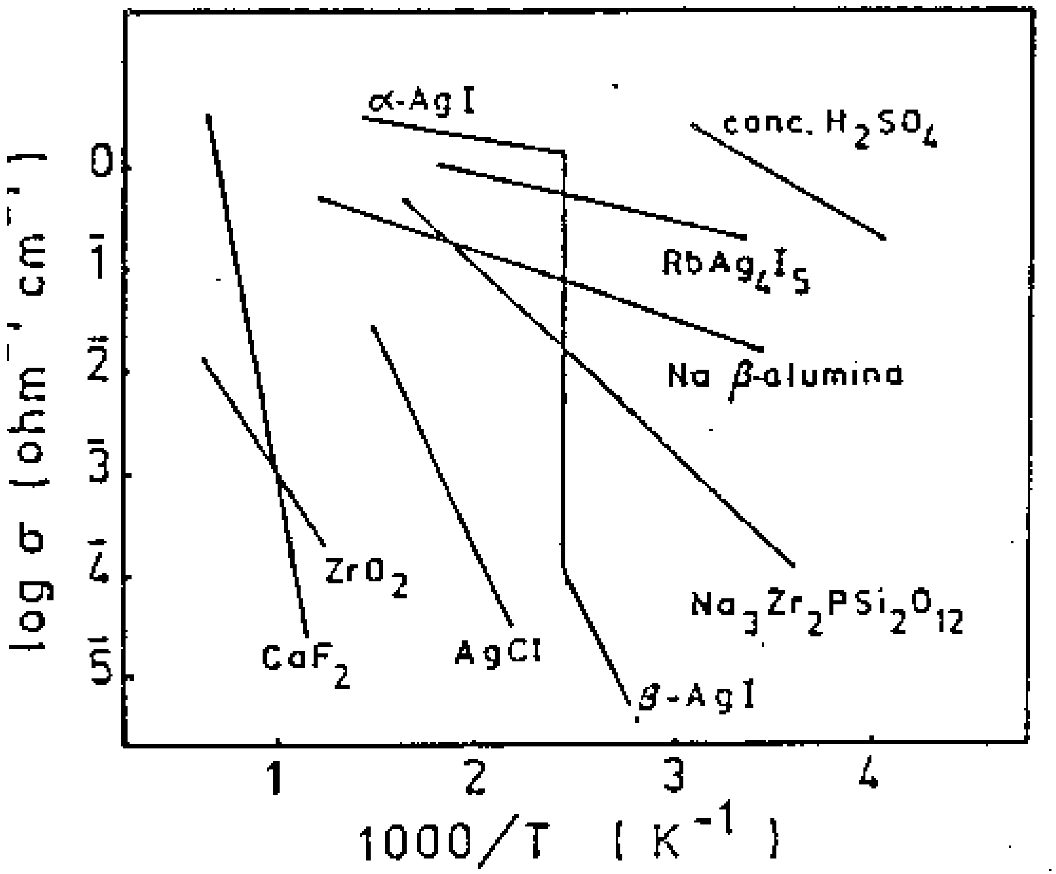
A - relates to number of carriers per unit volume,

d^2,

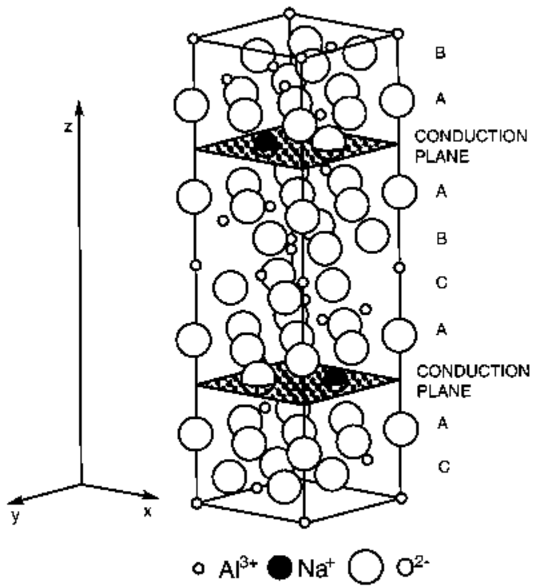
jump frequency

E_a = Activation Energy

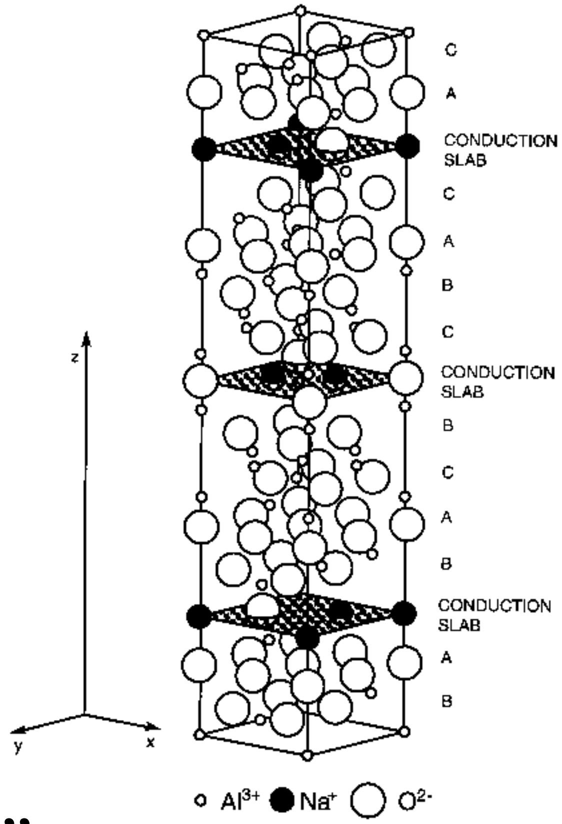
SOLID ELECTROLYTES



Structure of Beta-Alumina



β



β”

<u>β-Alumina</u>

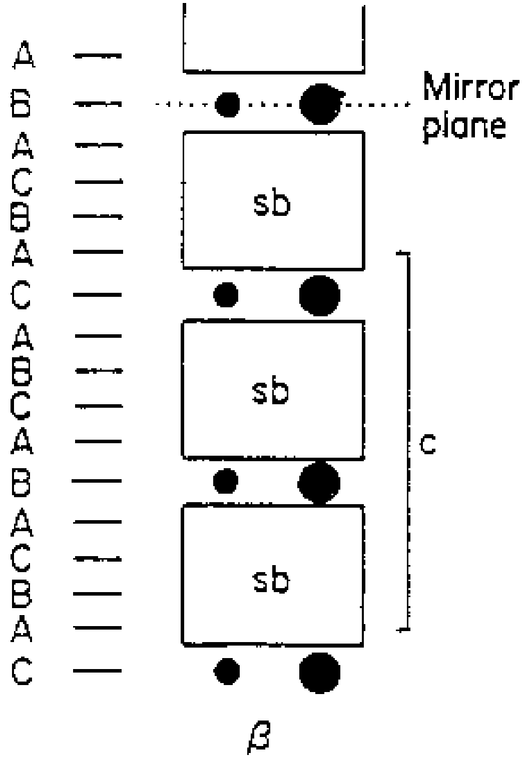
$M_2O.nX_2O_3$ - M - Alkali, Cu, Ag, H_3O,
X - Al, Ga, Fe

$NaAl_{11}O_{17}$ ideal
Na - β (8-11), β"(5-7)

Structure consists of spinel blocks separated by less dense
layers - conduction planes.

2 dimensional Na conductor

E_a ~ 0.16 eV



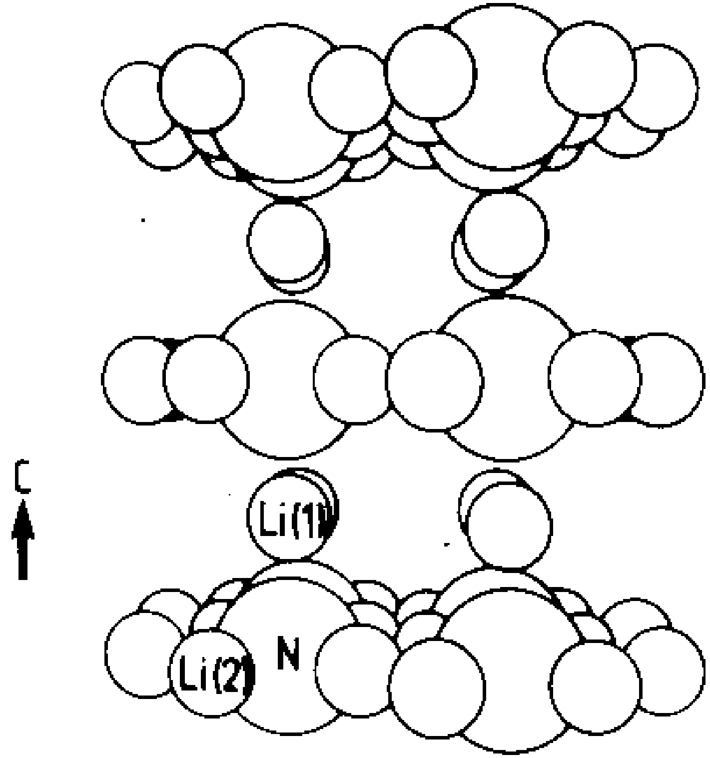
Li ion Conductors

Best are 1-2 orders of magnitude less conductive than Na β- alumina, ie 10^{-3} - 10^{-4} Scm^{-1}

Li_3N - layered structure Li, LiN_2
Li β alumina
$Li_{0.5}La_{0.5}TiO_3$
Various Li silicate frameworks - LISICON

Li polymer electrolytes are good alternative.

$LiClO_4$/ polyethylene oxide



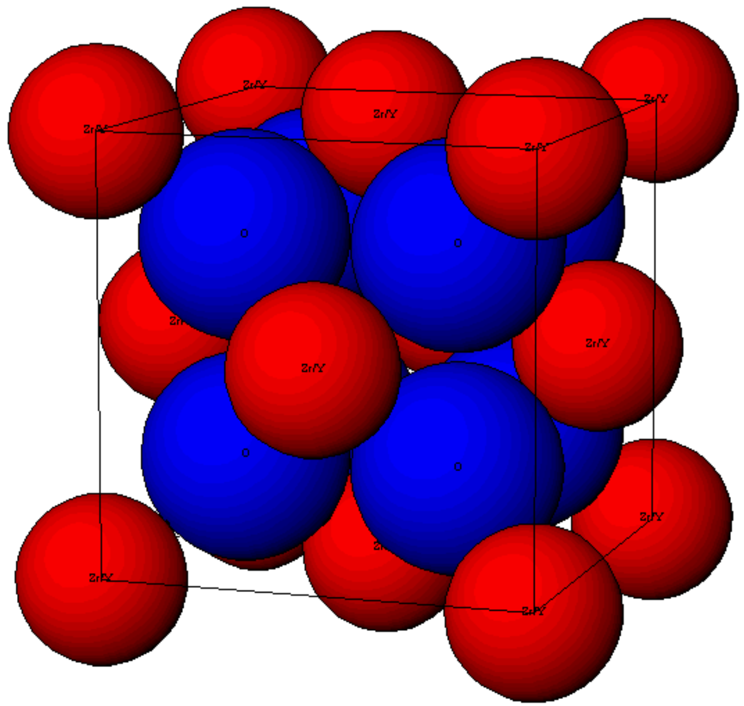
ANION CONDUCTORS

Fluorite anion conductors

PbF_2, $SnPbF_4$ 10^{-1} Scm^{-1} at room temperature
$La_xSr_{1-x}F_2$

ZrO_2 based ion conductors, Y_2O_3 and CaO doping

Conductivities 10^{-2} Scm^{-1} at 1000°C



Electrolytes

Solid electrolytes not widely used now

Considerable interest in incorporating batteries into printed circuit boards - crystalline electrolytes

LiI formed in situ has been used, similar to AgI

Polymer electrolytes are particularly promising-safety

However, liquids now widely commercialised in solid state batteries.

Organic electrolyte encapsulated in polymer mesh