Ionic Conductivity

Fundamental to batteries, fuel cells and many sensors

Conduction electrons or ions, usually one or the other but some materials can show both.

Two requirements:

- charge carriers, n_i (charge carried, e_i)
- charge carrier mobility, μ_i

$$\sigma = \Sigma\, n_i e_i \mu_i$$

Typical conductivities: specific conductivity, σ, Units $\text{ohm}^{-1}\text{m}^{-1}$ or Sm^{-1} where S is the siemen (equivalent to ohm^{-1})

	Material	σ Sm^{-1}
Ionic conduction	Ionic crystal	$<10^{-18}$ - 10^{-4}
	Solid electrolyte	10^{-3} - 10^{1}
	Liquid electrolyte	10^{-3} - 10^{1}
Electronic conduction	Metal	10^{1} - 10^{5}
	Semiconductor	10^{-5} - 10^{2}
	Insulator	$<10^{-12}$

Ionic materials
- conductivity only by crystal defects.

High temperatures:
- increase in defect concentration
- ion mobility

Special case

Solid electrolytes - rather special crystal structures: open tunnels or layers through which mobile ions may move e.g 10^{-3} for Na^+ ions in β-alumina at 25°C.

Perfect ionic crystal
- no ion diffusion is possible because all the available sites are occupied.

Na	Cl	Na	Cl	Na	Cl
Cl	Na	Cl	Na	Cl	Na
Na	Cl	Na	Cl	Na	Cl
Cl	Na	Cl	Na	Cl	Na
Na	Cl	Na	Cl	Na	Cl
Cl	Na	Cl	Na	Cl	Na

- limited ion mobility
    - absence of a route for diffusion
    - bottlenecks between interstitial sites

Defect types

Inherent/intrinsic (Schottky, Frenkel)

- Present in all crystals
- Energy fluctuations which occur above absolute zero
- Point defects, < 0.001 atom %.

Schottky

Cation and anion vacancies occur in pairs

- maintains electrical neutrality
- for NaCl typically 250 $kJmol^{-1}$
- <3 x 10^{-5} of lattice site in NaCl

$$NaCl = \square_{Na} + \square_{Cl}$$

Frenkel

Cation or anion is moved from the close-packed structure onto an interstitial site.

- E_F = 42-420 $kJmol^{-1}$

$$Ag^{+} + \square_{i} = Ag_{i}^{+} + \square_{Ag}$$

Extrinsic

- Introduced into a structure
- Dopant of different valency and aliovalent impurity, such as $MnCl_2$ in NaCl.
- Solubility limited

The Mn occupies the same lattice site as the Na but for electric neutrality there must be less present. Hence a sodium ion vacancy is created, V_{Na} or $\square_{Na}$.

$$MnCl_2 = Mn_{Na} + \square_{Na} + 2Cl_{Cl}$$

Structure specific

Defects present in a material by virtue of the structure type

Temperature dependence

Overall the temperature dependence of the ionic conductivity given by the Arrhenius equation.

$$\sigma = A\exp\left(\frac{-E}{RT}\right)$$

E is the activation energy

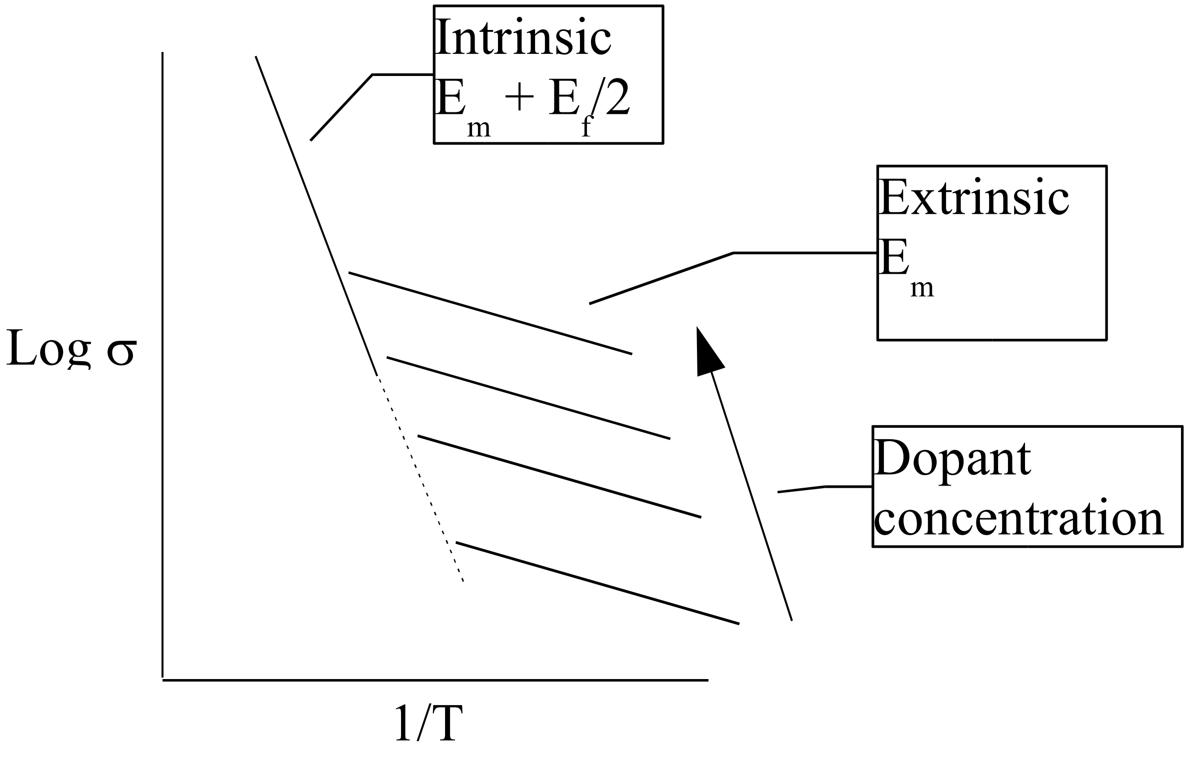
- creation of the defect, E_f
- defect migration, E_m

For example

NaCl doped with $MnCl_2$

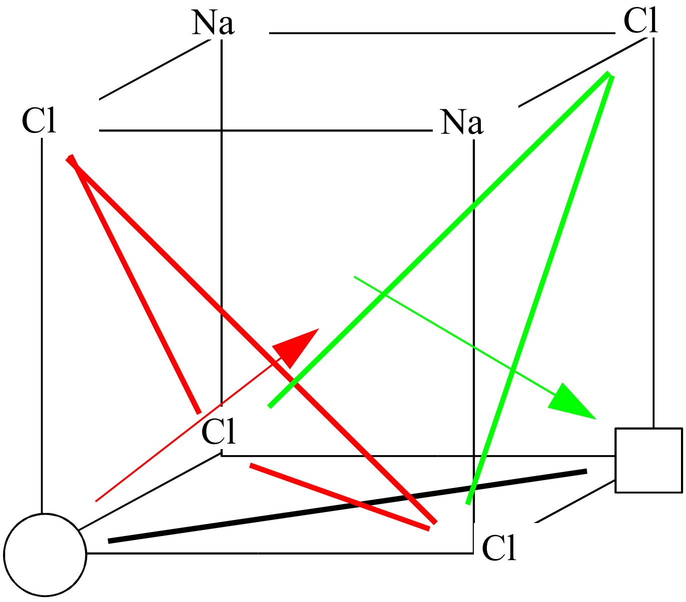
$$NaCl = \square_{Na} + \square_{Cl}$$

$$MnCl_2 = Mn_{Na} + \square_{Na} + 2Cl_{Cl}$$



Origin of the activation energy

- consider the possible paths
- Na^+ ion jumping from its lattice site to an adjacent vacancy .



Direct jump

- black line not possible
- two Cl^- ions are too close

Indirect jump

- through the middle of the cube, red line
- interstitial site at cube centre.
- triangular windows of chloride ions.
- radius of the triangular window is 0.45 Å (based on the close-packed structure)

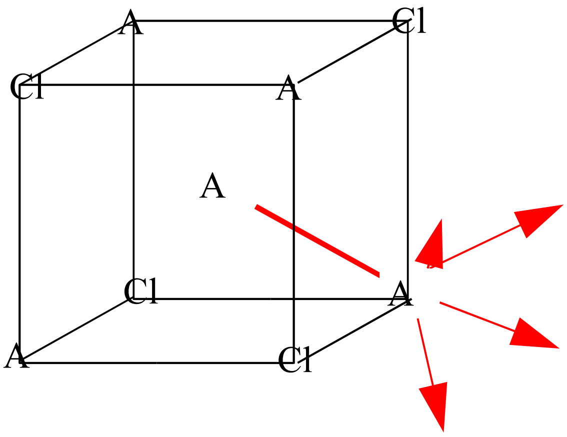
Radius of the interstitial site, 0.59 Å.
Ionic radius of Na^+ is ~0.95Å

Hence an ion can only get through when the structure becomes distorted, through the presence of thermal motions.

Silver chloride

Also has the NaCl structure.
Defects are however Frenkel. The Ag^+ ion moves off the lattice site and becomes an interstitial ion.
Two mechanisms for ion migration:

- direct interstitial:
  interstitial jumps to an adjacent interstitial site
- indirect, a knockon process.
  interstitial ion causes one of the neighbouring Ag^+ ions to move into the adjacent interstitial site and in turn occupies the newly created vacancy.



Aliovalent Cation Impurity

Now what happens if an aliovalent cation impurity is added. Add $CdCl_2$

$$CdCl_2 \quad = \quad Cd_{Ag} + \quad \square_{Ag} \quad + \quad 2Cl_{Cl}$$

cation vacancies are increased.
But the equilibrium constant continues to hold for:

$$Ag^{+} + \quad \square_{i} \quad = \quad Ag_{i}^{+} \quad + \; \square_{Ag}$$

So if $\square_{Ag}$ is increased then Ag_i^+ must decrease.

But this is the charge carrier so the specific conductivity will fall with dopant. It is displaced to lower levels.

Variation of specific conductivity with dopant concentration:

- initial decrease as number of Ag_i^+ falls
- a minimum will be reached when cation vacancy takes over as charge carrier
- at high enough dopant concentrations $\square_{Ag}$ increases so the conductivity begins to increases again

Structure Specific Conducitvity

Solid electrolytes

Requirements

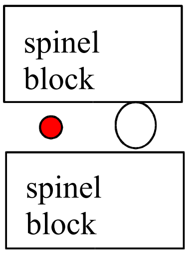
- large number of charge carriers
  simple ideas: if S present replace with P/Si more cations present
- high mobility
  open three dimensional structures, large windows (but not too large *cf* zeolites, otherwise the ions will prefer to stay on the sides)
- a number of vacant lattice sites
  (symmetry equivalent, so of the same energy, but unoccupied)

Within these general rules there are a number of classes of solid electrolytes: Most developed applications are based on β-alumina

β-alumina

Application: used in a sodium-sulphur battery.
Ford Motor Co. (1963) Na^+ ions mobile
Family of compounds of general formula
$M_2O.nX_2O_3$
Most important M= Na^+ and X=Al^{3+}
Structure slabs of spinel containing only Al^{3+} ions with Na^+ ions in oxide deficient layers
Good conductivity

- more Na^+ sites than ions available to fill them
- radius of Na^+ smaller than O^{2-}



Only two-dimensional conduction, cannot penetrate dense spinel blocks. Actual conduction mechanism somewhat complicated to envisage, many different possible sites. $S = 10^{-1}$ Sm^{-1} at 300°C.

Sodium-sulphur battery: uses Na^+ β-alumina as a solid electrolyte, high density secondary battery (high energy/power to mass ratio).
Molten sodium anode, molten sulphur cathode separated by the β-alumina electrolyte.
Cell reaction:

$$2Na + 5S = Na_2S_5 \qquad E = 2.08\ V$$

Operates at 300-350°C, this is a requirement based on the nature of the product. Only at this temperature are the products always molten.
Energy storage about 100-200 Wh kg^{-1}

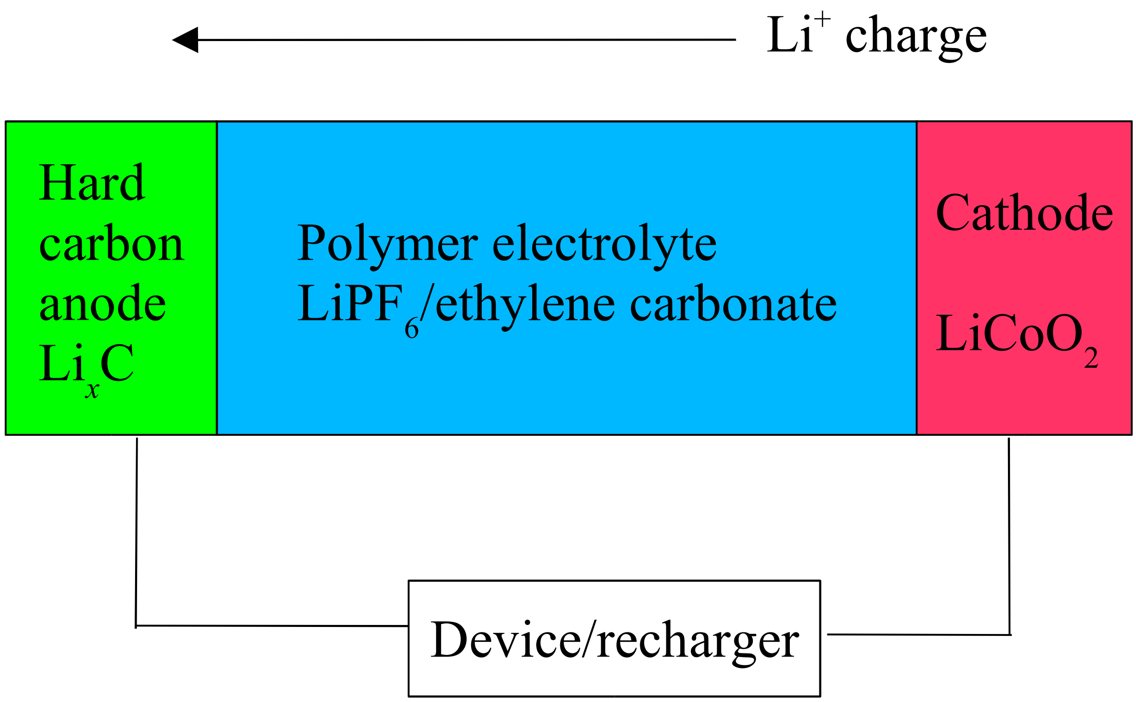
Lithium ion conductors are being developed. Why? Think about what determines the power

$$Li^+ + e^- = Li \qquad E = 3.05\ V$$

$$Na^+ + e^- = Na \qquad E = 2.71\ V$$

Rechargeable lithium batteries

Introduced by Sony in 1990



Li^+ charge

Hard carbon anode Li_xC

Polymer electrolyte
$LiPF_6$/ethylene carbonate

Cathode

$LiCoO_2$

Device/recharger

Known as rocking-chair, swing or LION cell

Fundamental expression of intercalation chemistry

- into graphitic carbon, Li_xC_6
  - between layers
  - lithium atoms intercalate – take up e^{-1}

- into Li_xCoO_2 : rock salt type
  - Co^{3+} in octahedral sites on alternate sheets
  - Li^+ in the remaining sheets
  - redox cycle Co^{3+} to Co^{4+} : 4V