CH5715
Energy Conversion and Storage

Electrolytes

For lecture notes: http://jtsigroup.wp.st-andrews.ac.uk/ch5715-energy-conversion-and-storage/

Textbook
Solid State Electrochemistry Cambridge - P. G. Bruce

Electrolytes

- Solution
- Polymer
- Ceramic – Solid electrolyte
- Physical aspects of solid electrolytes

Solution Electrolytes

salt + solvent → solution

-ve ΔG

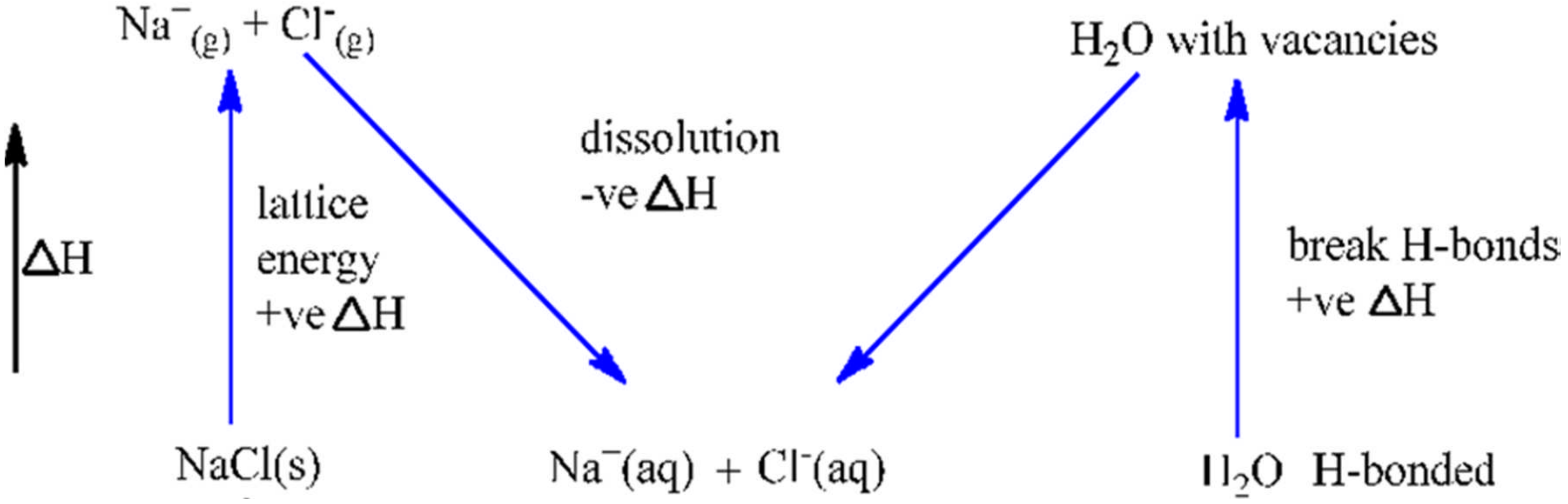
$\Delta G = \Delta H - T\Delta S$

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



Water as a solvent - is it unique?

1. Strong H-bonding - a network

2. Large dielectric constant $\varepsilon=80$

3. Both cations and anions are solvated

$Li^+(OH_2)_6$ $F^-(H_2O)_4$

LiF highly soluble, both Li^+ and F^- stabilised in water

In water, solubility depends on the enthalpy of cation and anion solvation being larger than the lattice energy

$$|\Delta H_{sol}| > |\Delta H_{latt}|$$

LiF soluble

MgO insoluble

Non-Hydrogen Bonded Solvents

Contrast with H_2O Aprotic

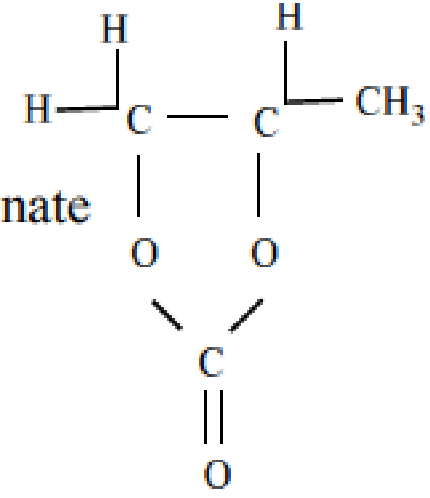
1. Only weakly associated - easy to create vacancies for ions.

2. Anions barely solvated - LiF insoluble
Br^-, I^- or better still ClO_4^-, BF_4^-, BPh_4^- are all soluble.

3. Dissolution depends on the strength of the cation - solvent bond vs. the lattice energy i.e. only the cations promote dissolution .

4. ε low 5-40 stabilisation of ions by dipole interactions less important.

Examples
acetonitrile CH_3CN propylene carbonate



Dissolution depends on local ion-solvent molecule interactions → solvation enthalpy.

Water - both cation and anion solvation competes with lattice energy.

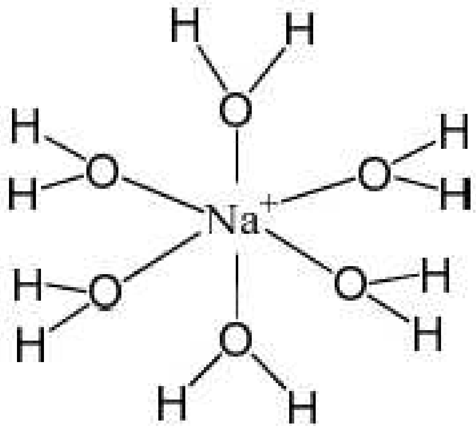
Non-aqueous → only cation competes with lattice

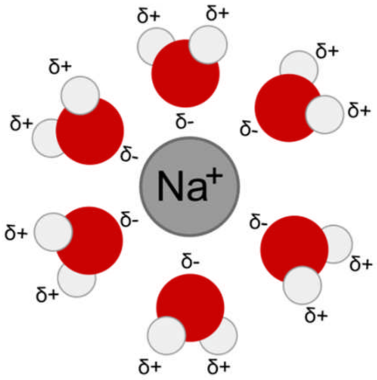
LiF	$LiClO_4$
Insoluble	soluble

Structure of Electrolyte Solutions

Cations strongly solvated

e.g.





Cations surrounded by a primary solvation sphere

Anions less strongly solvated; barely solvated in non-aqueous solvents.

First: ions interact with the solvent molecules immediately surrounding them
ion-solvent interactions

Second: ions interact with each other. Around any ion there will be an atmosphere of oppositely charged ions. Net negative charge around each cation will interact electrostatically with it
→ lower energy.

This is termed Debye-Hückel ion atmosphere ion-ion interactions

If ions highly charged and/or solvent has low dielectric constant, ε, then

ION PAIRING

$M^+ + X^- + (MX)^{\circ}$

e.g. $LiClO_4$ in THF

Electrolytes

Polymer electrolytes are particularly promising-safety

However, liquids now widely commercialised in solid state batteries.

Organic electrolyte encapsulated in polymer mesh

Solid Polymer Electrolytes

Many salts can be dissolved in organic solvents.

e.g. $LiClO_4$ in $CH_3O\text{-}[CH_2\text{-}CH_2\text{-}O]_2\text{-}CH_3$
(linear chain ether)

instead of $[CH_2\text{-}CH_2\text{-}O]_2$ we can have $[CH_2\text{-}CH_2\text{-}O]_n$ where n=100, 1000, etc
⇒ organic polymer - polyethylene oxide

When n is large → polymer is a solid at room temperature.

But salts may still be dissolved in the high m.wt. polymers by e.g. melting polymer

Films may be prepared 100nm thick of polymeric solids with dissolved salts

The cations and anions are mobile within the solid polymer film

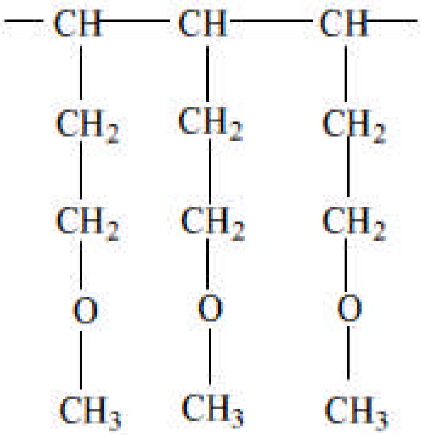
$LiClO_4$ in polyethylene oxide (1 million molecular weight) has a conductivity of

$10^{-3}\ \Omega^{-1}\mathrm{cm}^{-1}$ at ~100C°

equal to 1M $LiClO_4$ in diethylether at RT

Polymer electrolytes with this conductivity at room temperature are now known

e.g.



$$-\mathrm{CH}(\mathrm{CH_2CH_2OCH_3})-\mathrm{CH}(\mathrm{CH_2CH_2OCH_3})-\mathrm{CH}(\mathrm{CH_2CH_2OCH_3})-$$

Flexible back-bone with ethylene oxide side chains ⇒ high conductivity

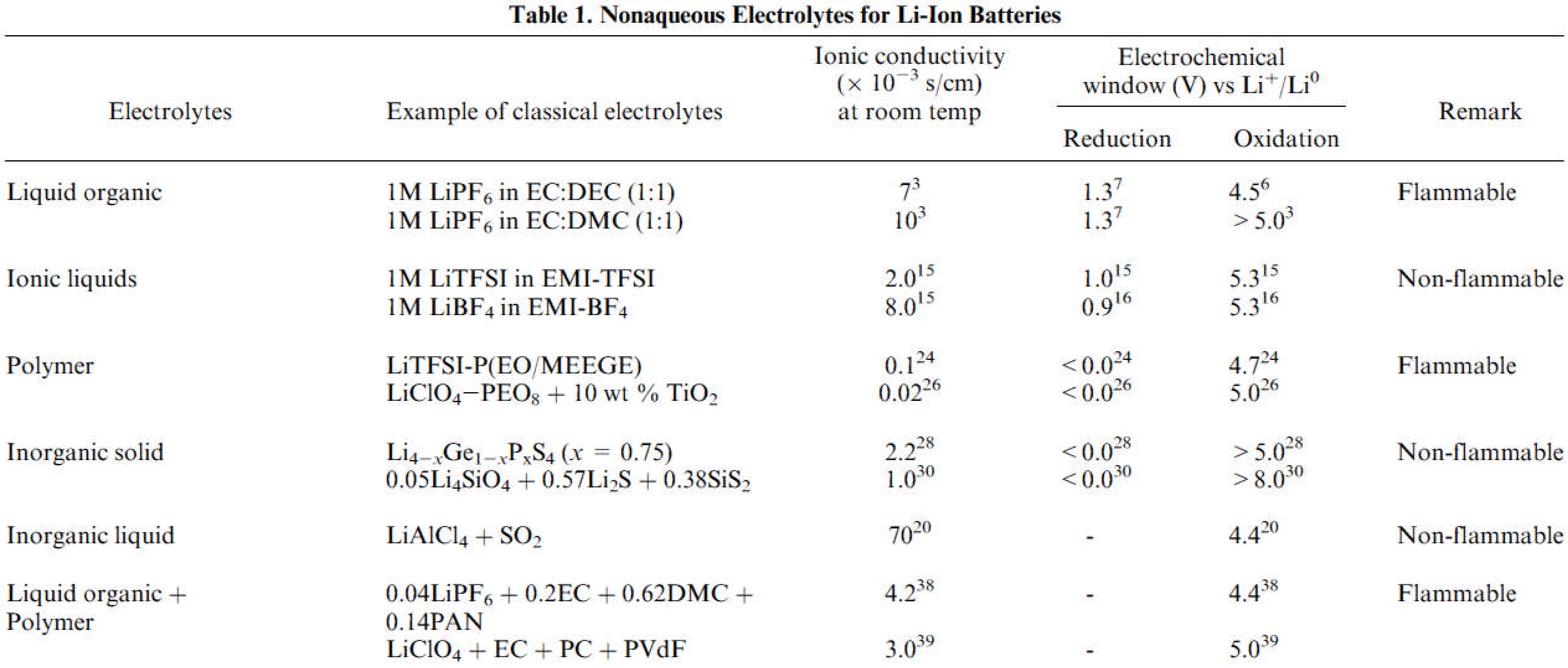


Table 1. Nonaqueous Electrolytes for Li-Ion Batteries

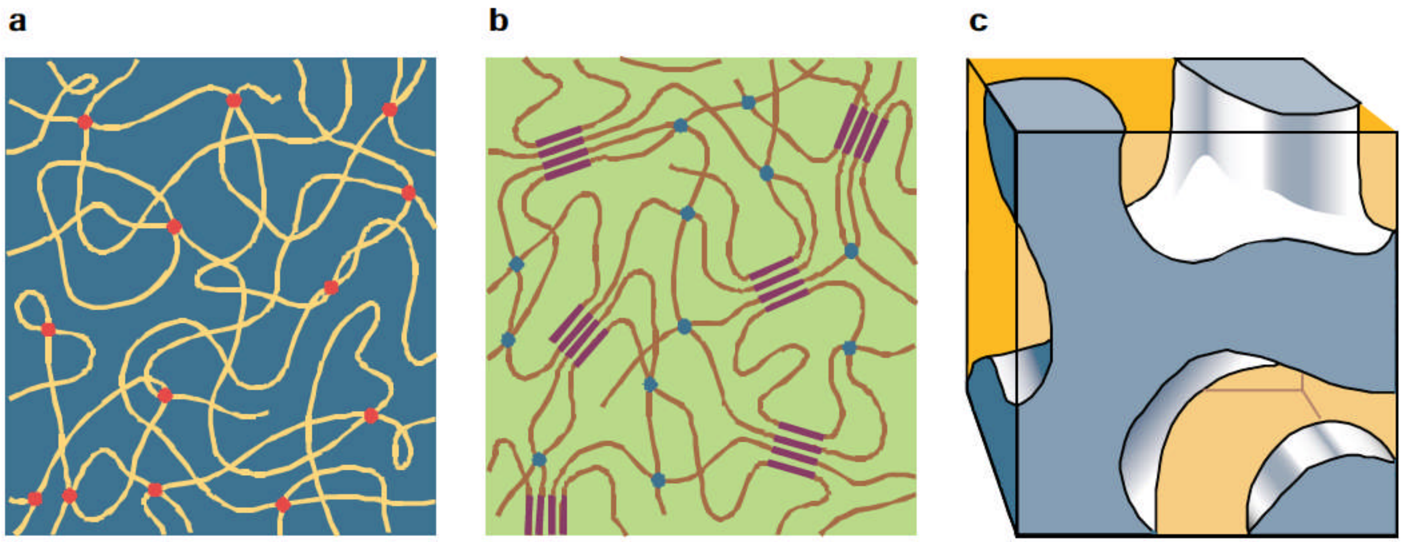
Electrolytes	Example of classical electrolytes	Ionic conductivity ($\times 10^{-3}$ s/cm) at room temp	Electrochemical window (V) vs Li^+/Li^0		Remark
			Reduction	Oxidation	
Liquid organic	1M $LiPF_6$ in EC:DEC (1:1) 1M $LiPF_6$ in EC:DMC (1:1)	7[3] 10[3]	1.3[7] 1.3[7]	4.5[6] $>$ 5.0[3]	Flammable
Ionic liquids	1M LiTFSI in EMI-TFSI 1M $LiBF_4$ in EMI-BF_4	2.0[15] 8.0[15]	1.0[15] 0.9[16]	5.3[15] 5.3[16]	Non-flammable
Polymer	LiTFSI-P(EO/MEEGE) $LiClO_4{-}PEO_8$ + 10 wt % TiO_2	0.1[24] 0.02[26]	$<$ 0.0[24] $<$ 0.0[26]	4.7[24] 5.0[26]	Flammable
Inorganic solid	$Li_{4-x}Ge_{1-x}P_xS_4$ ($x = 0.75$) $0.05Li_4SiO_4 + 0.57Li_2S + 0.38SiS_2$	2.2[28] 1.0[30]	$<$ 0.0[28] $<$ 0.0[30]	$>$ 5.0[28] $>$ 8.0[30]	Non-flammable
Inorganic liquid	$LiAlCl_4 + SO_2$	70[20]	-	4.4[20]	Non-flammable
Liquid organic + Polymer	$0.04LiPF_6 + 0.2EC + 0.62DMC + 0.14PAN$ $LiClO_4$ + EC + PC + PVdF	4.2[38] 3.0[39]	- -	4.4[38] 5.0[39]	Flammable

J.B. Goodenough and Y.S. Kim
Chem. Mater., 22, (2010) 587- 603

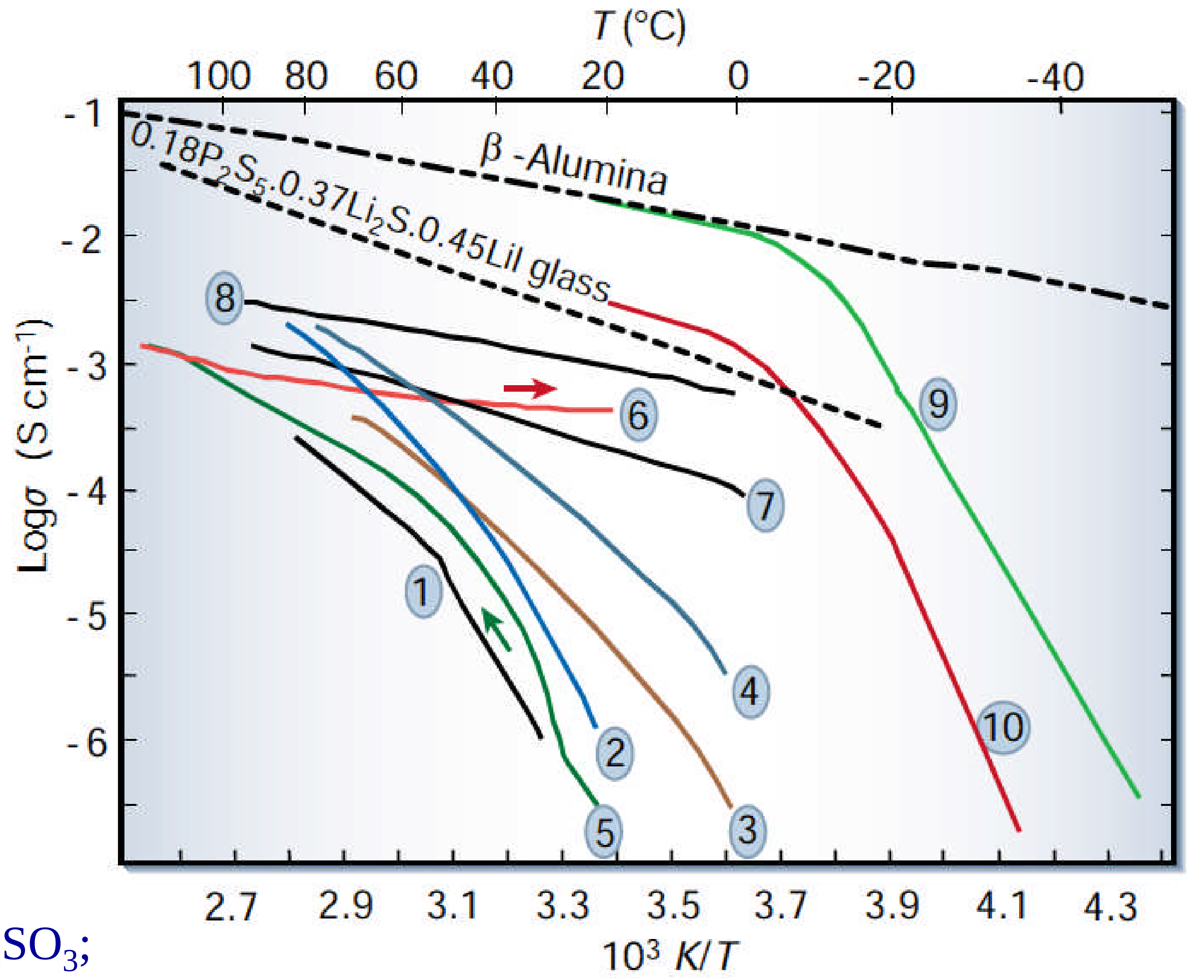
Electrolyte characteristics for Batteries

1) Large electrolyte potential window Eg so does not decompose across potential range:
2) Retention of the electrode/electrolyte interface during cycling when the electrode particles are changing their volume.
3) A Li -ion conductivity $\sigma_{Li} > 10^{-4}$ S/cm over the temperature range of battery operation.
4) An electronic conductivity $\sigma_e < 10^{-10}$ S/cm.
5) A transference number $\sigma_{Li}/\sigma_{total} \sim 1$
6) Chemical stability over ambient temperature ranges and temperatures in the battery under high power.
7) Chemical stability with respect to the electrodes, including the ability to form rapidly a passivating solid/electrolyte-interface (SEI) layer.
8) Safe materials, i.e., preferably nonflammable and nonexplosive if short-circuited.
9) Low toxicity and low cost.

Polymer Electrolytes



Schematic representations of polymer electrolyte networks.
a, Pure (dry) polymer consisting of entangled chains, through which the Li ions (red points) move assisted by the motion of polymer chains.
b, A hybrid (gel) network consisting of a semicrystalline polymer, whose amorphous regions are swollen in a liquid electrolyte, while the crystalline regions enhance the mechanical stability.
c, A poly-olefin membrane (Celgard for instance) in which the liquid electrolyte is held by capillaries.



1 PEO-$LiCF_3SO_3$;

2 new solutes with high-dissociation PEO-Li $[(CF_3SO_2)_2N]$ bis(trifluoromethanesulfone)imide (TFSI)

3 low-Tg combination polymer;

4 plasticized polymer electrolyte PEO-Li$[(CF_3SO_2)_2N]$ +25% w/w PEG-dimethylether (mol wt, 250)

5,6 liquid crystalline polymer electrolytes

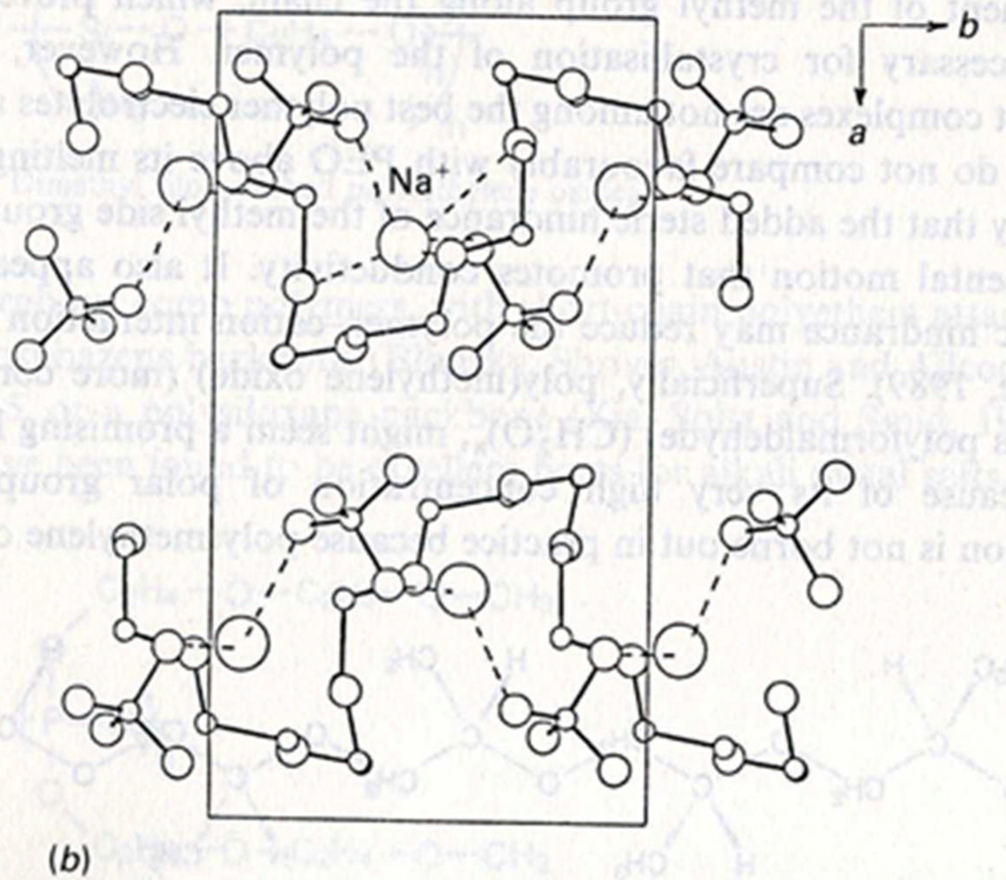
7 gel-type polymer (X-linked PEO-dimethacrylate- Li $[(CF_3SO_2)_2N]$-PC 70%);

8 liquid electrolyte PC/DME $LiCF_3SO_3$; trifluoromethanesulfonate

9 liquid electrolyte EC/DMC-$LiPF_6$ at low temperature ;

10 gel electrolyte P(VDF-HFP)/EC/DMC-$LiPF_6$.

Local Coordination



(*b*) Crystal structure of the (PEO)$_3$:NaClO$_4$ complex.

Crab-like motion assisted by chains

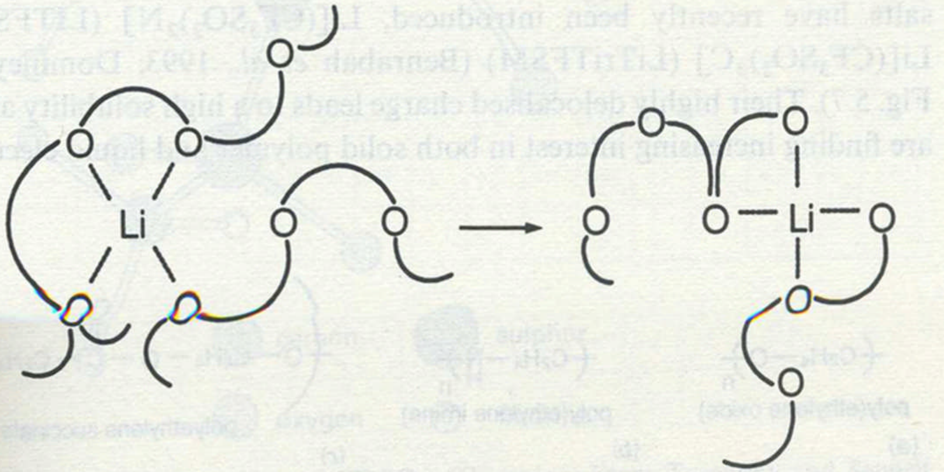


Fig. 5.5 Cartoon of ion motion in a polymer.

Solid State Electrochemistry Bruce

Crystalline vs Amorphous Polymer Electrolytes

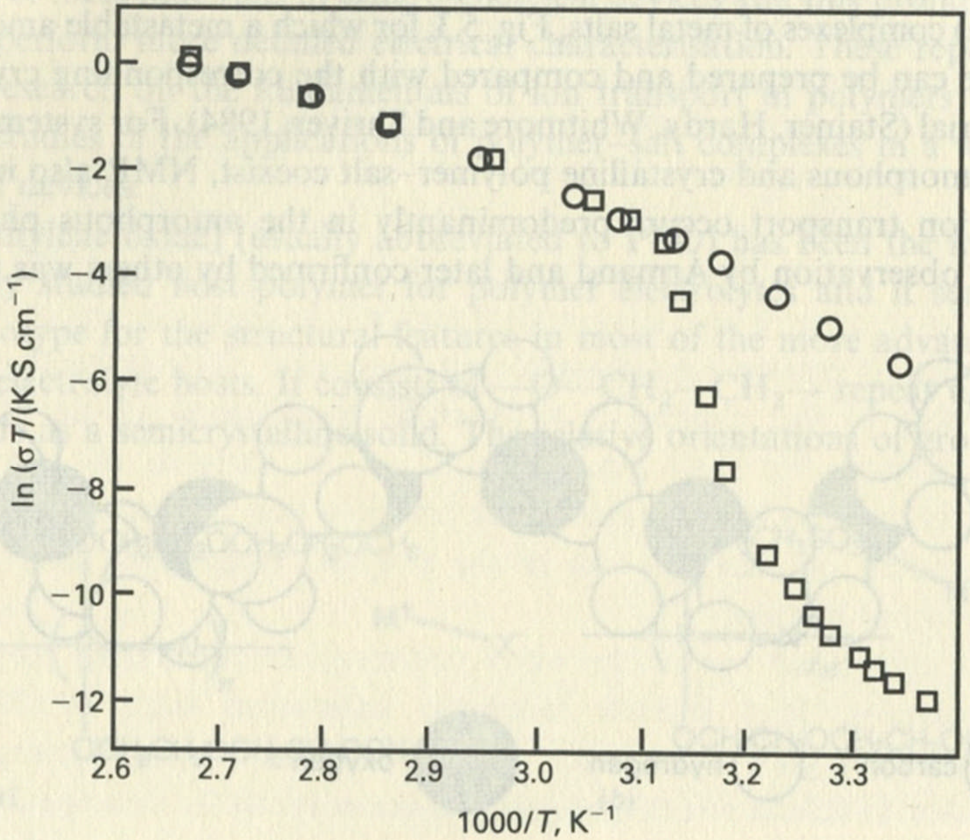


Fig. 5.3 Comparison of the temperature-dependent conductivities for amorphous PEO:NH_4SCN (circles) and crystalline PEO:NH_4SCN (squares).

Polymer Electrolytes do form Crystalline Phases with salts

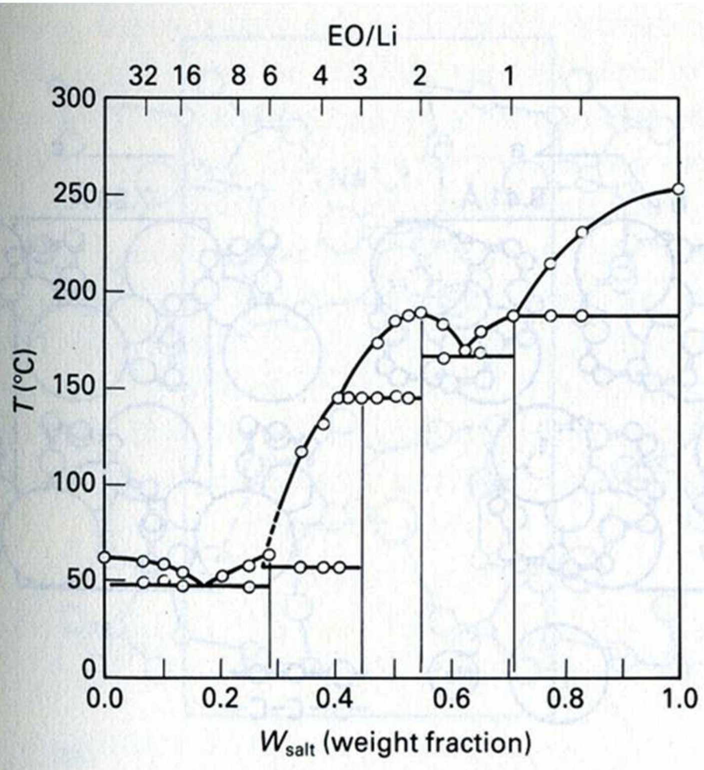


Fig. 5.10 Phase diagram of the PEO–$LiClO_4$ system. From Vallée *et al.* (1992).

Crystal Structure

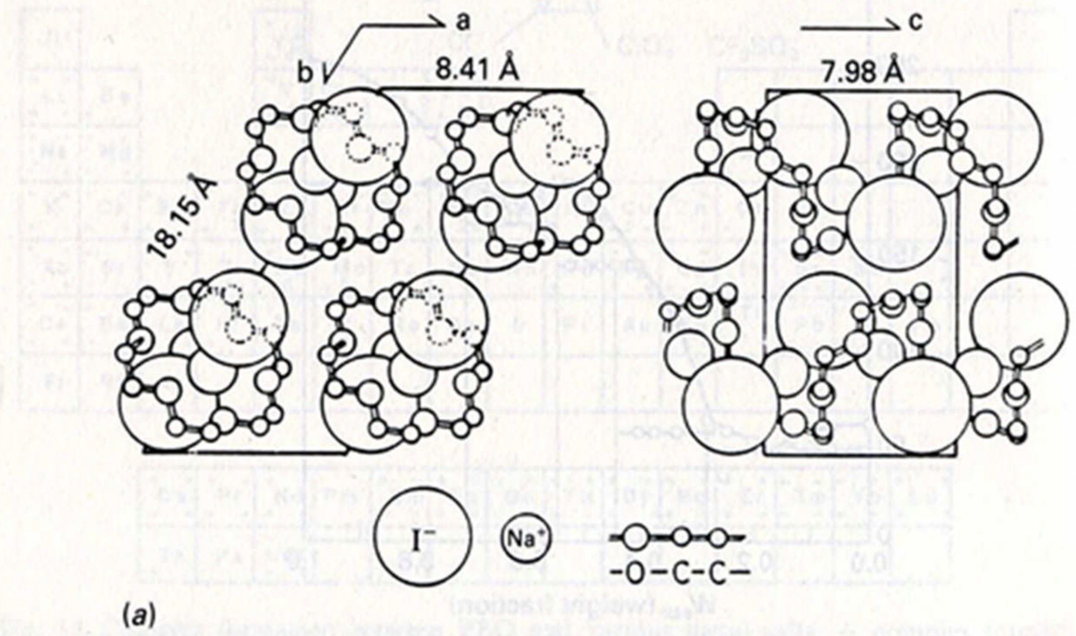
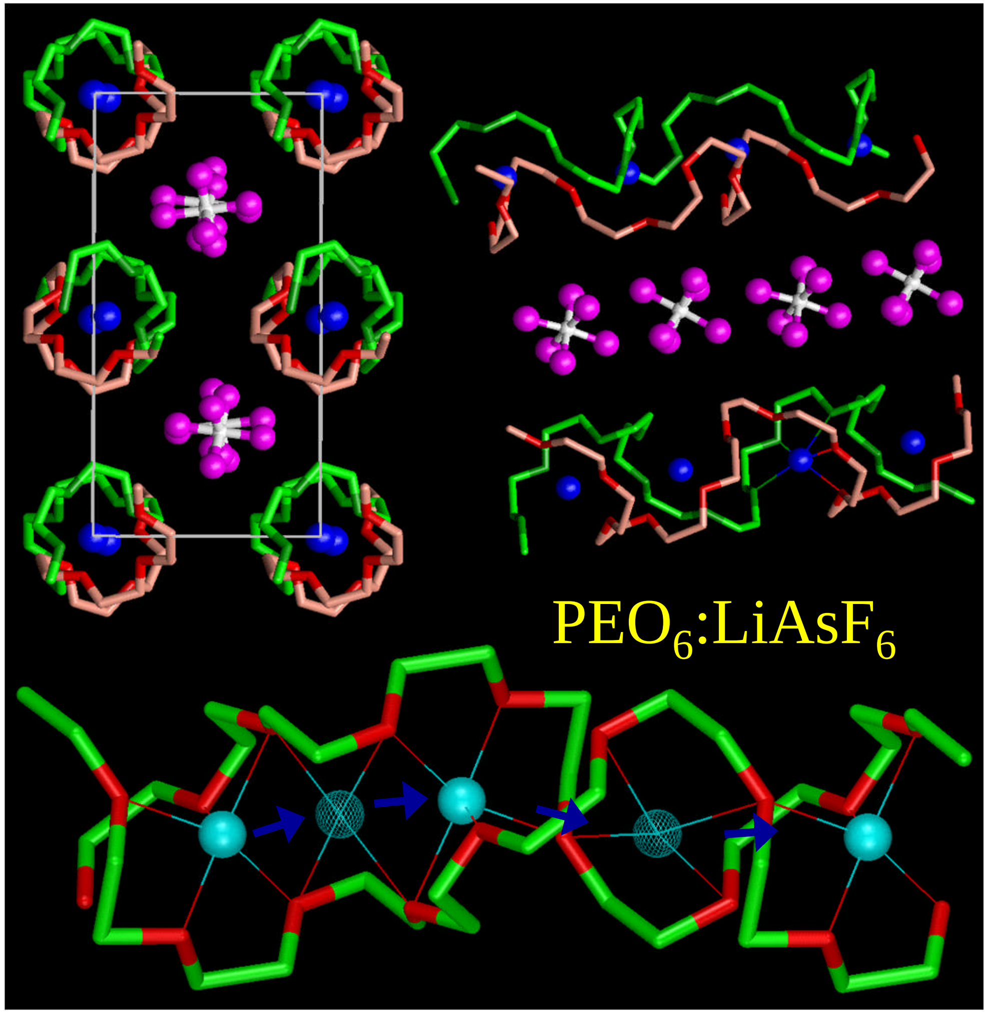


Fig. 5.11 (*a*) Crystal structure of the $(PEO)_3$:NaI complex.

Crystalline polymer electrolytes



P. G. Bruce *et al.* *Nature* **398**, 72 (1999)
P. G. Bruce *et al.* *Nature* **412**, 520 (2001);
P. G. Bruce *et al.* *Nature* **433**, 50 (2005).

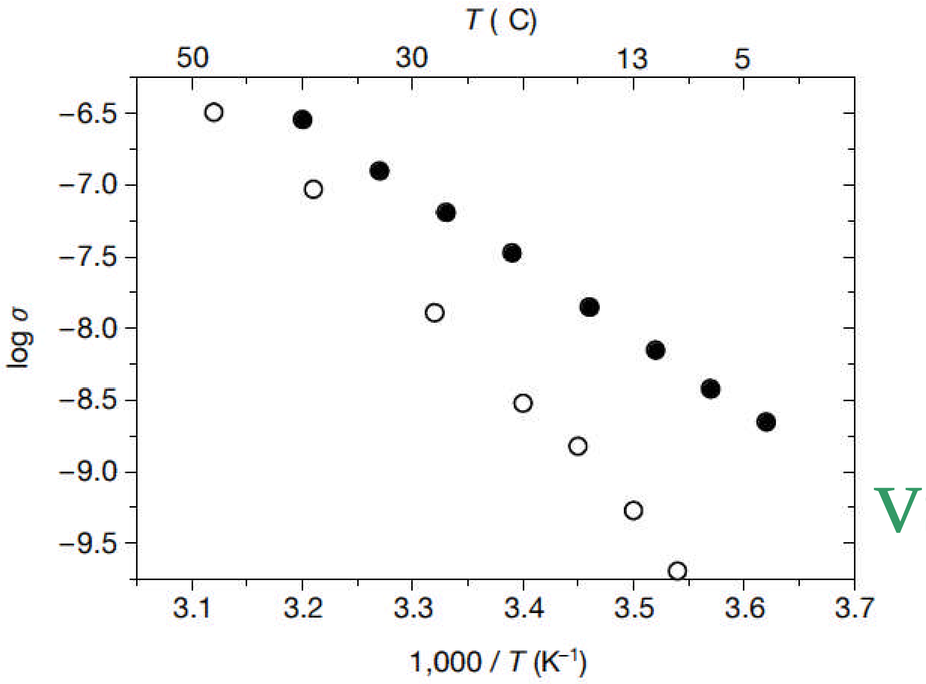


Figure 2 Ionic conductivity σ ($S\,cm^{-1}$) of amorphous (open circles) and crystalline (filled circles) PEO_6:$LiSbF_6$ as a function of temperature.

Note
MWt 1000 Xlline
vs 100,000 Amorphous

Zlatka Gadjourova, Yuri G. Andreev, David P. Tunstall* & Peter G. Bruce
http://www.nature.com/nature/journal/v412/n6846/full/412520a0.html

Putting together a lithium battery

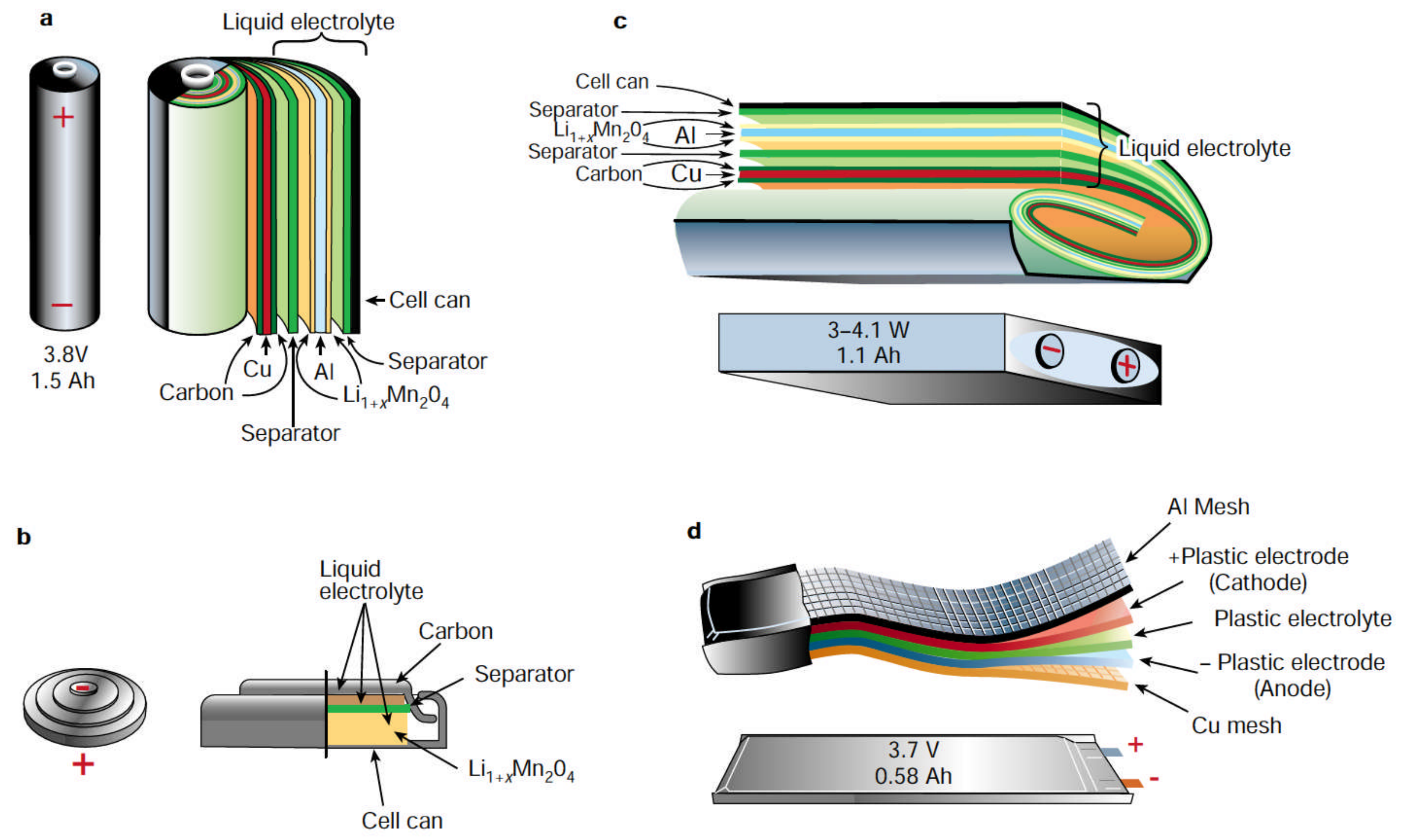


Figure 4 Schematic drawing showing the shape and components of various Li-ion battery configurations. **a**, Cylindrical; **b**, coin; **c**, prismatic; and **d**, thin and flat. Note the unique flexibility of the thin and flat plastic LiION configuration; in contrast to the other configurations, the PLiION technology does not contain free electrolyte.

CH5715
Energy Conversion and Storage

Ionic Conduction 2

John T.S. Irvine
Room 216
jtsi@st-and.ac.uk

Electrolytes

Polymer electrolytes are particularly promising-safety

However, liquids now widely commercialised in solid state batteries.

Organic electrolyte encapsulated in polymer mesh

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

Ion-Conducting Membranes

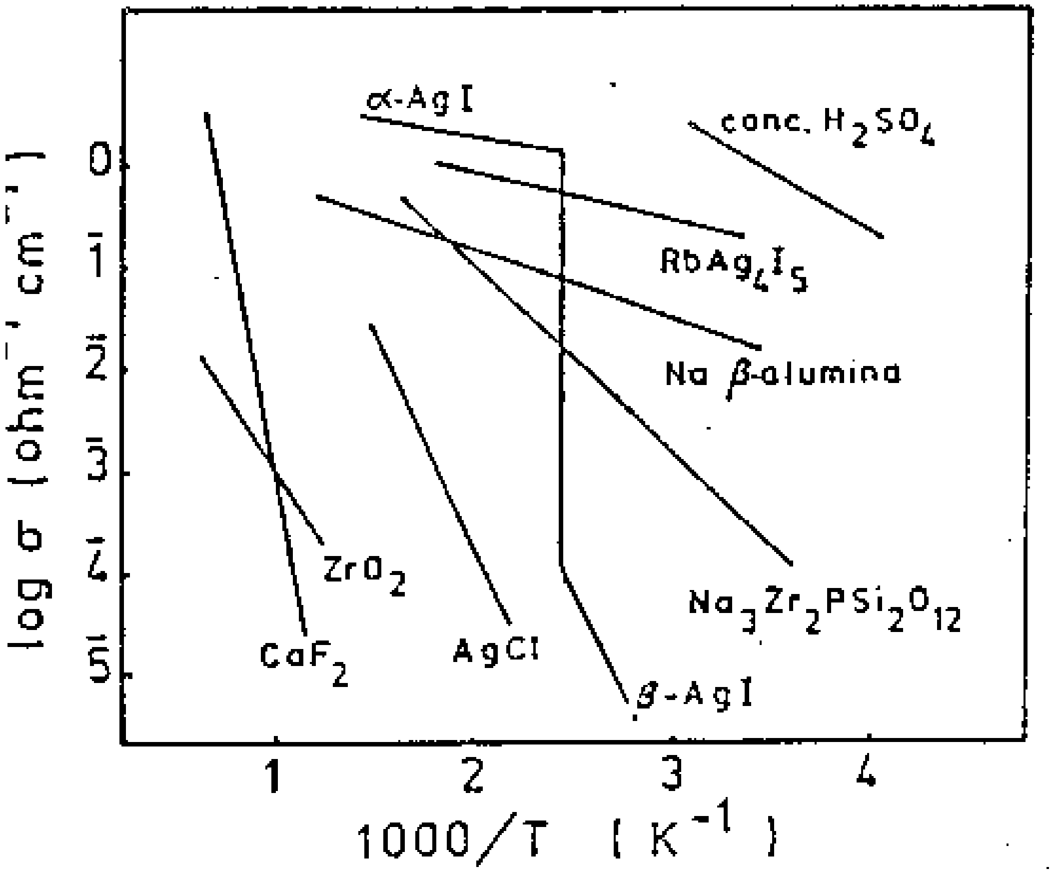
Ionic Conductivity (Scm^{-1})

Ionic crystals < 10^{-13} - 10^{-4}
Solid Electrolytes 10^{-4} - 10 - ceramic membranes
Ion-conducting polymers 10^{-4} - 10^{-2}
Strong liquid electrolytes 10^{-3} - 10^{1}

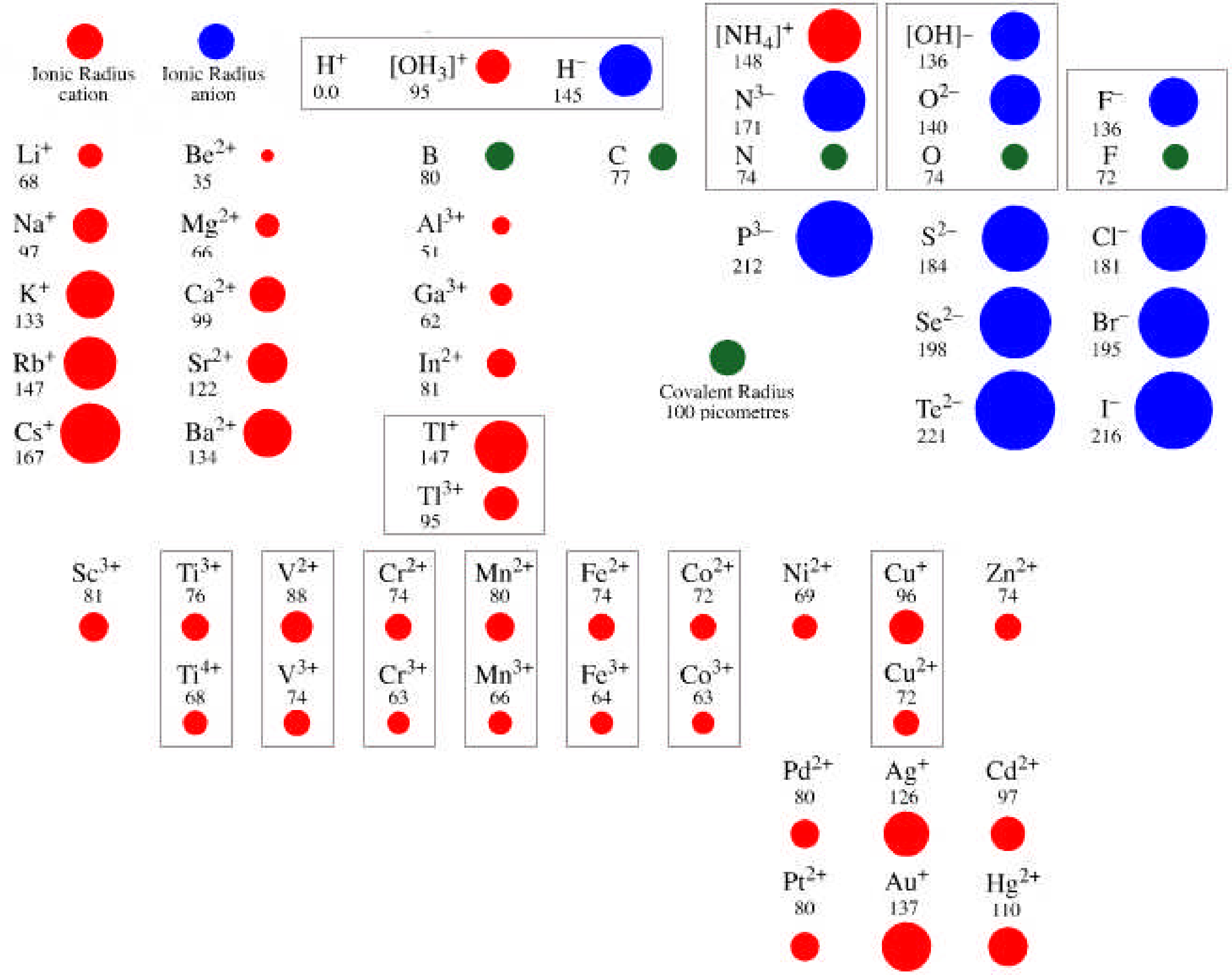
$$\sigma = ne\mu$$

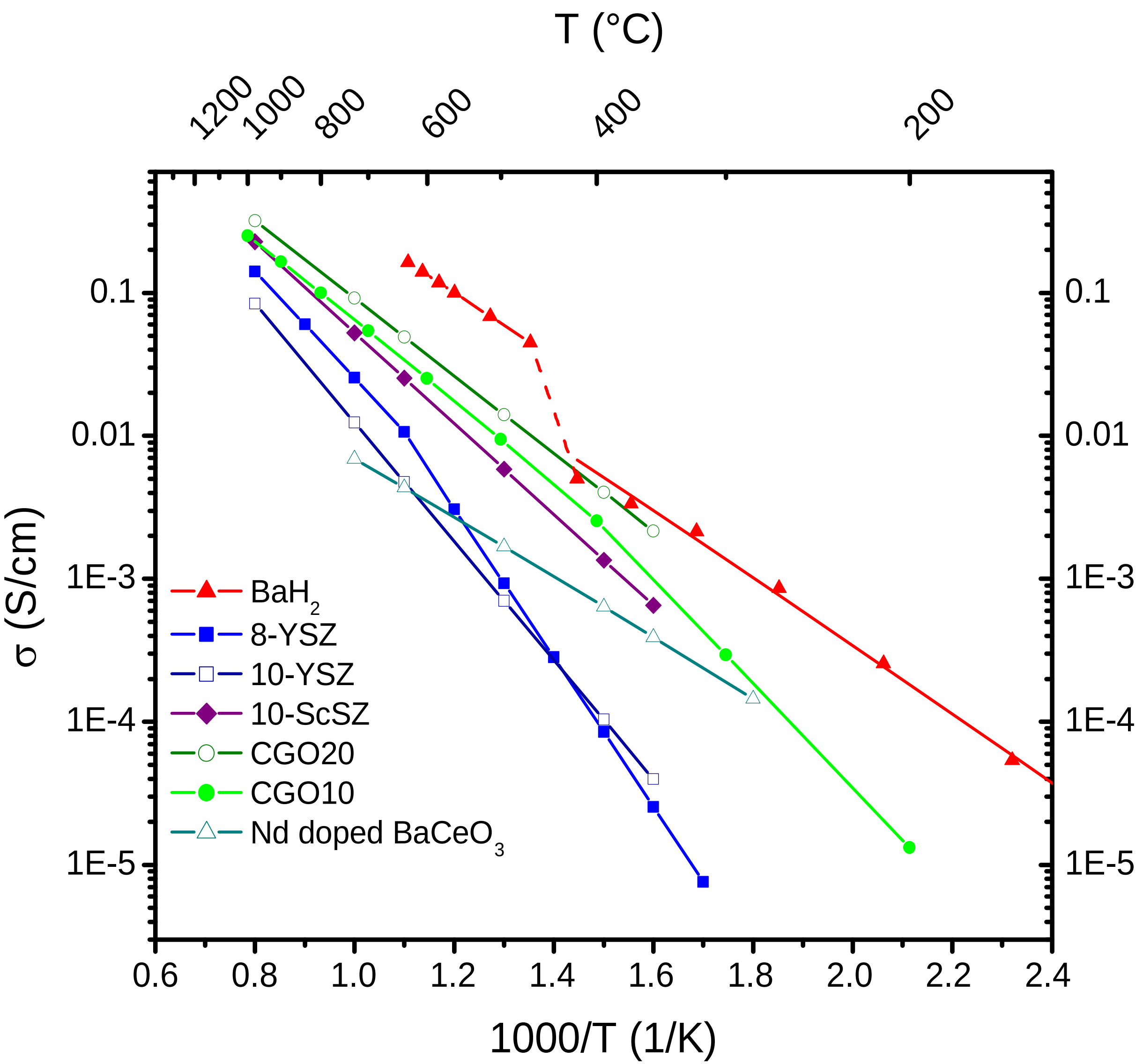
$\mu = f(T)$ Nernst Einstein relation $\mu = qD/kT$.

SOLID ELECTROLYTES



Ionic Radii


Ionic Radius cation
Ionic Radius anion
H^+ 0.0
$[OH_3]^+$ 95
H^- 145
$[NH_4]^+$ 148
N^{3-} 171
N 74
$[OH]^-$ 136
O^{2-} 140
O 74
F^- 136
F 72
Li^+ 68
Be^{2+} 35
B 80
C 77
Na^+ 97
Mg^{2+} 66
Al^{3+} 51
P^{3-} 212
S^{2-} 184
Cl^- 181
K^+ 133
Ca^{2+} 99
Ga^{3+} 62
Se^{2-} 198
Br^- 195
Rb^+ 147
Sr^{2+} 122
In^{2+} 81
Covalent Radius 100 picometres
Cs^+ 167
Ba^{2+} 134
Tl^+ 147
Tl^{3+} 95
Te^{2-} 221
I^- 216
Sc^{3+} 81
Ti^{3+} 76
Ti^{4+} 68
V^{2+} 88
V^{3+} 74
Cr^{2+} 74
Cr^{3+} 63
Mn^{2+} 80
Mn^{3+} 66
Fe^{2+} 74
Fe^{3+} 64
Co^{2+} 72
Co^{3+} 63
Ni^{2+} 69
Cu^+ 96
Cu^{2+} 72
Zn^{2+} 74
Pd^{2+} 80
Ag^+ 126
Cd^{2+} 97
Pt^{2+} 80
Au^+ 137
Hg^{2+} 110



- Verbraeken Nature Materials 2015

CRYSTALLINE IONIC CONDUCTORS

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

How do ions move in solid electrolytes?

General requirements

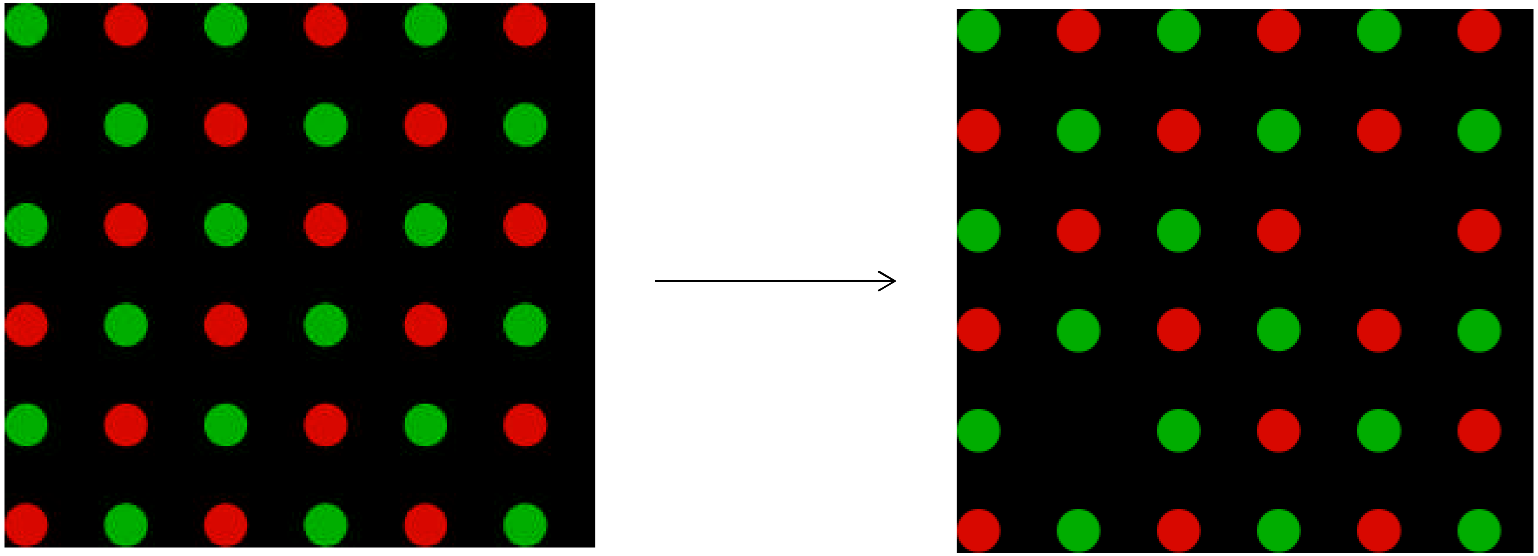
1. Mobile ions must partially occupy a set of energetically equivalent or near equivalent sites.

2. The sites must be interconnected by continuous pathways.

1. **Partial occupancy**

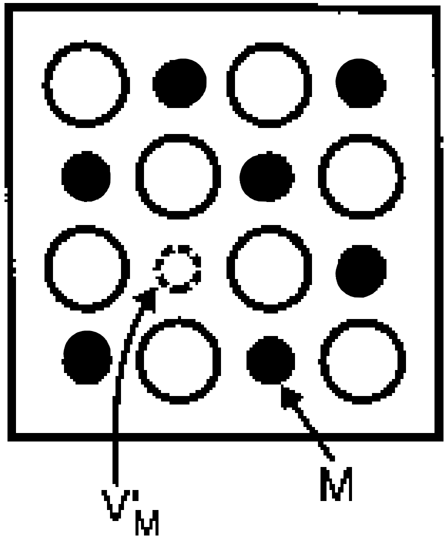
A perfect crystal of NaCl would not support ionic conductivity. Schottky defects → a few Na^+ and Cl^- vacancies → ions can move.

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

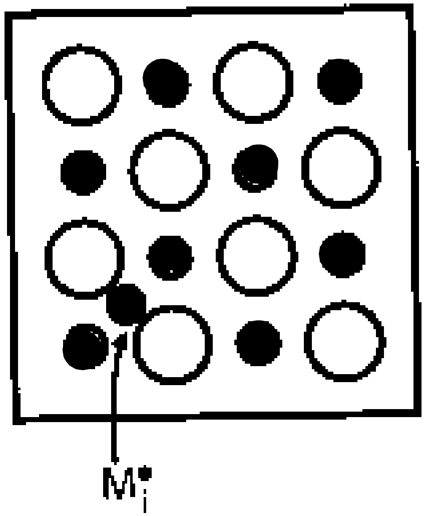


Schottky Vacancies

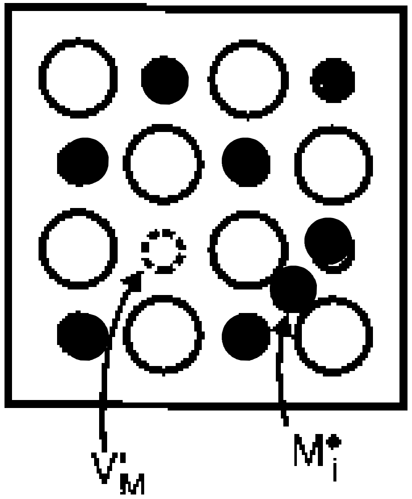
Point defects and cation migration



(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

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

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

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

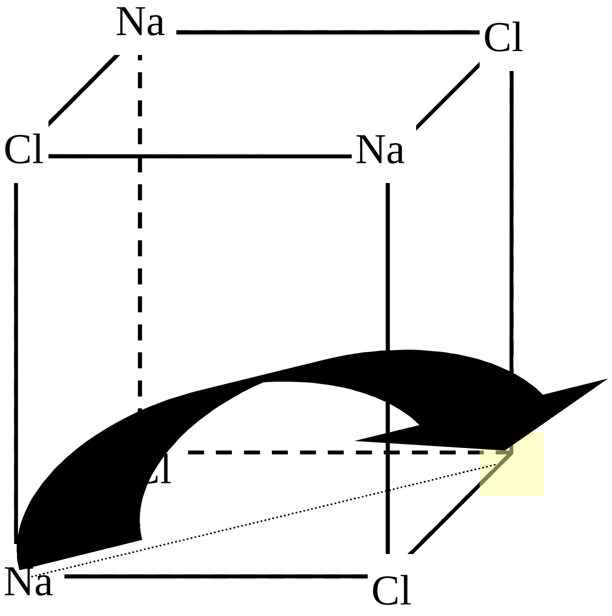
$$\therefore N_V = N\sqrt{C\exp(-E_f/kT)}$$

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

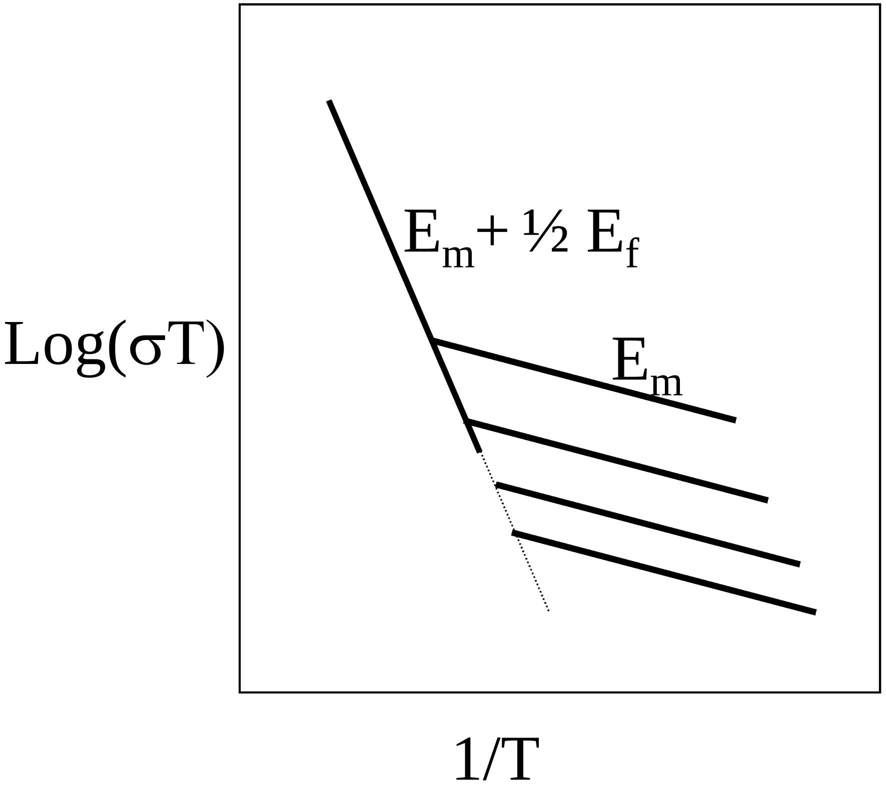
Extrinsic conductivity

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

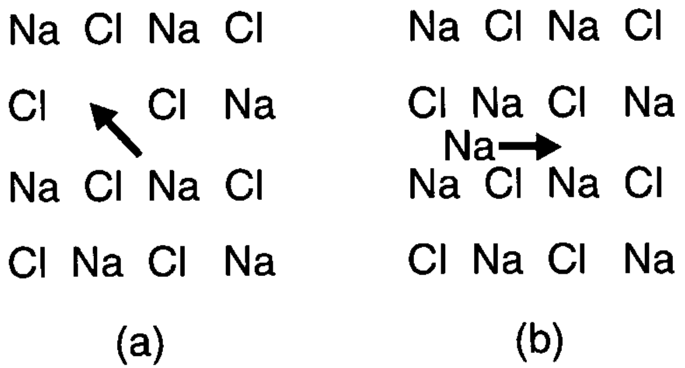


Jump mechanism in 3d space



Influence of dopants on conductivity behaviour in NaCl

Vacancy and Interstitial Conduction Mechanisms



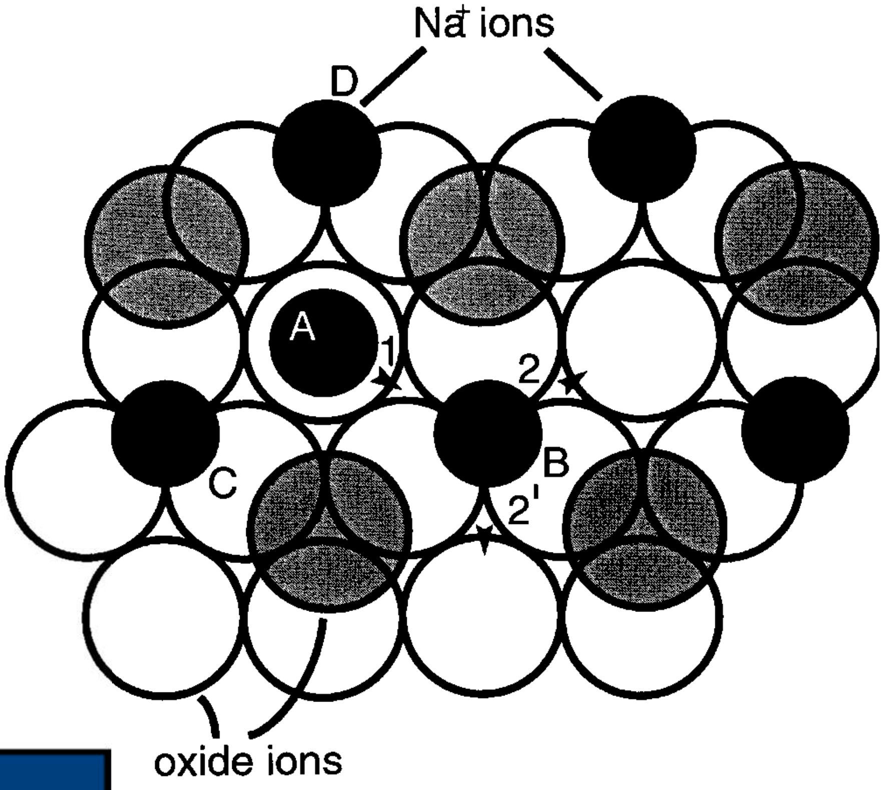
Na Cl Na Cl
Cl Cl Na
Na Cl Na Cl
Cl Na Cl Na

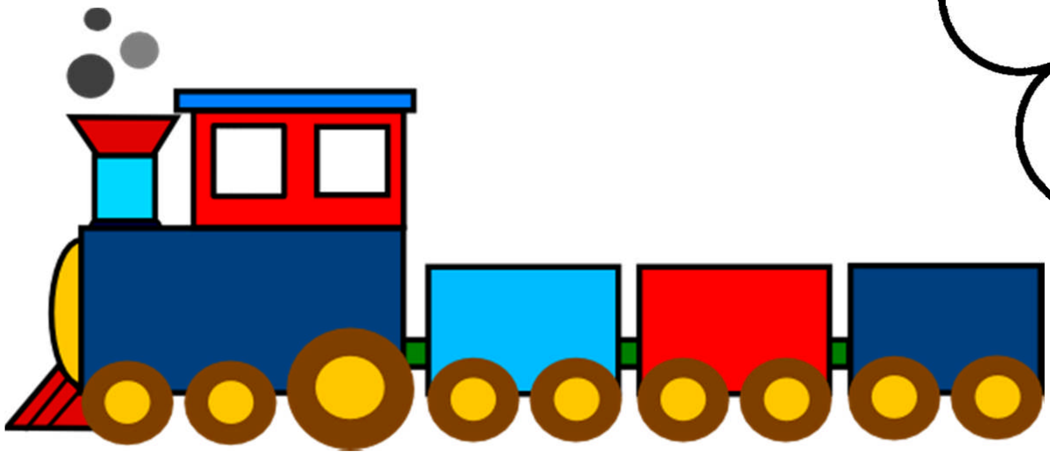
(a)

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

(b)

Interstitialcy mechanism





Ionic Migration/Ionic Conductivity

Ionic Conductivity (Scm^{-1})

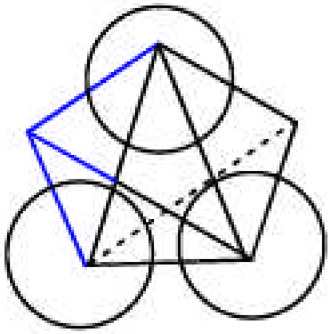
Ionic crystals < 10^{-13} - 10^{-4}
Solid Electrolytes 10^{-4} - 10
Strong liquid electrolytes 10^{-3} - 10^{1}

$$\sigma = ne\mu$$

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

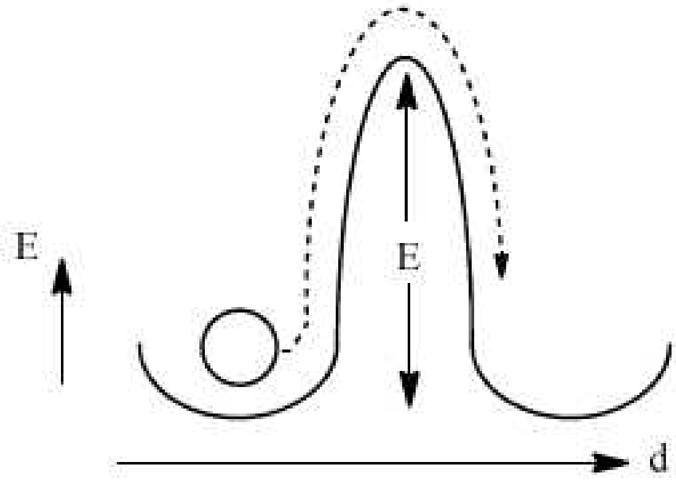
2. Pathways

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

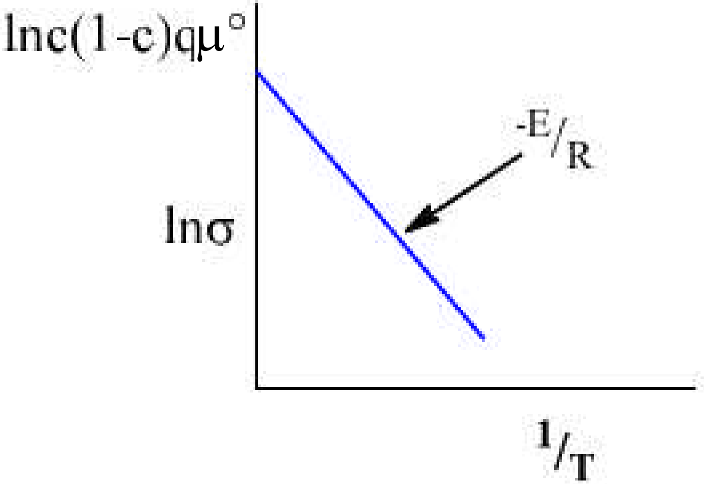
μ s function of (ν, d)

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

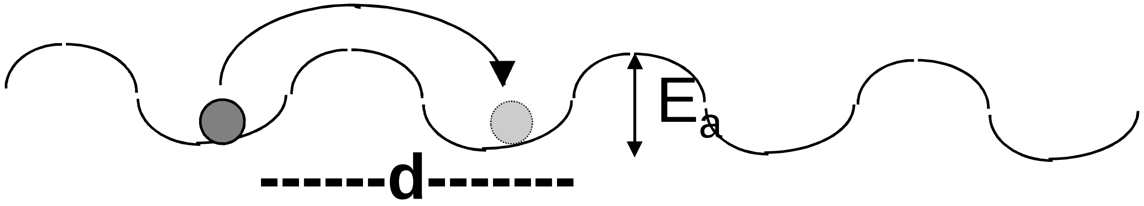
$\mu = \mu^\circ \exp\left(^{-E}/_{RT}\right)$

$\sigma = c(1-c)q\mu^\circ \exp\left(^{-E}/_{RT}\right)$

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,

a_0^2,

jump frequency

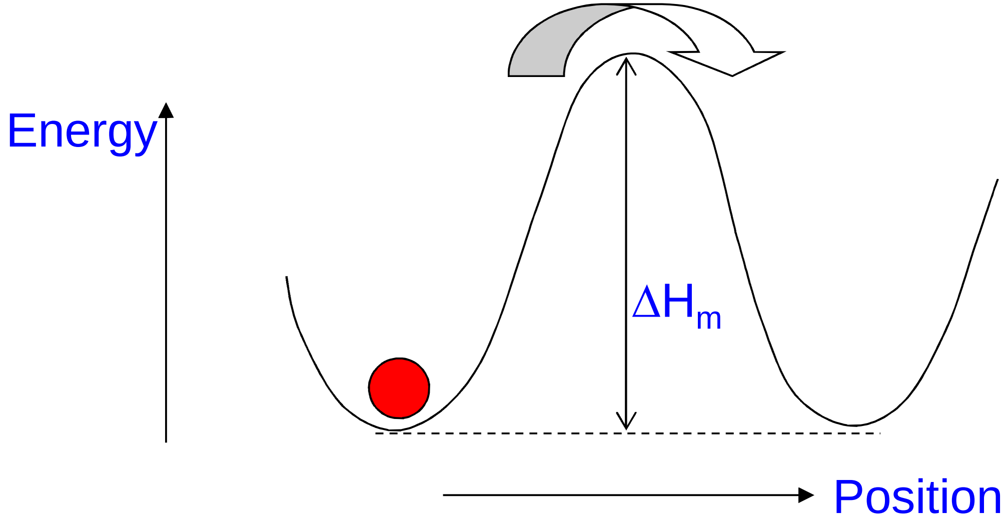
E_a = Activation Energy

Ionic Conductivity

$$\sigma = N\frac{q^2}{kT}\gamma\left[V_O^{\cdot\cdot}\right]_S(1-\left[V_O^{\cdot\cdot}\right]_S)a_0^2\nu_0\exp\left\{\frac{-\Delta H_m}{kT}\right\}$$

Equation for conductivity contains number of vacancies plus a term which indicates how easily they move through the crystal lattice.

ΔH_m is “migration enthalpy”

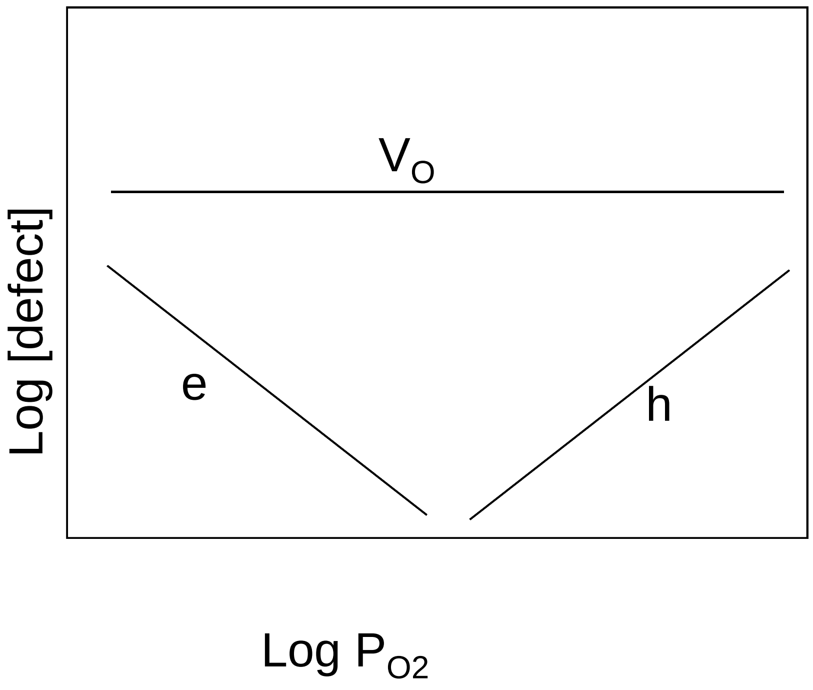


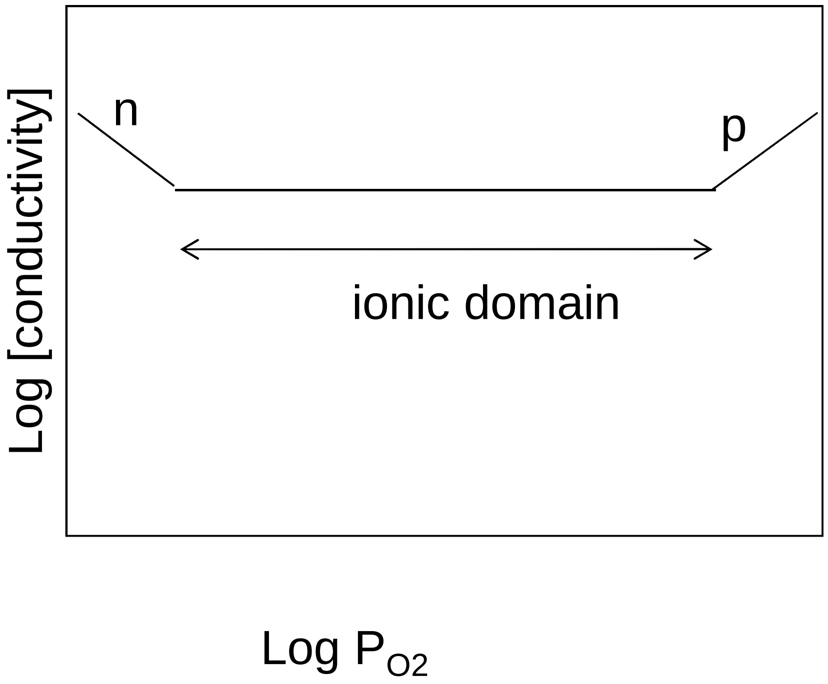
- Ions jump from site to site
- Requires a vacant site to jump into
- Jumps biased by electric field
- Jumps require thermal energy to get over energy barrier.
- Need low ΔH_m for high ionic conductivity

Electrolytic domain

Electrons and holes have higher mobilities than ions

Variable valence metal ions (e.g. transition metals) are bad for solid oxide electrolytes





$LaGaO_3$ Oxide ion electrolyte

$La_{0.8}Sr_{0.2}Ga_{0.9}Mg_{0.1}O_?$

$V_O^{\bullet\bullet}$ oxide ion conduction

$2V_O^{\bullet\bullet} + 1/2O_2 \rightarrow O_O^X + 2h^+$

Below 300^{o}C in air electronic

Ionic transference number

$$t_{ion} = \frac{\sigma_{ion}}{\sigma_{ion} + \sigma_{el}}$$

For a SOFC electrolyte working over a range of P_{O2}

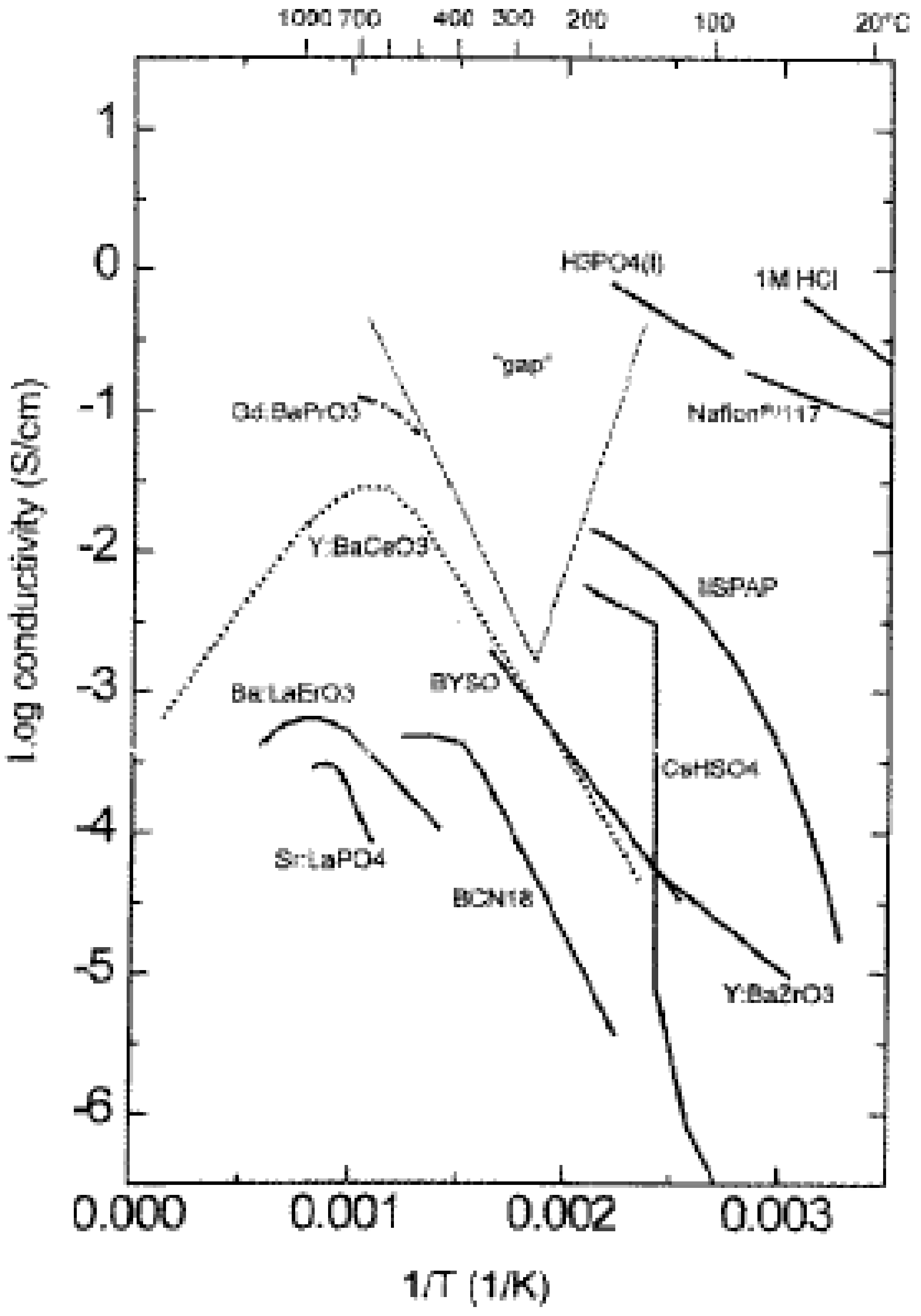
$$\langle t_{ion} \rangle = \frac{\int_{anode}^{cathode} t_{ion} \, d\left(\ln\left(P_{O2}\right)\right)}{\ln\left(P_{O2}^{cathode}\right) - \ln\left(P_{O2}^{anode}\right)}$$

Need $<t_{ion}>$ to be close to 1 e.g.>0.99

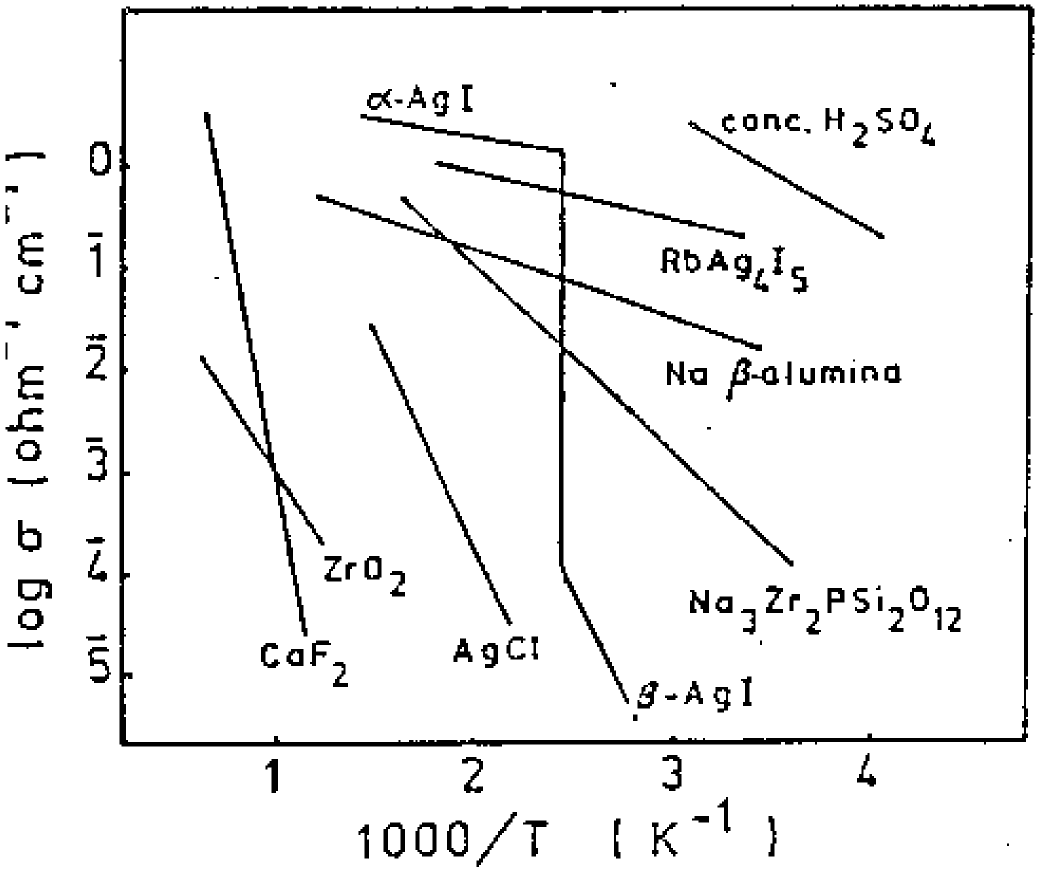
In proton conductors there is a temperature gap where proton conduction is too low

→ The Norby Gap

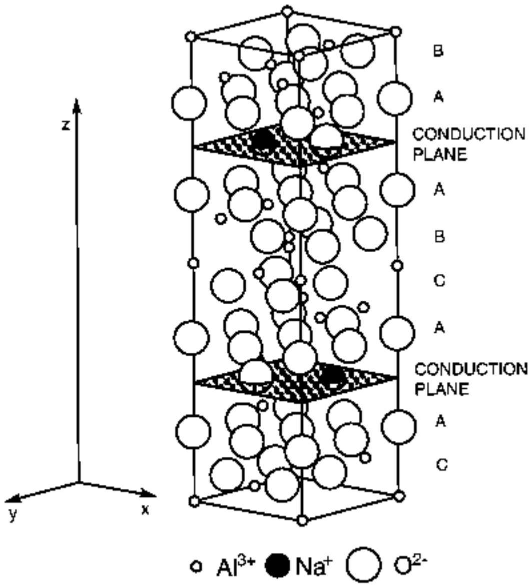
T. Norby, Solid State Ionics 125 (1999) 1



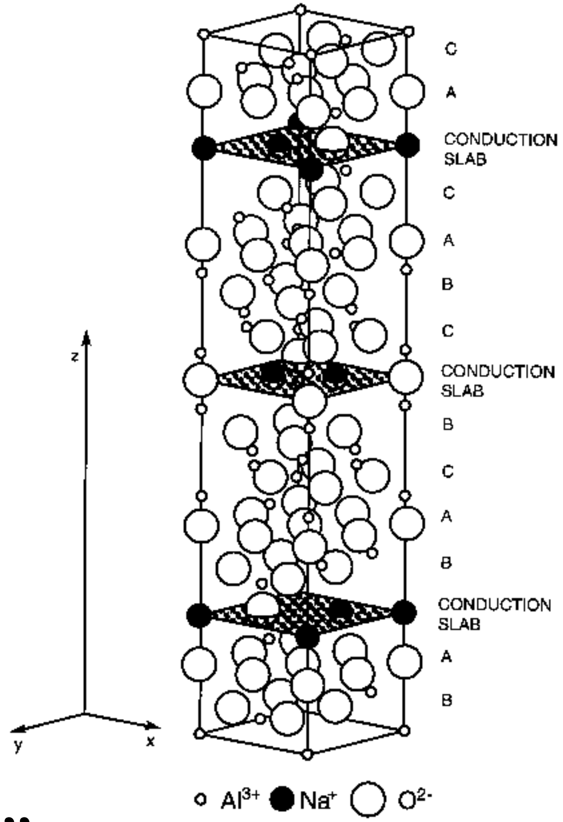
SOLID ELECTROLYTES



Structure of Beta-Alumina



β



β”

β-Alumina

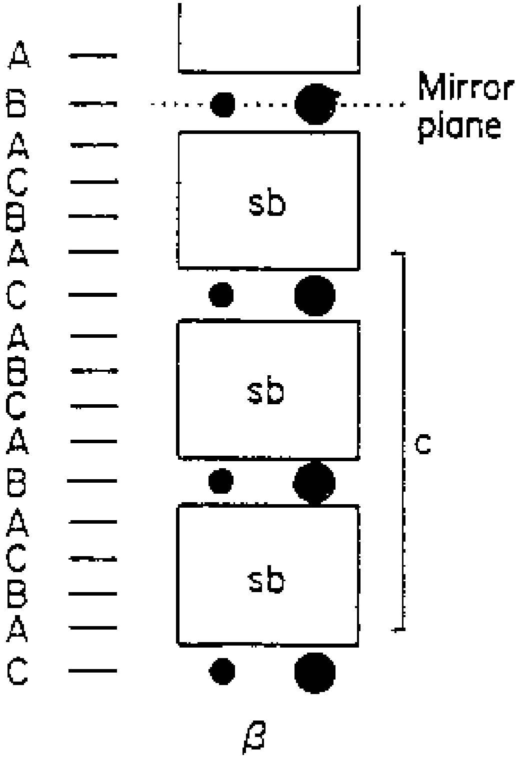
$M_2O.nX_2O_3$ - M - Alkali, Cu,
Ag, H_3O,
X - Al, Ga, Fe

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

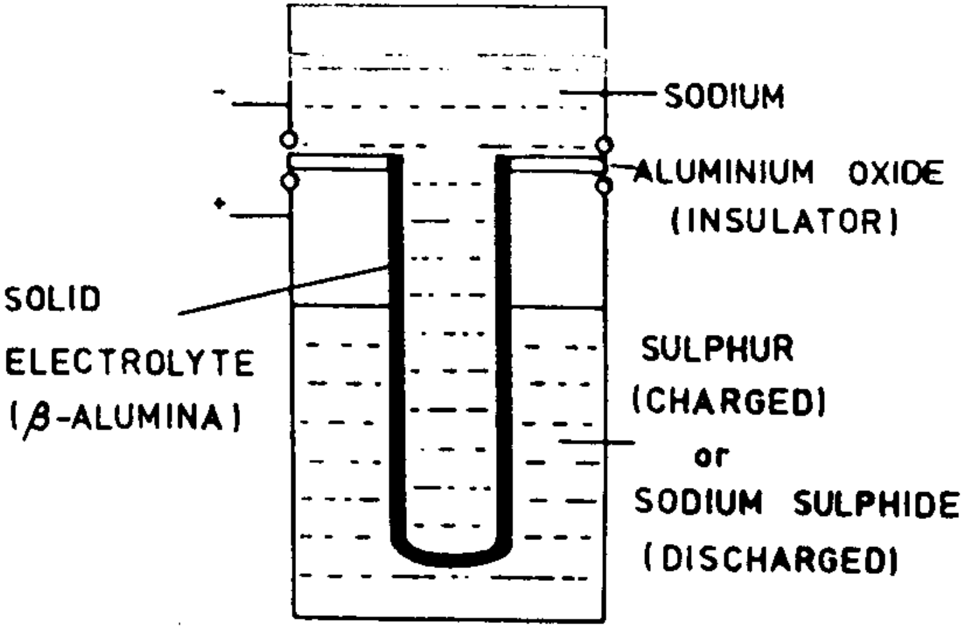
Structure consists of spinel blocks separated by less dense
layers - conduction planes.

2 dimensional Na conductor

E_a ~ 0.16 eV

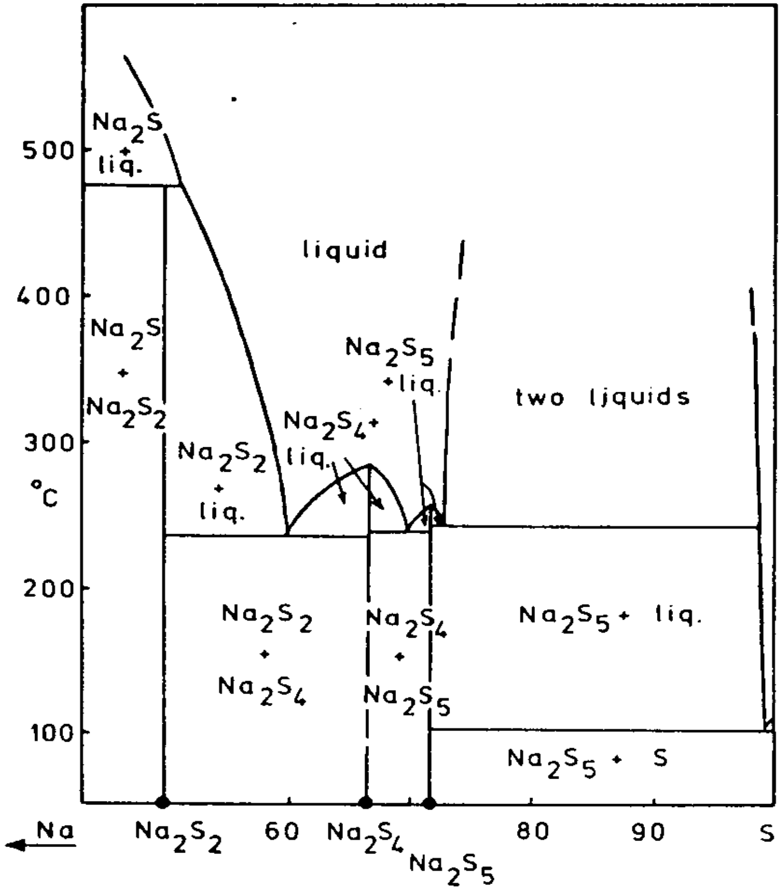


Beta battery
Na/S operates at 300-350^{o}C



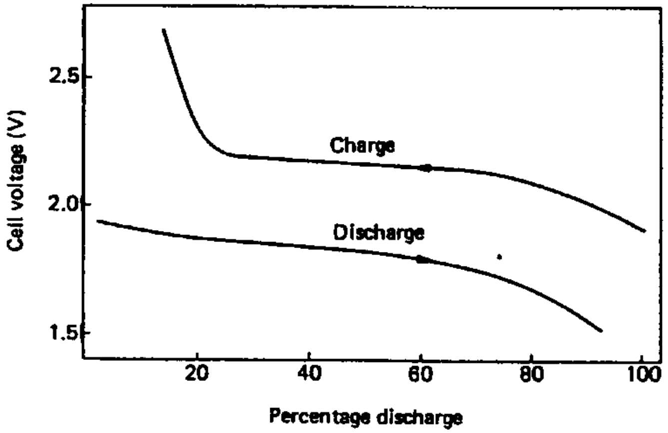
CELL REACTION: $2Na + 5S \rightleftharpoons Na_2S_5$ 2·08 V

The sodium–sulphur cell

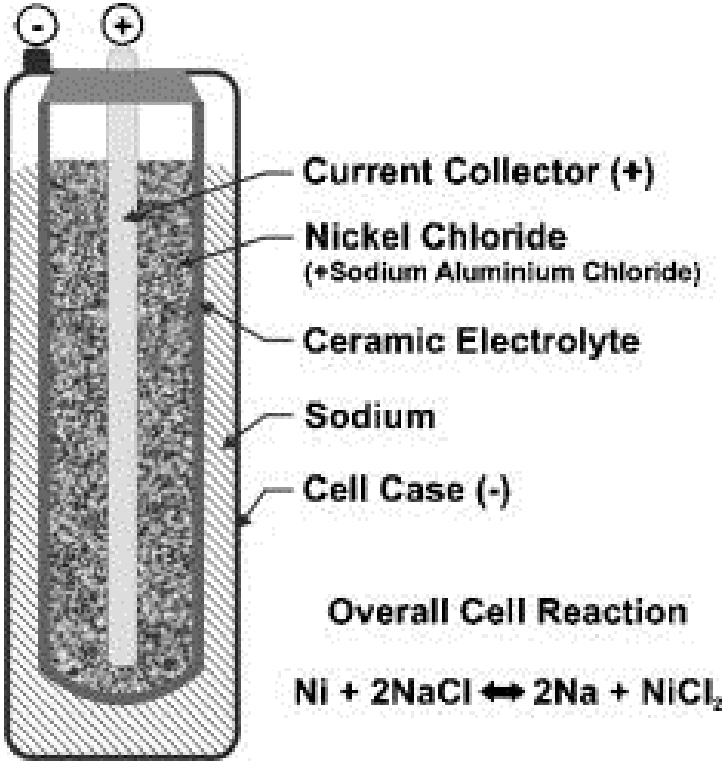


Phase diagram for the sodium–sulphur system

practical sodium–sulphur cells. (By courtesy of British Railways Board)

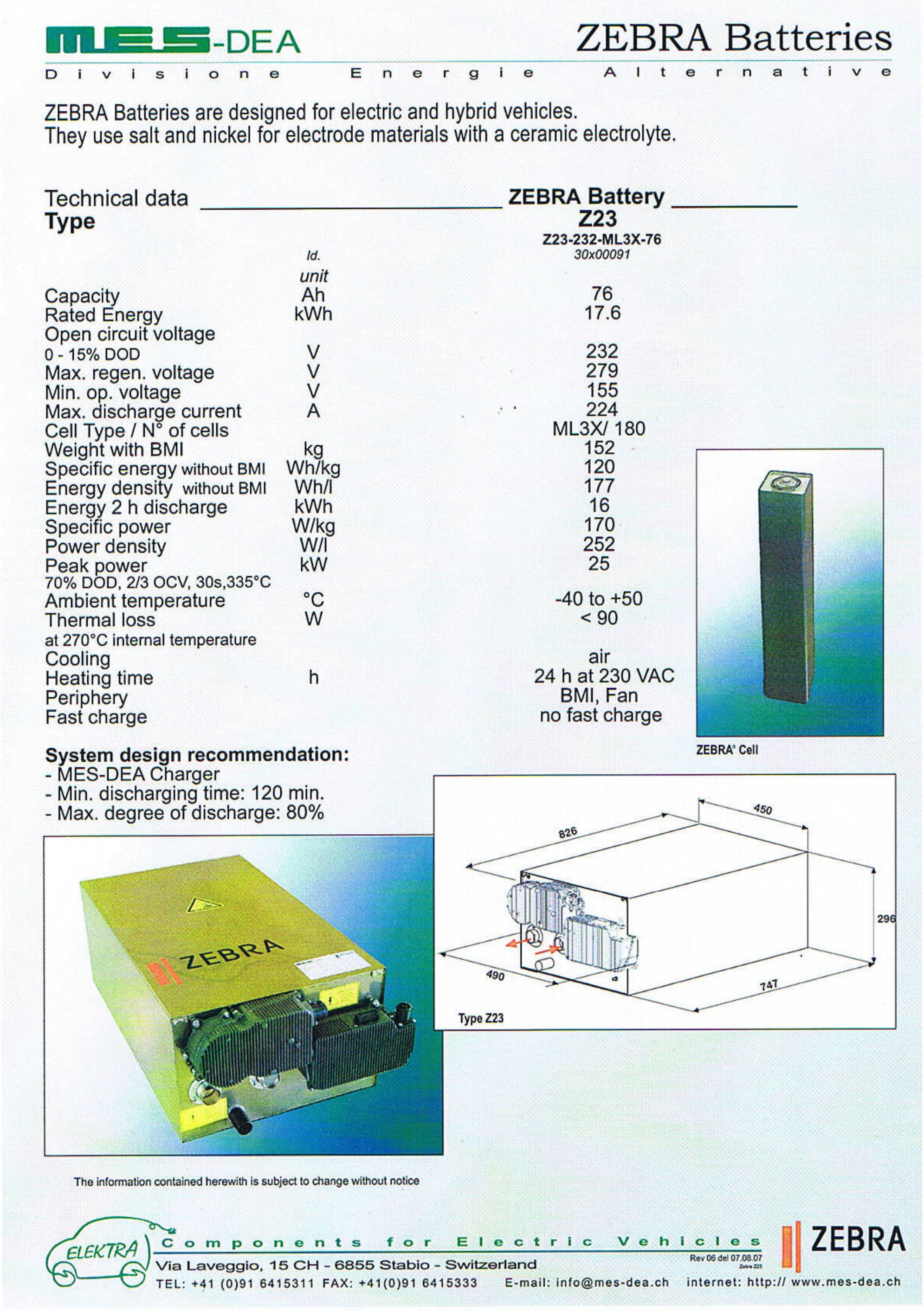


Zebra battery



Overall Cell Reaction

$$Ni + 2NaCl \leftrightarrow 2Na + NiCl_2$$



MES-DEA ZEBRA Batteries
Divisione Energie Alternative

ZEBRA Batteries are designed for electric and hybrid vehicles.
They use salt and nickel for electrode materials with a ceramic electrolyte.

Technical data **Type**	*Id.* *unit*	**ZEBRA Battery** **Z23** **Z23-232-ML3X-76** *30x00091*
Capacity	Ah	76
Rated Energy	kWh	17.6
Open circuit voltage		
0 - 15% DOD	V	232
Max. regen. voltage	V	279
Min. op. voltage	V	155
Max. discharge current	A	224
Cell Type / N° of cells		ML3X/ 180
Weight with BMI	kg	152
Specific energy without BMI	Wh/kg	120
Energy density without BMI	Wh/l	177
Energy 2 h discharge	kWh	16
Specific power	W/kg	170
Power density	W/l	252
Peak power 70% DOD, 2/3 OCV, 30s,335°C	kW	25
Ambient temperature	°C	-40 to +50
Thermal loss at 270°C internal temperature	W	< 90
Cooling		air
Heating time	h	24 h at 230 VAC
Periphery		BMI, Fan
Fast charge		no fast charge

ZEBRA® Cell

System design recommendation:
- MES-DEA Charger
- Min. discharging time: 120 min.
- Max. degree of discharge: 80%

Type Z23

The information contained herewith is subject to change without notice

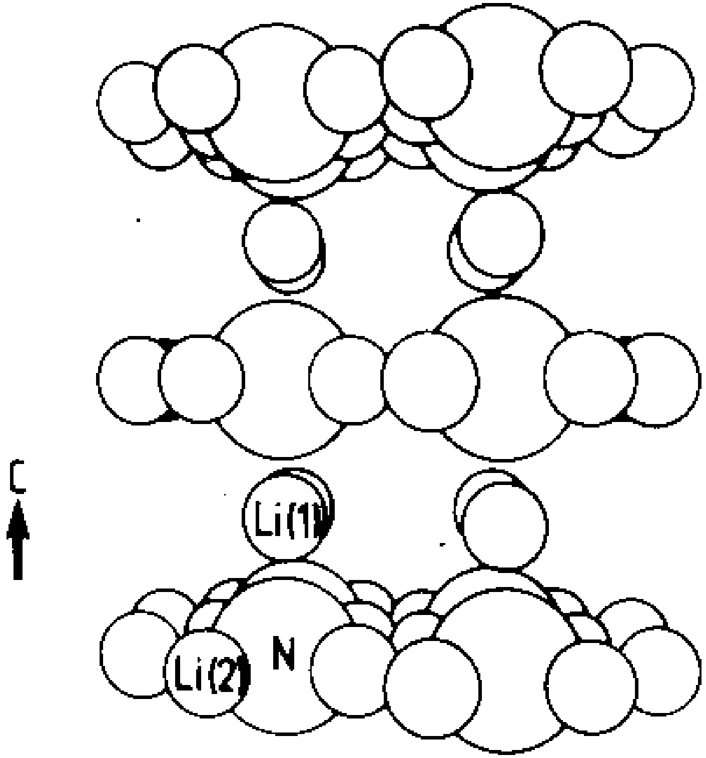
ELEKTRA Components for Electric Vehicles
Via Laveggio, 15 CH - 6855 Stabio - Switzerland
TEL: +41 (0)91 6415311 FAX: +41(0)91 6415333 E-mail: info@mes-dea.ch internet: http:// www.mes-dea.ch
Rev 06 del 07.08.07
ZEBRA

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.



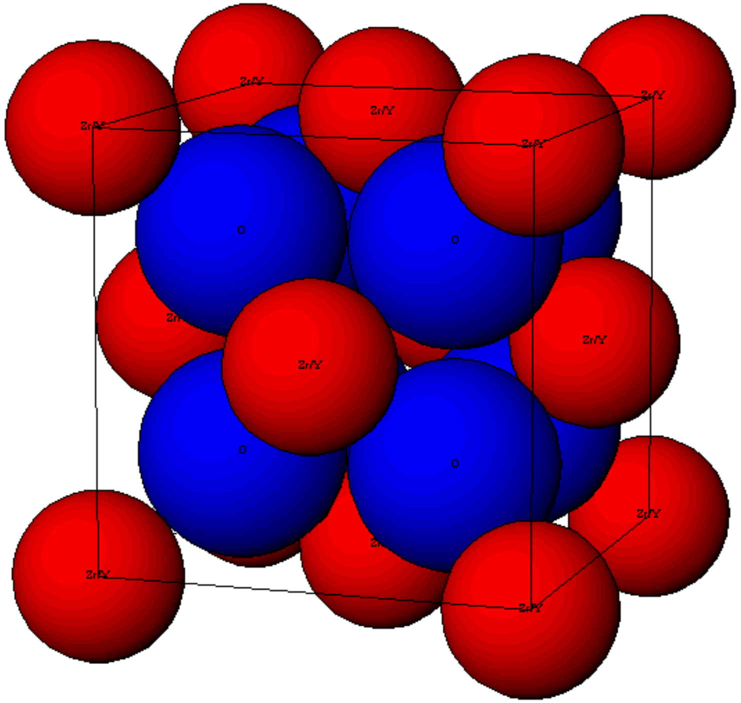
ANION CONDUCTORS

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^oC



Question

The ionic resistance of 1%$CdCl_2$ doped NaCl decreases with temperature according to Arrhenius behaviour, with an increase in activation energy for conduction from 0.7eV to 1.3 eV at 500^oC as temperature increases. Sketch this on a schematic Arrhenius type plot and suggest why this change occurs. Also add to this diagram a plot showing how the traces for 2% and 3% doping of NaCl with $CdCl_2$ would appear.