

Defects

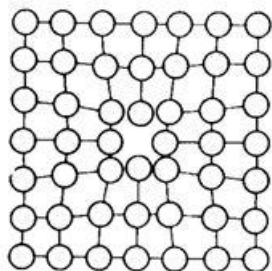
CML102

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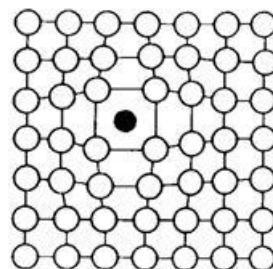
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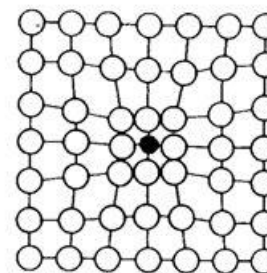
Point Defects



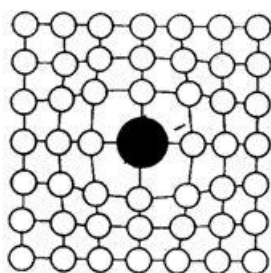
vacancy



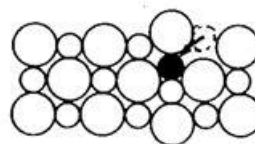
interstitial



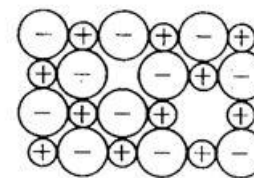
small substitutional atom



large substitutional
atom



Frenkel defect



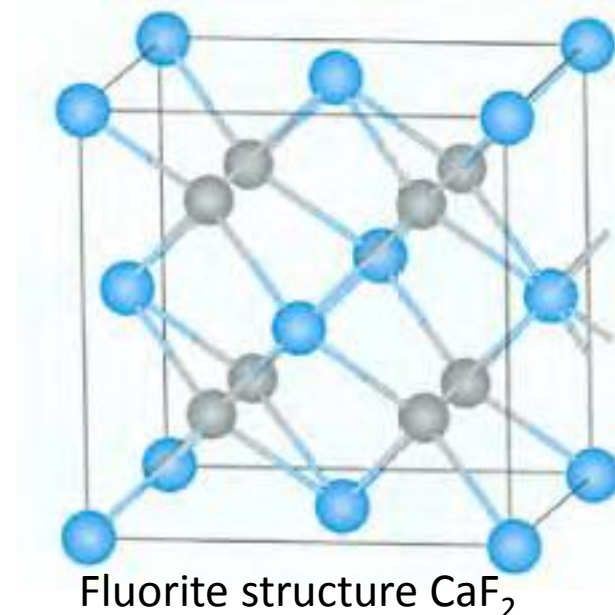
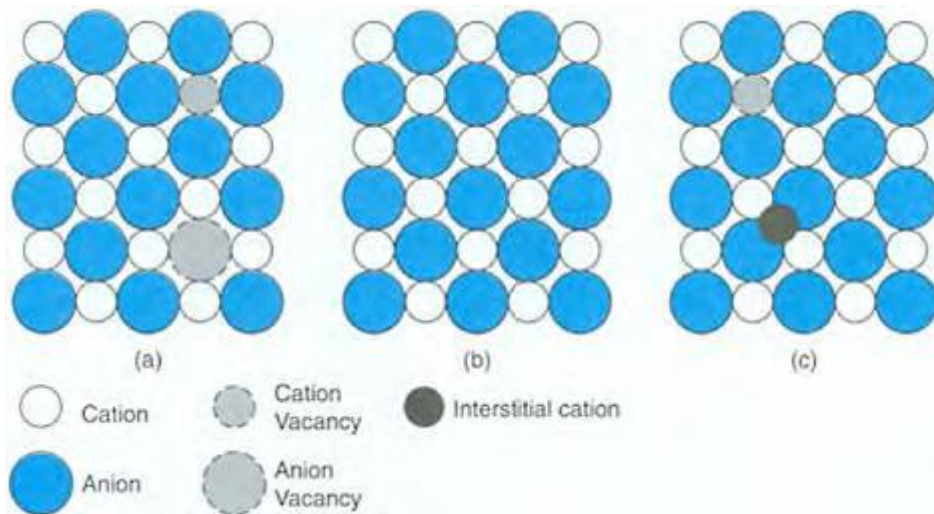
Schottky defect

All of these defects disrupt the perfect arrangement of the surrounding atoms – relaxation effects

Schottky and Frenkel normally v low conc. since formation energy high

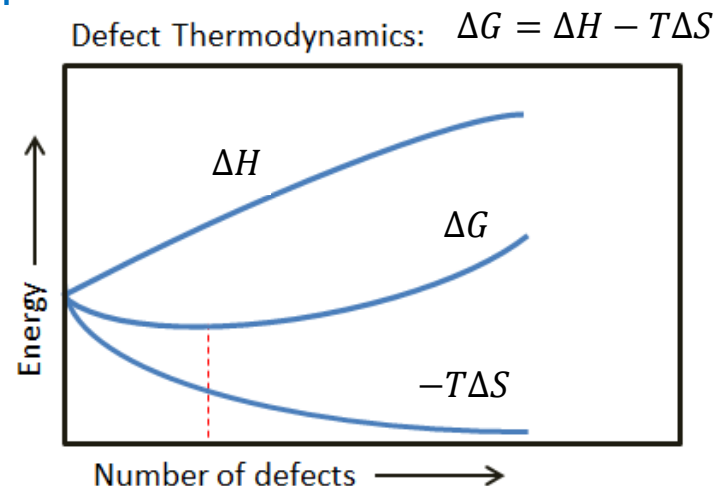
Schottky and Frenkel Defects

- **Schottky defect:** vacancies in lattice. In MX a pair of vacant sites are generated due to a missing cation and anion. MX_2 ? E.g. NaCl, ZnS, CsCl
 - ~ 1 defect per 10^{15} atoms
 - responsible for optical and electrical properties
- **Frenkel defect:** The cation (usually) moves to an interstitial position. E.g. AgCl, AgBr – photography.
 - Fluorite structures (CaF_2 , PbF_2 , SrF_2 , ThO_2 , UO_2 , ZrO_2) do have anion Frenkel defects.
 - Lower charge of anion compared to cation
 - Structure of fluorite – large O_h holes are empty

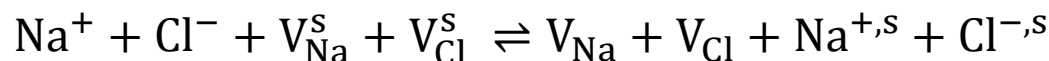


Thermodynamics of defect formation

- Schottky and Frenkel – intrinsic defects. thermodynamically must.
 - high T crystallization favors more defects



Schottky equilibria



(s = surface $\rightarrow$ vacancy on surface for chloride V_{Cl}^s)

$$K = \frac{[V_{\text{Na}}][V_{\text{Cl}}][\text{Na}^{+,s}][\text{Cl}^{-,s}]}{[\text{Na}^+][\text{Cl}^-][V_{\text{Na}}^s][V_{\text{Cl}}^s]} = \frac{[V_{\text{Na}}][V_{\text{Cl}}]}{[\text{Na}^+][\text{Cl}^-]} = \frac{(N_v)^2}{(N - N_v)^2} \sim \frac{(N_v)^2}{(N)^2}$$

$$K \propto e^{-\Delta G/RT} \propto e^{-\Delta H/RT} e^{\Delta S/R} = \text{const} \times e^{-\Delta H/RT}$$

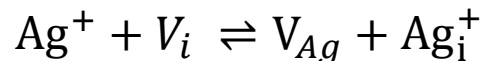
$$N_v = N \times \text{const} \times e^{-\Delta H/2RT}$$

monatomic crystals $N_v = NK$
(all molar quantities)



Frenkel equilibria

AgCl - fcc



(s = surface $\rightarrow$ vacancy on surface for chloride V_{Cl}^s)

$$K = \frac{[\text{Ag}_i^+][V_{Ag}]}{[\text{Ag}^+][V_i]} = \frac{(N_i)^2}{(N - N_i)(\alpha N)} \sim \frac{(N_i)^2}{\alpha N^2}$$

$$[V_{Ag}] = [Ag_i] = N_i = N \times \sqrt{\alpha} \times e^{-\Delta G/2RT} = \text{const} \times N e^{-\Delta H/2RT}$$

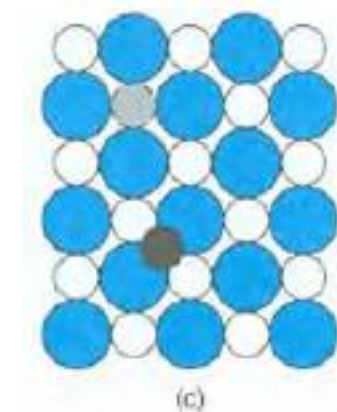
(all molar quantities)

log-log plot – straight line

At $\sim 450^\circ\text{C}$ (AgCl m.p. = 456°C) 0.6% Frenkel defects. 1 in 200 occupy Td site.

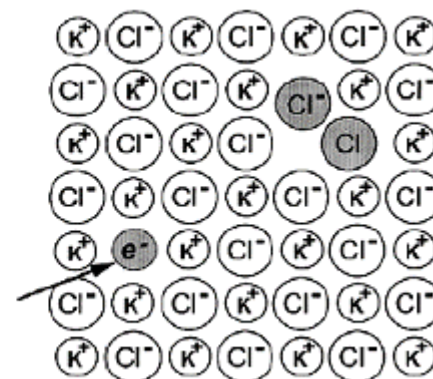
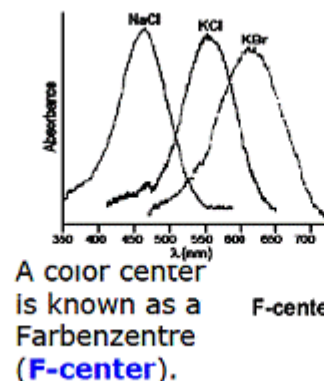
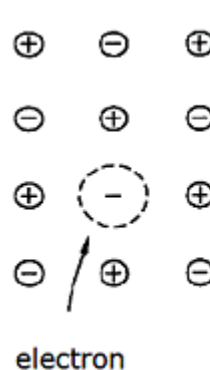
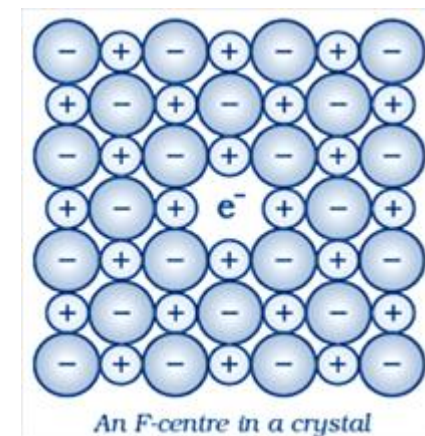
ΔH , Frenkel, AgCl $\sim 1.35\text{ eV}$ (130 kJ mol^{-1})

ΔH , Schottky, NaCl $\sim 2.3\text{ eV}$ (220 kJ mol^{-1})



Color Centres

- F-centre (*Farbenzentre*) – electron trapped on an anion vacancy
 - $\text{NaCl} + \text{Na vapors} = \text{Na}^+ \text{ ions on surface} + \text{e}^- \text{ in anion site}$
 $= \text{Na}_{1+\delta}\text{Cl}$: $\delta \ll 1$
 - $\text{NaCl} + \text{K vapors} = \dots$
 - e^- responsible for color, not cation – yellow color – PIB
 - $\text{KCl} + \text{K} = \text{violet color}$
- H-centre, V-centre



Defects

- Extrinsic defects

- Ca^{2+} in NaCl – each Ca^{2+} replaces two Na^+
- $\text{ZrO}_2 + \text{Ca}^{2+}$ - anion vacancies – CSZ (to be taught later)

TABLE 5.1 The formation enthalpy of Schottky and Frenkel defects in selected compounds

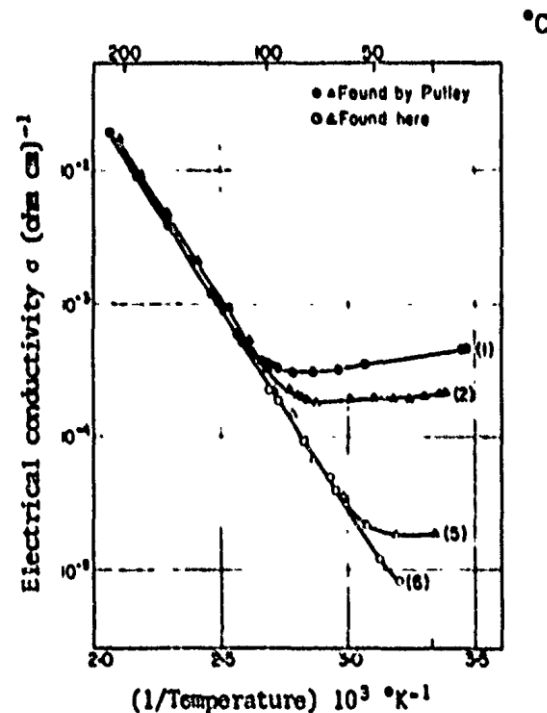
	Compound	$\Delta H/10^{-19} \text{ J}$	$\Delta H/\text{eV}^a$
Schottky defects	MgO	10.57	6.60
	CaO	9.77	6.10
	LiF	3.75	2.34
	LiCl	3.40	2.12
	LiBr	2.88	1.80
	LiI	2.08	1.30
	NaCl	3.69	2.30
	KCl	3.62	2.26
Frenkel defects	UO_2	5.45	3.40
	ZrO_2	6.57	4.10
	CaF_2	4.49	2.80
	SrF_2	1.12	0.70
	AgCl	2.56	1.60
	AgBr	1.92	1.20
	$\beta\text{-AgI}$	1.12	0.70

^aThe literature often quotes values in eV, so these are included for comparison. $1 \text{ eV} = 1.60219 \times 10^{-19} \text{ J}$.



Ionic conductivity

- $\sigma = nZe\mu$
- $\mu = \mu_0 \exp -E_a/kT$
- $\sigma = \sigma_0 \exp -E_a/kT$
- Plot $\log \sigma$ vs. $1/T$ – extrinsic and intrinsic regions



Electrical conductivity of p-type silicon single crystals as a function of the temperature. The curves (1) and (2) are taken from a paper by Putloy and Mitchell. Samples 5 and 6 are intrinsic. Boron impurity level reduced to 10^{11} cm^{-3} .



Ionic conductivity: Activated behavior

• Ionic conductivity (S cm^{-1})

- ionic crystals $< 10^{-18} - 10^{-4}$
- solid/liquid electrolytes $10^{-3} - 10^1$

Electronic conductivity (S cm^{-1})

metals $10^1 - 10^5$
 semiconductors $10^{-5} - 10^2$
 insulators $< 10^{-12}$

• specific conductivity $\sigma = \sum_i \overset{\text{\# of charge carriers}}{n_i} e_i \overset{\text{mobility of ions}}{\mu_i}$

- NaCl $\rightarrow$ r.t. insulator, $\sim 800^\circ\text{C}$ $10^{-3} \text{ S cm}^{-1}$
- Arrhenius behavior $\sigma = Ae^{-E_a/RT}$
- due to mobility of ions $\mu = \mu_0 e^{-E_a/RT}$

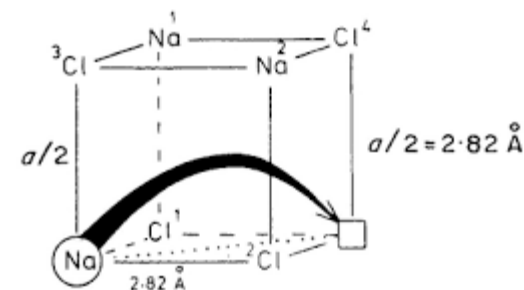


Fig. 7.16 Pathway for Na^+ migration in NaCl

• Na-Cl bond length = $2.82 \text{ \AA}$ ($r_{\text{Na}^+} = 0.95, r_{\text{Cl}^-} = 1.85 \text{ \AA}$)

• $\text{Cl}_1\text{-Cl}_2 = \frac{\sqrt{2}a}{2} = 3.99 \text{ \AA}$, $2r_{\text{Cl}^-} = 3.7 \text{ \AA} \rightarrow$ adjacent Cl not in contact, some space available

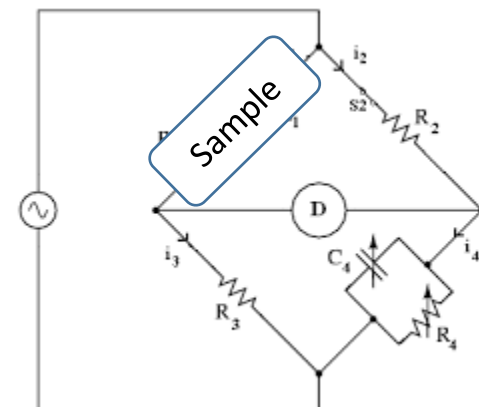
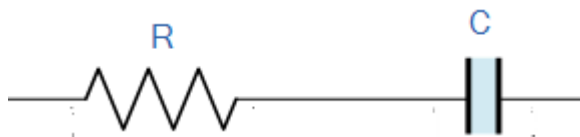
• radius, r' of Δ window $\text{Cl}_1\text{-Cl}_2\text{-Cl}_3$:

- $\cos 30 = \frac{x/2}{y} = \frac{1.995}{r' + r_{\text{Cl}^-}} \rightarrow r' + r_{\text{Cl}^-} = 2.30 \text{ \AA} \rightarrow r' = 0.45 \text{ \AA}$
- $r_{\text{Na}^+} = 0.95 \text{ \AA}$

Conductivity measurements

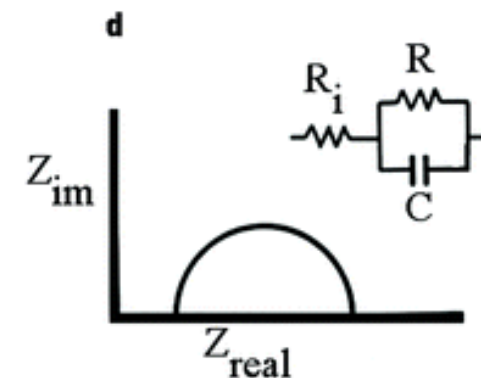
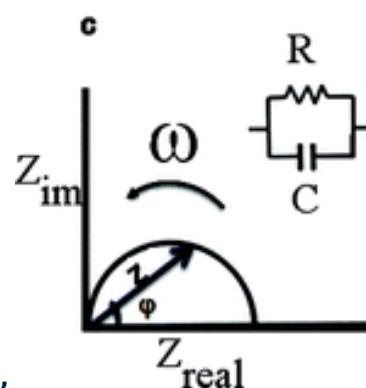
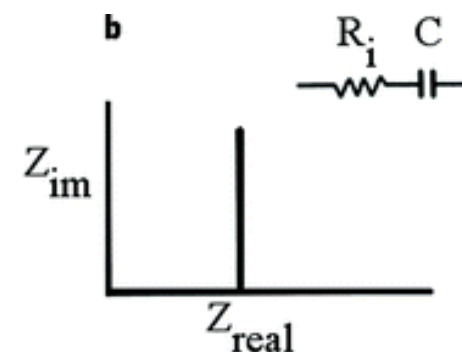
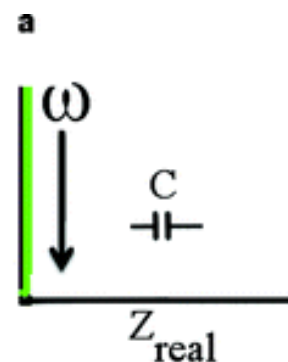
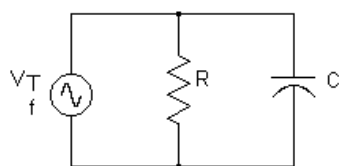
• RC in series

- For R, $I = E_1/R$
- For C, $I = j\omega CE_2$
- $E = E_1 + E_2$
- $Z = R + \frac{1}{j\omega C} = R - j\omega C = Z^* = Z' + Z''$ complex impedance
- complex admittance, $A^* = \frac{1}{Z^*} = \frac{1}{R} + j\omega C = A' + jA''$



• RC in parallel

- $Z^* = (A^*)^{-1} = \left(\frac{1}{R} + j\omega C\right)^{-1}$
- $= \frac{R}{1+j\omega RC} = \frac{R}{1+j\omega RC} \frac{1-j\omega RC}{1-j\omega RC}$
- $= \underbrace{\frac{R}{1+(\omega RC)^2}}_{Z'} - \underbrace{\frac{jR\omega RC}{1+(\omega RC)^2}}_{jZ''}$



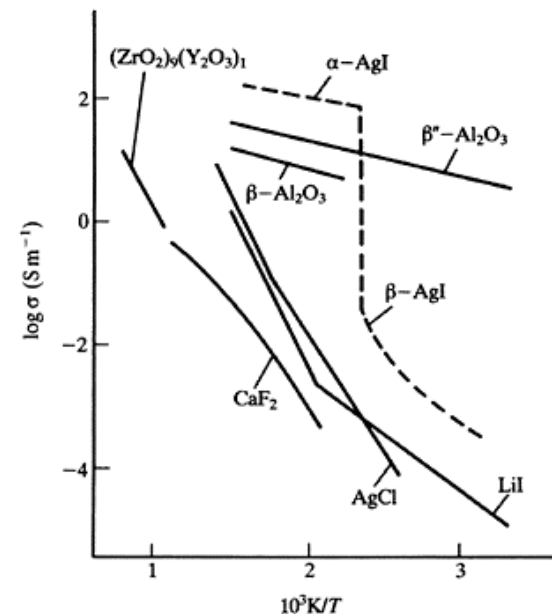
Solid Electrolytes

- preferred over liquid electrolytes
- solid state batteries – long life (small size possible), spill proof
- primary and secondary batteries
- sensors
- electrochromic devices
- fuel cells

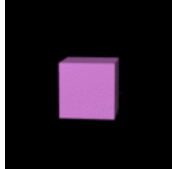


Fast-ion conductors: Silver ion conductors - α -AgI

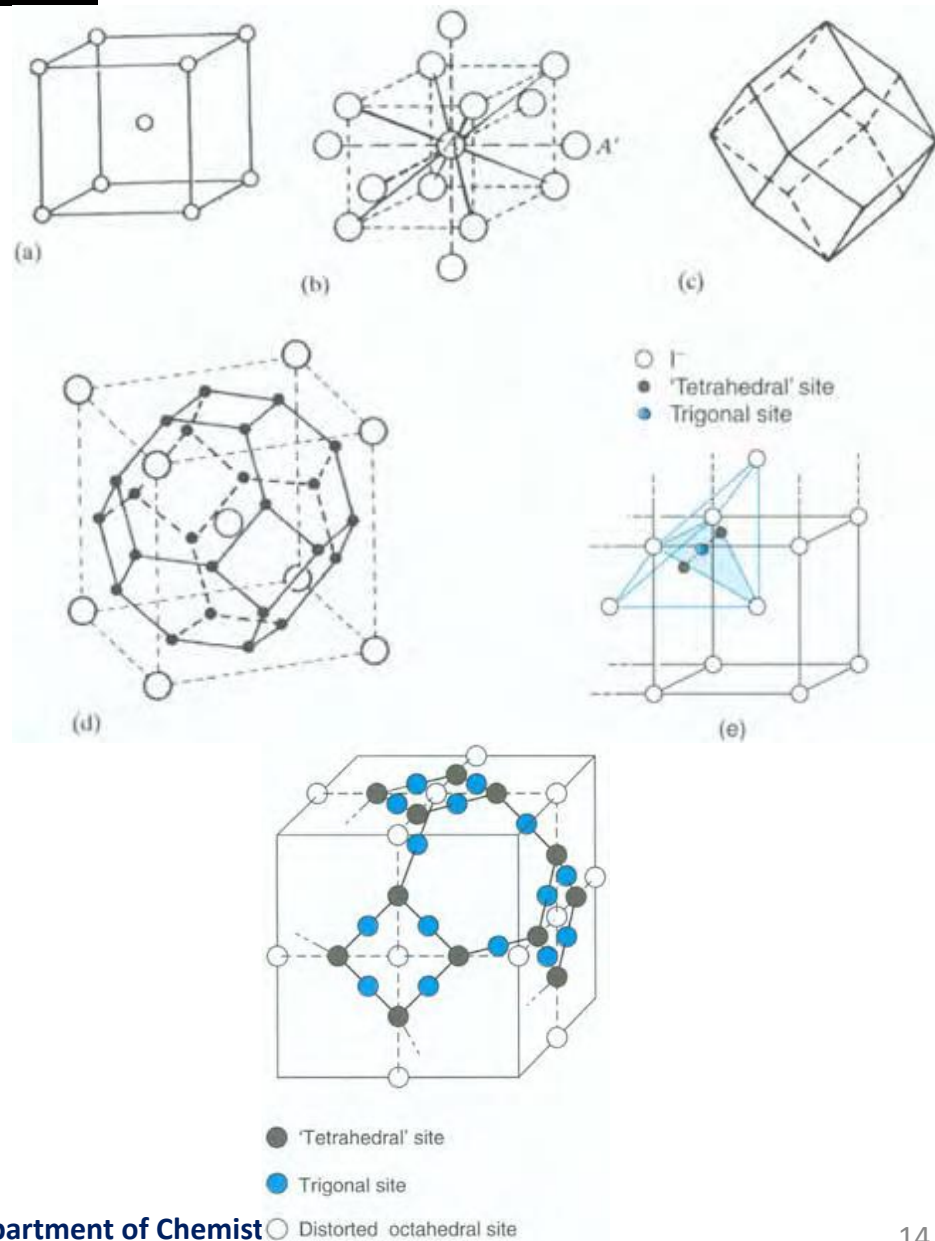
- 1913, Tubandt and Lorenz, α -AgI
- Below 146 °C $\rightarrow$ closed packed array of iodide ions with half the Td holes occupied by Ag
 - γ -AgI, zinc blende
 - β -AgI, wurtzite
- Above 146 °C $\rightarrow$ iodide ions have a BCC lattice
 - α -AgI
 - high conductivity = 131 S m^{-1} ($\sim 10,000$ times higher than β, γ phase)
- Crystal structure is the key to understanding!



α -AgI crystal structure



- Iodide BCC lattice
 - 8 nearest neighbors + 6 next nearest neighbors (only 15% farther) = 14 atoms on the vertices of a rhombic dodecahedron
 - or as the truncated Oh (6 square and 8 hexagonal faces). **Domain** – region belonging to the atom.
- Domain – each vertex lies at the center of an interstice (Td or Oh holes)
- In α -AgI, many positions for Ag^+ (42 possible)
 - the two tetrahedra share a triangular face - 12
 - between two Td sites a trigonal site - 24
 - site at the center of the 4 I^- is Oh (distorted) – 6
- BCC $\rightarrow$ 2 I^- ions $\rightarrow$ 2 Ag^+ ions but many possibilities
 - expt: C.N. 4 $\rightarrow$ 3 $\rightarrow$ 4
 - low $E_a = 0.05$ eV



α -AgI – high conductivity

- low charge on ions
- large number of vacant sites
- open framework structure with pathways that allows ions to move through
- CN is low $\rightarrow$ low E_a
- polarizable anions $\rightarrow$ e- cloud is easily distorted
- RbAg_4I_5
 - r.t. 25 S m^{-1}
 - E_a 0.07 eV
 - Rb^+ and I^- form a rigid array, Ag^+ moves around
 - used as solid electrolyte in batteries with electrodes of Ag and RbI_3 .

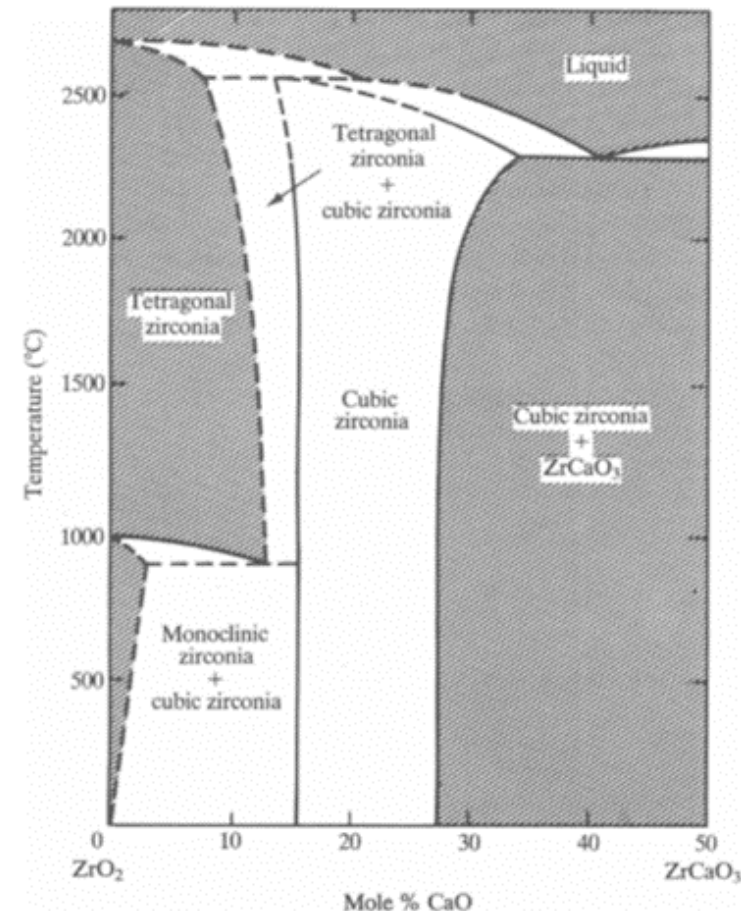
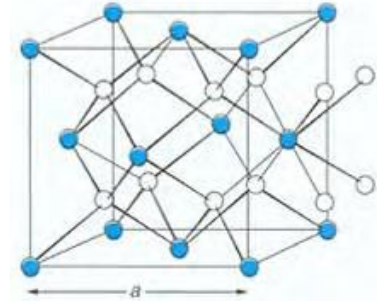
Anion structure	bcc	ccp	hcp	other
	α -AgI	α -CuI	β -CuBr	RbAg_4I_5
	α -CuBr	α -Ag ₂ Te		
	α -Ag ₂ S	α -Cu ₂ Se		
	α -Ag ₂ Se	α -Ag ₂ HgI ₄		

related
ionic
conductors



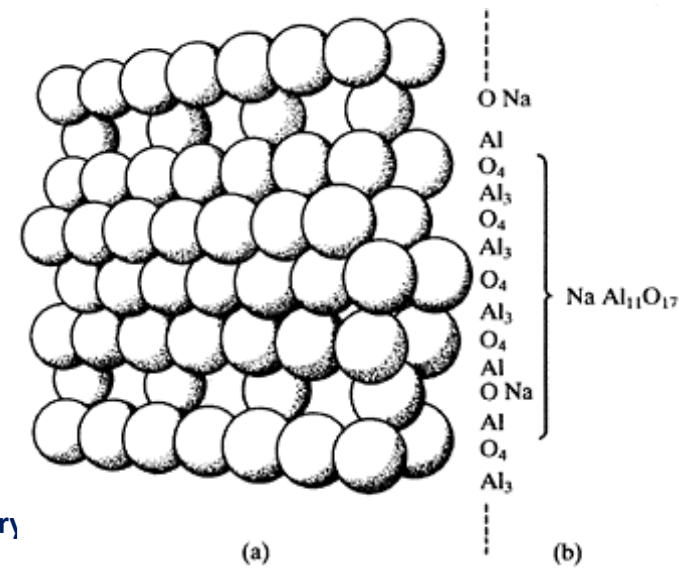
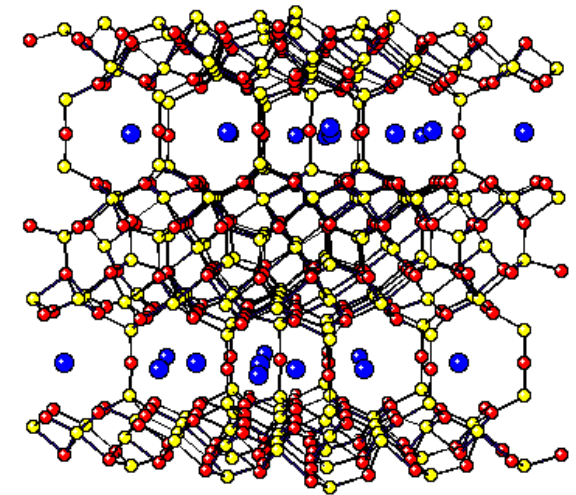
Fast-ion conductors: Oxygen ion conductors - Zirconias

- Fluorite structure: empty space for movement of F^- ions.
- PbF_2 : r.t. low $\rightarrow 500^\circ C \sim 500 S m^{-1}$
- ZrO_2 – cubic fluorite phase at high temp
 - Nernst: mixed Y_2O_3 and ZrO_2 – glow white hot when electric current is passed $\rightarrow$ conduction of oxide ions
 - at r.t. mix ZrO_2 with other oxides to stabilize
 - YSZ – Y_2O_3
 - CSZ – $CaO \rightarrow Ca^{2+}$ in Zr^{4+} sites $\rightarrow$ vacancies in the O^{2-} sublattice $\rightarrow$ good fast-ion oxide conductors
 - best conductivity when the dopant ion is the same size (no lattice distortion)
 - zirconia doped with Sc_2O_3
 - ceria doped gadolinia (Gd_2O_3) CGO
 - YSZ – SOFC, oxygen sensors – these are based on electrochemical cells
- perovskites
 - $LaGaO_3$ Sr^{2+} doped induces O^{2-} vacancies
 - Sr doped $LaMnO_3$, $LaCrO_3$ – both ionic and electronic conductors



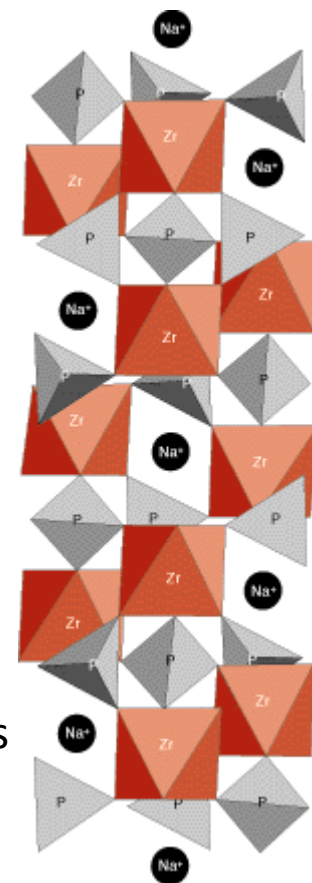
Fast-ion conductors: Sodium ion conductors - β -Alumina

- $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ ($\text{NaAl}_{11}\text{O}_{17}$)
- byproduct of glass industry – originally thought to be a polymorph of Al_2O_3 . Later it was found to have sodium ions
- General formula $\text{M}_2\text{O} \cdot n\text{X}_2\text{O}_3$ ($n = 5$ to 11).
 - M monovalent ion (alkali metal, Cu^+ , Ag^+ , NH_4^+)
 - X is a trivalent ion Al^{3+} , Ga^{3+} , Fe^{3+} .
- 1966, Ford demonstrated Na^+ - high mobility at r.t.
 - ccp layers of oxide ions (spinel blocks)
 - 4 ccp layers have Al^{3+} in both Oh and Td holes
 - 5th layer $\frac{3}{4}$ O^{2-} ions are missing
 - Na^+ ions reside in these layers
 - B(ABCA)C(ACBA)B... 5th layer is a mirror plane
 - conduction planes
 - At 300 °C, ionic conductivity $\approx$ liquid electrolytes
- Used in electrochemical cells for power supplies



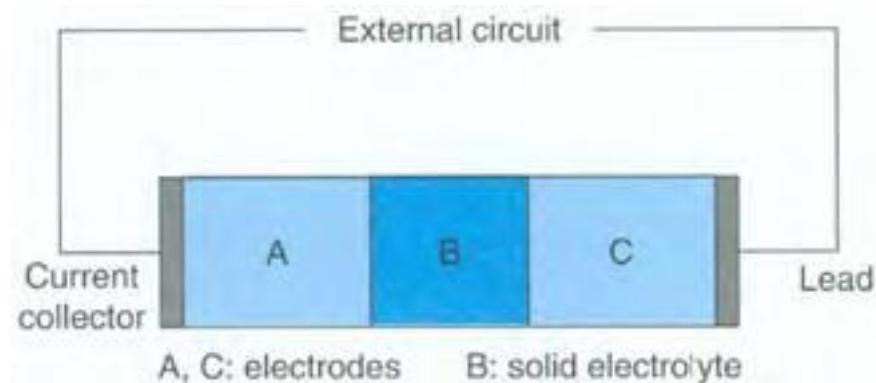
NASICON – Na SuperIonic CONductor

- 1968, Hagman and Kierkegaard – $\text{NaZr}_2(\text{PO}_4)_3 = \text{NZP}$
- corner linked ZrO_6 octahedra joined by PO_4 tetrahedral
 - each Td corner-shares to 4 Oh
- 3-D system of channels with 2 type of vacant sites
 - Type I – single distorted Oh site (occupied by Na^+)
 - Type II – three large sites – vacant in NZP
 - General formula $\text{A}_x\text{M}_2((\text{Si}, \text{P})\text{O}_4)_3$ - hundreds of compounds
 - A = alkali or alkaline earth; M=Ti, Zr, Nb, Cr, Fe
 - NASICON 20 S m^{-1} at 300 °C. $\text{Na}_3\text{Zr}_2(\text{PO}_4)_3(\text{SiO}_4)_2$
 - 3 out of 4 vacant sites are occupied – correlated motion of Na^+ ions
 - ions diffuse through the channels



Applications

- Solid State Ionic devices (SSIs)
 - batteries
 - fuel cells
 - electrochromic displays
 - sensors
- Solid electrolyte 'B' conducts ions but not electrons



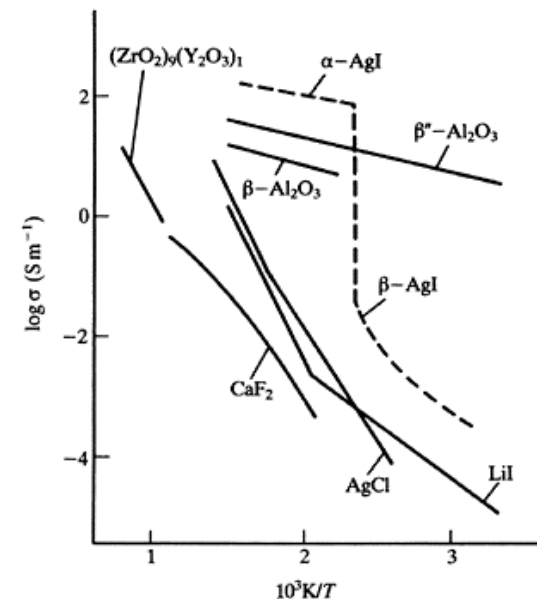
Applications: Batteries

- ions taking part in the reaction pass through an electrolyte
 - red/ox at electrode
 - electrode where oxidation takes place = anode (anion moves towards anode)
 - electrode where reduction takes place = cathode (cation towards cathode)
 - solid electrolyte in a battery
 - high ionic conductivity & electronic insulator
 - it can separate two reactants by allowing only ions (and not e⁻s) to travel. Else device would short-circuit
 - electrons travel round the external circuit
- EMF, $\Delta G^0 = -nFE^0$ ($F = 96485 \text{ C mol}^{-1}$ or 96485 J V^{-1})
- Energy stored in battery $\propto$ energy generated by the cell and amount of materials used
 - expressed in Watt-hours (current x voltage x discharge time)
- Advantage of solid state batteries
 - perform over a wide temperature range
 - long shelf life
 - high density, small lightweight batteries possible



Lithium batteries

- Lithium – light weight
 - energy density = W-h/battery volume in liters
 - specific energy = W-h/battery weight in kg
- LiI
 - low ionic conductivity
 - still used for pacemaker – low current requirement
 - hermetically sealed batteries
- A B C
 Li //LiI// I₂ and polymer
 - Anode A: $2\text{Li(s)} = 2\text{Li}^+(\text{s}) + 2\text{e}^-$
 - Cathode C: $\text{I}_2(\text{s}) + 2\text{e}^- = 2\text{I}^-(\text{s})$
- LiI contains intrinsic Schottky defects $\rightarrow \text{Li}^+$ ions are able to pass through
- Li ion batteries – challenge
- Rechargeable Li-ion batteries (Sony, 1990s)
 - challenge - Li redeposit in a finely divided state – catches fire
 - Li + TMO = intercalation compound e.g. Li_xCoO_2 . Li^+ rocks between two intercalation compounds. No lithium metal is present.
- A B C
 Li/C //polymer gel// CoO₂ and polymer
 - Anode A: $\text{Li}_x\text{C}_6(\text{s}) = x\text{Li} + 6\text{C} + x\text{e}^-$
 - Cathode: $x\text{Li}^+ + \text{CoO}_2(\text{s}) + x\text{e}^- = \text{Li}_x\text{CoO}_2(\text{s})$
- Cathode materials: CoO₂, NiO₂, TiS₂, MnO₂ ...



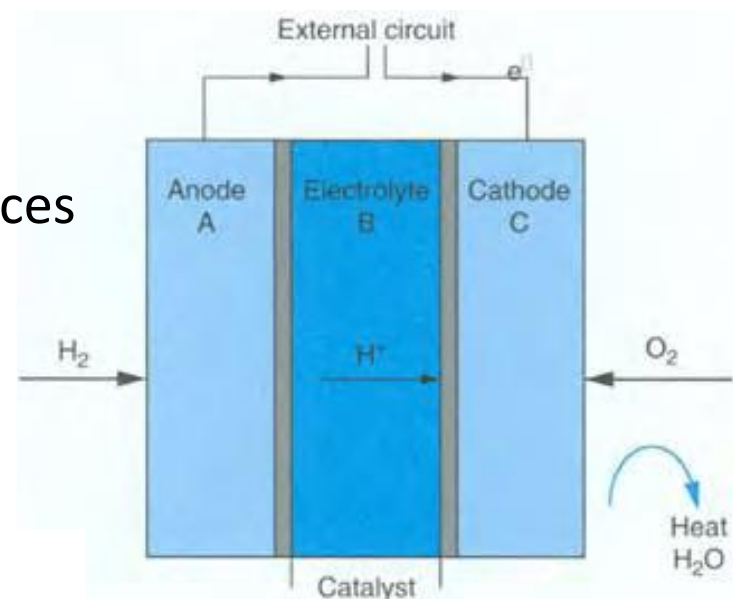
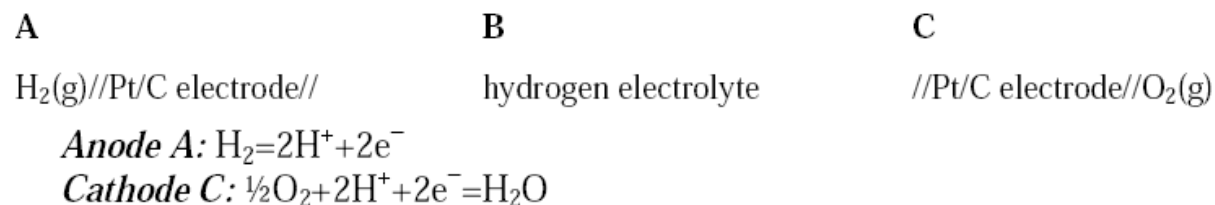
Sodium batteries

- **sodium sulfur batteries** – use NASICON $\{Na_3Zr_2(PO_4)_2(SiO_4)_2\}$ or β -alumina
A B C
Na(l) // β -alumina // S(l) and graphite
 - Anode A: $2Na(l) = 2Na^+ + 2e^-$
 - Cathode C: $2Na^+ + 5S(l) + 2e^- = Na_2S_5(l)$
 - Overall: $2Na(l) + 5S(l) = Na_2S_5(l)$
- low polysulfides are formed and discharge is terminated at a composition of Na_2S_3 .
- operation temp. 300 °C
- **ZEBRA battery**
 - β -alumina,
 - Cathode: Nickel chloride or mixture of Fe and Ni chlorides (solids)
 - poor contact so use second liquid electrolyte $NaAlCl_4$
 - Overall reaction: $2Na + NiCl_2 = Ni + 2NaCl$
 - high specific energy ($>100 \text{ Wh kg}^{-1}$)
 - electric vehicles can run upto 250 km, maintenance free for 100,000 km



Applications: Fuel Cells

- similar to battery except that the fuel is now fed externally
- non-polluting byproducts
- efficiency > 50% (ICE ~ 20%, diesel ~ 30%)
- electric vehicles – hybrids, homes, smaller devices
- expensive Pt catalyst
 - $E^\ominus = 1.23 \text{ V}$ at 298 K, 1 V at 500 K



- storage of H_2 gas
 - CNT
- generation of H_2 gas
 - reforming reaction: $\text{CH}_4/\text{CH}_3\text{OH} + \text{steam} \rightarrow \text{H}_2$



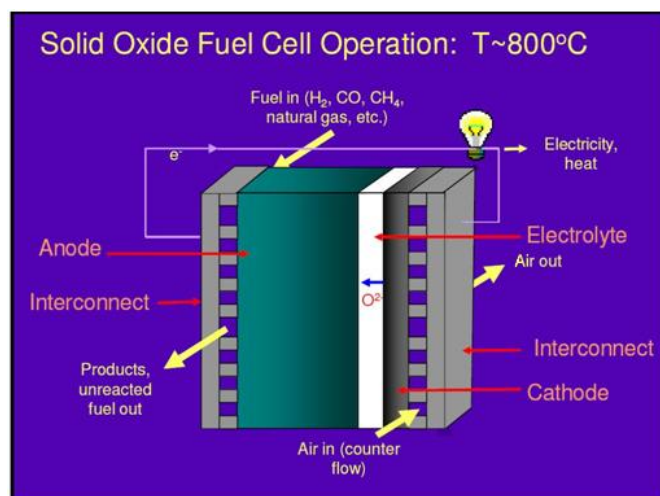
Fuel Cells – a short history

- 1839: Wiliam Grove, Welsh physicist – first working fuel cell
- 1959: Tom Bacon, Cambridge University – stack of 40 alkaline fuel cells, 5 kW power
- Willard Grub and Leonard Niedrach at GE developed a conducting membrane with Pt catalyst on Ti gauze – used in Gemini earth-orbit programme
- 1965, Pratt & Whitney – Alkaline fuel cells (AFC) for Apollo missions
 - provided power and drinking water
- 1983: first fuel cell buses, Canada (2017 in India)



SOFC: Solid Oxide Fuel Cells

- ceria- or yttria-doped zirconia, $\text{Y}_2\text{O}_3/\text{ZrO}_2$ electrolyte
 - O^{2-} conducting at very high temperatures (800-1000 °C)
 - high temp. allows for reforming reaction
 - no Pt catalyst
 - no H_2 storage issues
 - high T $\rightarrow$ long time $\rightarrow$ good for powering buildings/industry, not for vehicles

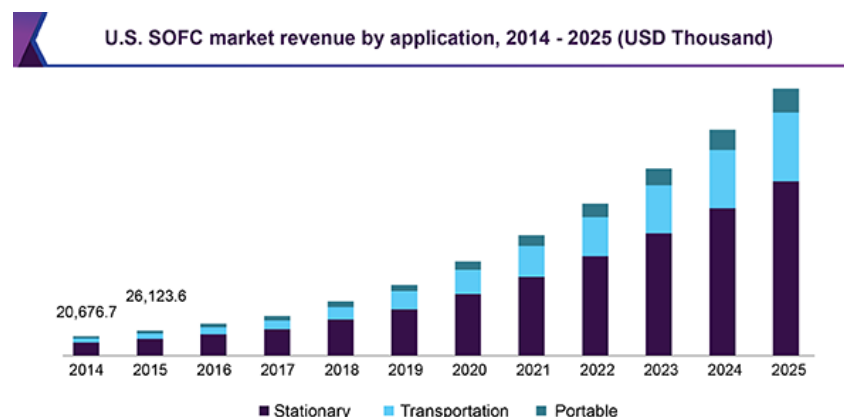


A

$\text{H}_2(\text{g}) // \text{electrode} //$

Anode A: $\text{H}_2 + \text{O}^{2-} = \text{H}_2\text{O} + 2e^-$

Cathode C: $\frac{1}{2}\text{O}_2 + 2e^- = \text{O}^{2-}$



B

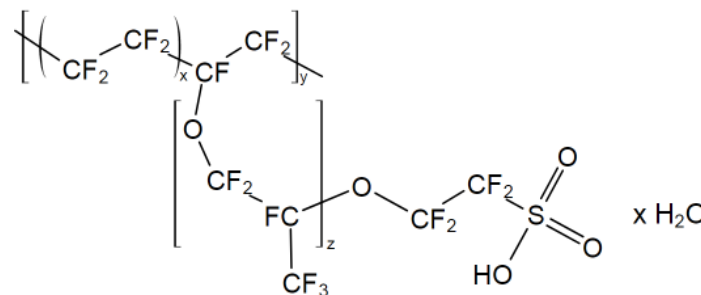
solid oxide electrolyte

C

$// \text{electrode} // \text{O}_2(\text{g})$

PEM: Proton exchange membrane fuel cell

- operate at $\sim 80\text{ }^{\circ}\text{C}$
- electrolyte – conducting polymer membrane (Nafion)
 - Nafion – sulfonate fluoropolymer by Dupont
 - strong acidic $-\text{SO}_2\text{OH}$ group allows H^+ ions
- $\sim 1\text{ V}$ at $80\text{ }^{\circ}\text{C}$, ohmic losses $\sim 0.5\text{ V}$, 0.5 A cm^{-2}
- 1 m^2 membrane $\sim 1\text{ kW}$
- stacks
- prototype zero emission vehicles



BMW i8

range: 310 miles

0-60 mph in 6s

200-400 stacks

life: 5000 hrs = 1,25,000 miles



Applications: Sensors – Oxygen sensors

- Calcia-stabilized zirconia (CSZ)
- If $p' > p''$, O_2 passes from right to left
 - produces a potential difference

Anode A: $2O^{2-} \rightarrow O_2(p'') + 4e^-$

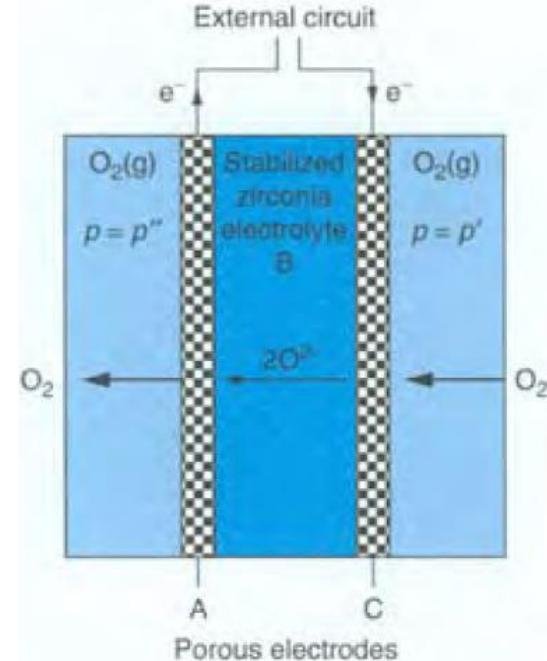
Cathode C: $O_2(p') + 4e^- \rightarrow 2O^{2-}$

Overall: $O_2(p') \rightarrow O_2(p'')$

- $\Delta G^0 = -nFE^0$
- let the cell reaction be $aA + bB + \dots + ne^- = xX + yY + \dots$
 - $E = E^0 - \frac{2.303RT}{nF} \log \left\{ \frac{a_X^x a_Y^y \dots}{a_A^a a_B^b \dots} \right\} = E^0 - \frac{2.303RT}{4F} \log \left\{ \frac{p''}{p'} \right\}$
- $E^0 = 0$ under standard conditions, both sides pr. is 1 atm
- to measure set p'' to known pr. (atmospheric O_2 or pure O_2)

$$E = \frac{2.303RT}{4F} \log \left\{ \frac{p'}{p_{ref}} \right\}$$

- NO ELECTRONIC CONDUCTANCE!!
- other gases – $H_2, F_2, Cl_2, CO_2, SO_x, NO_x$



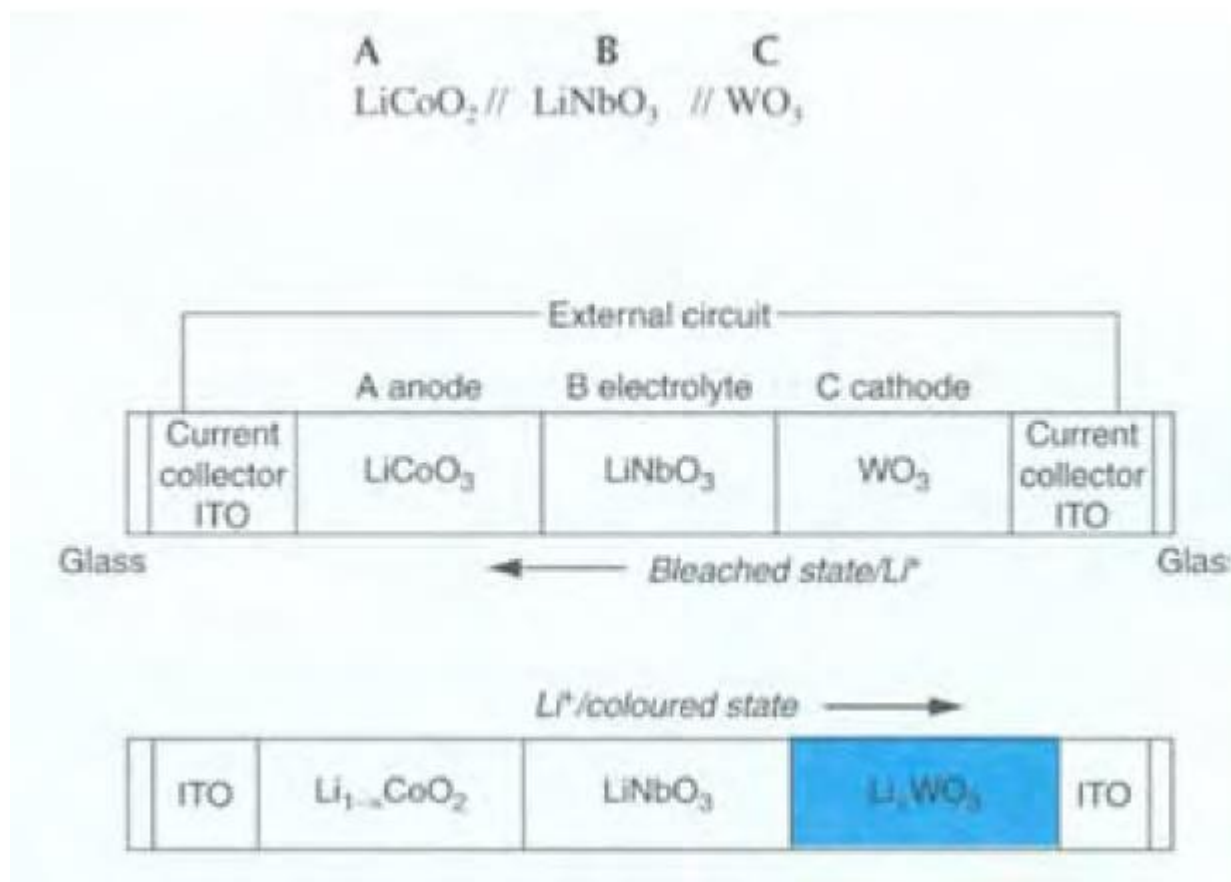
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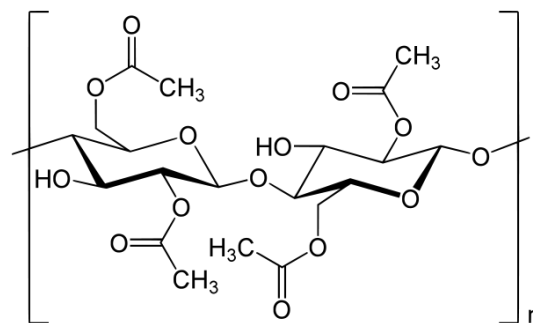
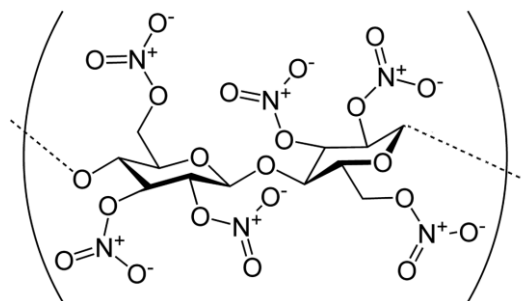
Applications: Electrochromic Devices

- Boeing 787 Dreamliner – electrochromic gels
- work opposite to electrochemical cells
 - apply current, cause ions to move



Photography

- Greek *photos* (light) + *graphe* (drawing)
- daguerreotype – silver-plated surface sensitized by iodine vapor, developed by Hg vapor and “fixed” with hot saturated salt water (1837).
- plastic film – nitrocellulose/celluloid (flammable) 1889-1951, cellulose acetate (safety film) 1908



Photography process

- Silver halide (AgBr, AgI) crystals in gelatin are coated on a film base – grains of AgX are present
- AgBr: fcc structure $a = 5.77 \text{ \AA}$, $E_g = 2.5 \text{ eV}$, solubility 0.14 mg/l , Frenkel defects
- $X^- + h\nu \rightarrow X + e^-$
- $e^- + Ag_i^+ \rightarrow Ag_i^0$ (crystals with large concentration of defects trap the electron faster)
- holes go to the Ag vacancies $h + Ag_v^- \rightleftharpoons h \cdot Ag_v$
- Bromine atoms go to the surface to be collected by the top layer of emulsion
- Growth of Ag atom speck
 - $Ag + e^- = Ag^-$
 - $Ag^- + Ag_i^+ = Ag_2$
 - $Ag_2 + Ag_i^+ = Ag_3^+$
 - $Ag_3^+ + e^- = Ag_3$
 - $Ag_3 + e^- = Ag_3^-$
 - $Ag_3^- + Ag_i^+ = Ag_4 \dots \dots$
- Sensitizers: Sulfur, organic dyes – to extend the range of AgBr towards red
- Developing: hydroquinone to reduce Ag^+ ions. Ag clusters act as catalysts. Grains that did not react with light are unaffected.
- Excess AgBr is washed with hypo ($Na_2S_2O_3$). This produces the negative.

