Ionic Conductivity and Solid Electrolytes I: The Basics

Chemistry 754
Solid State Chemistry
Lecture #26
June 2, 2003

References

A.R. West – "*Solid State Chemistry and it's Applications*", Chapter 13, Wiley (1984)

C.N.R Rao and J. Gopalakrishnan – "New Directions in Solid State Chemistry", pp. 409-416, Cambridge (1997)

A. Manthiram & J. Kim – "Low Temperature Synthesis of Insertion Oxides for Lithium Batteries", Chem. Mater. **10**, 2895-2909 (1998).

J.C. Boivin & G. Mairesse – "Recent Material Developments in Fast Oxide Ion Conductors", Chem. Mater. **10**, 2870-2888 (1998).

Craig Fisher (Japan Fine Ceramic Institute) http://www.spice.or.jp/~fisher/sofc.html

Solid Electrolytes

Electrolyte - A substance that conducts electricity through the movement of ions.

Most electrolytes are solutions or molten salts, but some electrolytes are solids and some of those are crystalline solids. Different names are given to such materials:

- -Solid Electrolyte
- -Fast Ion Conductor
- -Superionic Conductor

Over the next two lectures we will be looking at materials which behave as solid electrolytes, their properties and applications.

Ionic vs. Electronic Conductivity

Let's begin by comparing the properties of ionic conductors with the conventional electronic conductivity of metals.

Metals

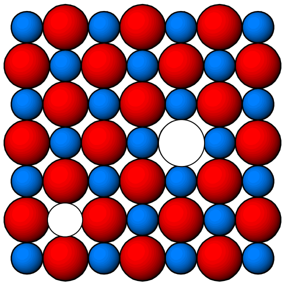
- -Conductivity Range = 10 S/cm < σ < 10^5 S/cm
- -Electrons carry the current
- -Conductivity Increases linearly as temperature decreases (phonon scattering decreases as T ↓)

Solid Electrolytes

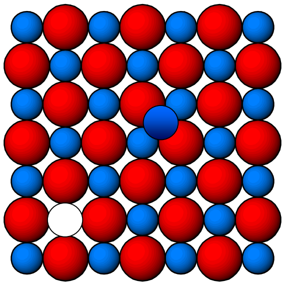
- -Conductivity Range = 10^{-3} S/cm < σ < 10 S/cm
- -Ions carry the current
- -Conductivity decreases exponentially as temperature decreases (activated transport)

Defects

In order for an ion to move through a crystal it must hop from an occupied site to a vacant site. Thus ionic conductivity can only occur if defects are present. The two simplest types of point defects are Schottky and Frenkel defects.



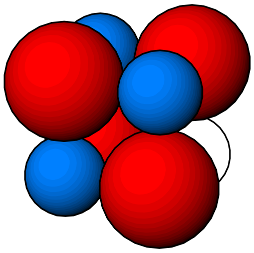
Schottky Defect
(i.e. NaCl)
$Na^+ + Cl^- \rightarrow V_{na} + V_{Cl}$

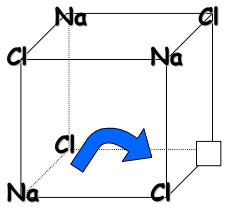


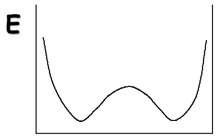
Frenkel Defect
(i.e. AgCl)
$Ag^+ \rightarrow V_{Ag} + Ag^+_{interstitial}$

Ion Migration (Schottky Defects)

Consider the movement of Na^+ ions in NaCl via vacancies originating from Schottky defects. Note that the Na^+ ion must squeeze through the lattice, inducing significant local distortion/relaxation. This is one factor that limits the mobility of ions. A second factor that contributes is the relatively high probability that the ion will jump back to it's original position, leading to no net ionic migration.



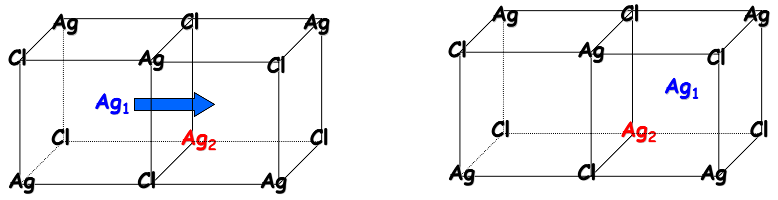




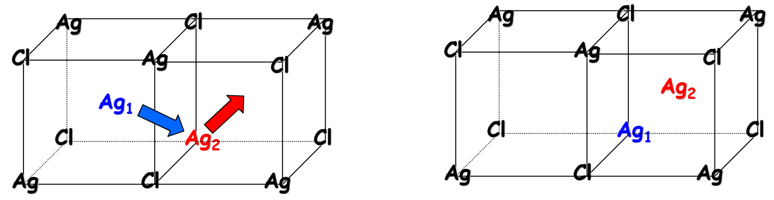
To get across the unit cell into the vacancy the Na^+ ion must hop through the center of the cube where it squeezes by 4 Cl^- and 2 Na^+. The energy of this "transition state" will determine the ease of migration.

Ion Migration (Frenkel Defects)

The Frenkel defects in AgCl can migrate via two mechanisms.



Direct Interstitial Jump

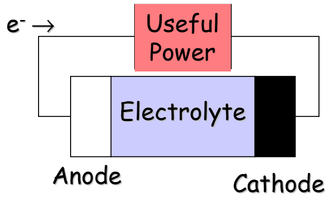


Interstitialcy Mechanism

Applications of Ionic Conductors

There are numerous practical applications, all based on electochemical cells, where ionic conductivity is needed and it is advantageous/necessary to use solids for all components.

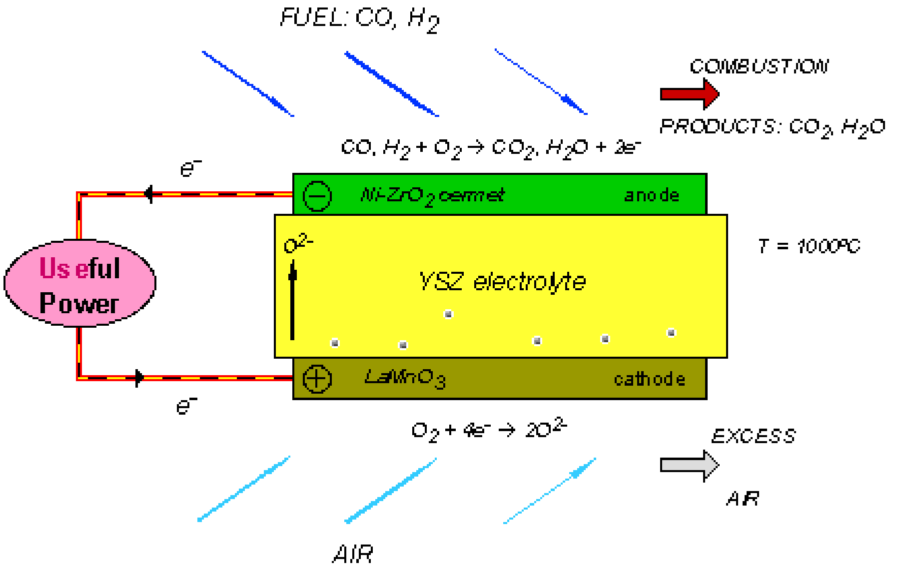
- **-Batteries**
- **-Fuel Cells**
- **-Gas Sensors**



In such cells ionic conductors are needed for either the electrodes, the electrolyte or both.

- **-Electrolyte** (Material needs to be an electrical insulator to prevent short circuit)
- **-Electrode** (Mixed ionic and electronic conductivity is needed to avoid open circuit)

Schematic of a Solid Oxide Fuel Cell



Taken from http://www.spice.or.jp/~fisher/sofc.html

Schematic of Rechargable Li Battery

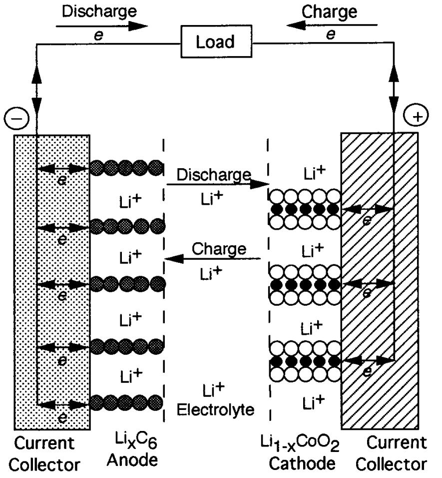


Figure 6. Schematic illustration of the discharge and charge processes in a rechargeable lithium ion battery. In the Li_x-CoO_2 cathode, the solid and open circles refer, respectively, to Co and O atoms (adapted from ref 14).

Taken from A. Manthiram & J. Kim – "Low Temperature Synthesis of Insertion Oxides for Lithium Batteries", Chem. Mater. **10**, 2895-2909 (1998).

Solid Electrolyte Materials

- **Ag^+ Ion Conductors**
  - -AgI & $RbAg_4I_5$
- **Na^+ Ion Conductors**
  - -Sodium β-Alumina (i.e. $NaAl_{11}O_{17}$, $Na_2Al_{16}O_{25}$)
  - -NASICON ($Na_3Zr_2PSi_2O_{12}$)
- **Li^+ Ion Conductors**
  - -$LiCoO_2$, $LiNiO_2$
  - -$LiMnO_2$
- **O^{2-} Ion Conductors**
  - -Cubic stabilized ZrO_2 ($Y_xZr_{1-x}O_{2-x/2}$, $Ca_xZr_{1-x}O_{2-x}$)
  - - δ-Bi_2O_3
  - -Defect Perovskites ($Ba_2In_2O_5$, $La_{1-x}Ca_xMnO_{3-y}$, …)
- **F^- Ion Conductors**
  - -PbF_2 & AF_2 (A = Ba, Sr, Ca)

Stabilized ZrO_2 is not a good ionic conductor at low temperature.

α-AgI & $RbAg_4I_5$ have ionic conductivities comparable to conc. H_2SO_4

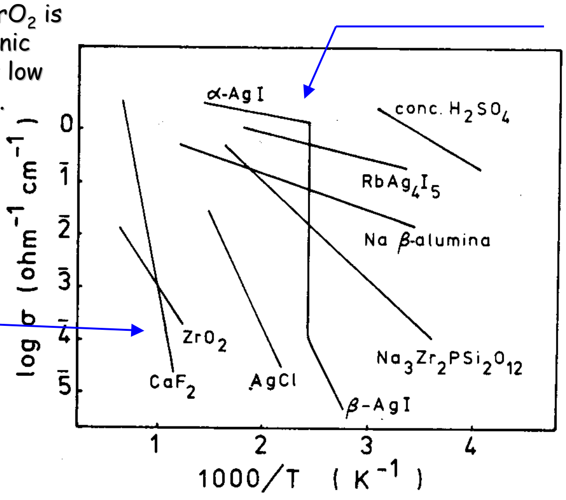


Fig. 13.10 Ionic conductivity of some solid electrolytes with concentrated H_2SO_4 for comparison. In searching for new materials, one aims for the top right-hand corner of the diagram (high σ, low T)

Taken from "Solid State Chemistry and it's Applications" by Anthony West

General Characteristics: Solid Electrolytes

1. A large number of the ions of one species should be mobile. This requires a large number of empty sites, either vacancies or accessible interstitial sites.
   - Empty sites are needed for ions to move through the lattice.
2. The empty and occupied sites should have similar potential energies with a low activation energy barrier for jumping between neighboring sites.
   - High activation energy decreases carrier mobility, very stable sites (deep potential energy wells) lead to carrier localization.
3. The structure should have solid framework, preferable 3D, permeated by open channels.
   - The migrating ion lattice should be "molten", so that a solid framework of the other ions is needed in order to prevent the entire material from melting.
4. The framework ions (usually anions) should be highly polarizable.
   - Such ions can deform to stabilize transition state geometries of the migrating ion through covalent interactions.

Molten Sublattice (1/2 Melting)

In the best ionic conductors one ion becomes so mobile that for all intensive purposes those ions are in a "molten" state. This behavior can be seen in part from the entropies of the observed phase transitions, where the Ag (and F respectively) sublattice melts prematurely.

(poor ionic conductor) β-AgI $\rightarrow$ α-AgI (excellent ionic conductor)

T = 146 °C, $\Delta S = 14.5$ J/mol-K

α-AgI $\rightarrow$ molten AgI

$\Delta S = 11.3$ J/mol-K

Compare with the an entropy of melting of 24 J/mol-K for NaCl.

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solid PbF_2 $\rightarrow$ molten PbF_2

$\Delta S = 16.4$ J/mol-K

Compare with the an entropy of melting of 35 J/mol-K for MgF_2

Ag^+ Ion Conductors

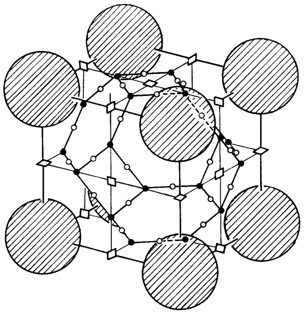

Figure 7.2 Structure of α-AgI, showing interstitial cation sites: large hatched circles, iodide ions; squares, octahedral 6*b* sites; solid circles, tetrahedral 12*d* sites; open circles, 24*h* sites.

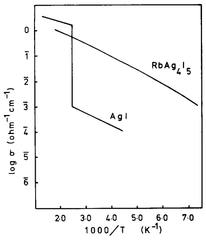

Fig. 13.16 Conductivity of Ag^+ in AgI and $RbAg_4I_5$

β-AgI

- Stable below 146 °C
- Wurtzite Structure (tetrahedral coordination)
- σ = 0.001 S/cm – 0.0001 S/cm

α-AgI

- Stable above 146 °C
- BCC Arrangement of I^-, molten/ disordered Ag^+
- $\sigma \sim 1$ S/cm, E_A=0.05 eV
- Conductivity decreases on melting

$RbAg_4I_5$

- Highest known conductivity at room temperature
- BCC Arrangement of I^-, molten/disordered Ag^+
- $\sigma \sim 0.25$ S/cm (25 °C), E_A=0.07 eV

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Na^+ Ion Conductors

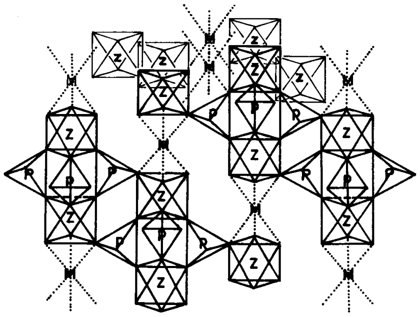

Figure 7.3 Structure of $NaZr_2(PO_4)_3$. (After Goodenough, 1984

$Na_3Zr_2PSi_2O_{12}$ (NASICON)

- Framework of corner sharing ZrO_6 octhahedra and PO_4/SiO_4 tetrahedra
- Na^+ ions occupy trigonal prismatic and octahedral sites, ¼ of the Na^+ sites are empty
- $E_A \sim 0.3$ eV

$NaAl_7O_{11}$ ($Na_2O{\cdot}nAl_2O_3$)

- FCC like packing of oxygen
- Every fifth layer ¾ of the O^{2-} ions are missing, Na^+ ions present. These layers are sandwiched between spinel blocks.
- 2D ionic conductor

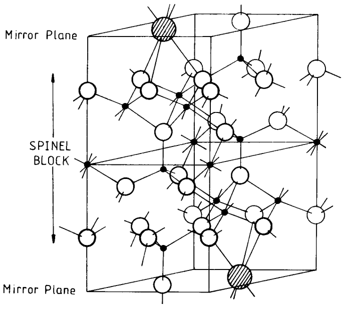

Figure 7.4 Structure of sodium β-alumina. Only half the unit cell is shown. Large hatched circles represent sodium, open circles oxygen, and small filled circles aluminium.