Chapter 5:
Defects and Non-stoichiometry

- Perfect Crystal
  - Extended Defects
    - Dislocations
  - Point Defects
    - Grain Boundaries
    - Intrinsic
    - Extrinsic
**Point Defect - Intrinsic**

![Diagram of Schottky and Frenkel defects](image)

**Schottky**
- Cation vacancy
- Anion vacancy

**Frenkel**
- Interstitial cation

\[
\text{Na}^+ + \text{Cl}^- \rightarrow V_{\text{Na}} + V_{\text{Cl}} \quad \text{Ag}^+ \rightarrow V_{\text{Ag}} + \text{Ag}^+_{\text{interstitial}}
\]

**Anion Frenkel defect in fluorite**

Example fluorites include CaF\(_2\), SrF\(_2\), PbF\(_2\), ThO\(_2\), UO\(_2\), ZrO\(_2\)

Cation Frenkel defects are common because of the typically smaller size of a cation compared to an anion.

- However, anions in the fluorite structure have a lower electrical charge than the cations and don’t find it as difficult to move nearer each other.

- The fluorite structure *ccp* cations with all tetrahedral holes occupied by the anions — thus all octahedral holes are unoccupied.
Concentration of defects

Energy is required to form a defect (endothermic process)

- Although there is a cost in energy, there is a gain in entropy in the formation of a defect.

- At equilibrium, the overall change in free energy of the crystal due to the defect formation is zero according to:

\[ \Delta G = \Delta H - T\Delta S \]

At any temperature, there will always be an equilibrium population of defects. The number of defects (for an MX crystal) is given by:

\[ n_s \approx N \exp \left( \frac{-\Delta H_s}{2kT} \right) \]

where \( n_s \) is the number of Schottky defects per unit volume, at \( T \) K, in a crystal with \( N \) cations and \( N \) anion sites per unit cell volume, and \( \Delta H_s \) is the enthalpy required to form one defect.

Concentration of defects, cont.

Estimate the configurational entropy, the change of entropy due to the vibrations of atoms around the defects and the arrangement of defects, using methods of statistical mechanics.

- If the number of Schottky defects is \( n_s \) per unit volume at \( T \) K, then there are \( n_s \) cation vacancies and \( n_s \) anion vacancies in a crystal containing \( N \) possible cation sites and \( N \) possible anion sites.

- The Boltzmann formula tells us that the entropy of such a system is:

\[ S = k \ln W \]

where \( W \) is the number of ways of distributing \( n_s \) defects over \( N \) possible sites at random, and \( k \) is the Boltzmann constant (1.38x10^{-23} J/K)

- Probability theory shows that \( W \) is given by:

\[ W = \frac{N!}{(N-n)!n!} \]

\( N! \) is 'factorial N'. \( N \times (N-1) \times (N-2) ... \times 1 \)
Concentration of defects, cont.

Number of ways on can distribute cation vacancies

$$W_c = \frac{N!}{(N-n_s)!n_s!}$$

Number of ways on can distribute anion vacancies

$$W_a = \frac{N!}{(N-n_a)!n_a!}$$

The total number of ways of distributing these defects, $W$, is:

$$W = W_c W_a$$

The change in entropy due to introducing defects into a perfect crystal:

$$\Delta S = k \ln W = k \ln \left( \frac{N!}{(N-n_s)!n_s!} \right)^2 = 2k \ln \left( \frac{N!}{(N-n_a)!n_a!} \right)$$

Concentration of defects, cont.

Simplify using Stirling’s approximation:

$$\ln N! \approx N \ln N - N$$

thus:

$$\Delta S = 2k \{ N \ln N - (N-n_s) \ln(N-n_s) - n_s \ln n_s \}$$

If the enthalpy change for the formation of a single defect is $\Delta H_s$ and then assume that the enthalpy change for the formation of $n_s$ defects is $n_s \Delta H_s$ then the Gibbs free energy change is given by:

$$\Delta G = n_s \Delta H_s - 2kT \{ N \ln N - (N-n_s) \ln(N-n_s) - n_s \ln n_s \}$$

At equilibrium, Gibbs free energy of the system must be a minimum with respect to changes in the number of defects, $n_s$. ($\frac{d\Delta G}{dn_s} = 0$)

$$\Delta H_s - 2kT \frac{d}{dn_s} \{ N \ln N - (N-n_s) \ln(N-n_s) - n_s \ln n_s \} = 0$$
Concentration of defects, cont.

\[ \Delta H_s - 2kT \frac{d}{dn_s} \left\{ N \ln N - (N - n_s) \ln(N - n_s) - n_s \ln n_s \right\} = 0 \]

MinN is a constant, so differential becomes zero

Differential of:

- \( \ln x \) is \( 1/x \)
- \( x \ln x \) is \( (1 + \ln x) \)

\[ \Delta H_s - 2kT \{ \ln(N - n_s) + 1 - \ln n_s - 1 \} = 0 \]

\[ \Delta H_s = 2kT \ln \left( \frac{(N - n_s)}{n_s} \right) \to n_s = (N - n_s) \exp \left( \frac{-\Delta H_s}{2kT} \right) \]

Since \( N >> N_s \), approximate \( N_n \) as \( N \)

\[ n_s \approx N \exp \left( \frac{-\Delta H_s}{2kT} \right) \]

in molar quantities \( \to n_s \approx N \exp \left( \frac{-\Delta H_s}{2RT} \right) \)

where \( R \) is 8.314 J/mol K

\( \Delta H_s \) is the enthalpy required to form one mole of Schottky defects

Concentration of defects, cont.

The number of Frenkel defects present in a MX crystal is:

\[ n_s \approx (NN_i)^{1/2} \exp \left( \frac{-\Delta H_F}{2kT} \right) \]

where \( n_i \) is the number of Frenkel defects per unit volume, \( N \) is the number of lattice sites, and \( N_i \) the number of interstitial sites available., and \( \Delta H_F \) is the enthalpy of formation of one Frenkel defect:

If \( \Delta H_F \) is the enthalpy of formation of one \textit{mole} of Frenkel defects:

\[ n_s \approx (NN_i)^{1/2} \exp \left( \frac{-\Delta H_F}{2RT} \right) \]

Knowing the enthalpy of formation for Schottky and Frenkel defects, one can estimate how many defects are present in a crystal.
Assuming $\Delta H = 5 \times 10^{-19}$ J, the proportion of vacant sites $n_s/N$ at 300 K is $6.12 \times 10^{-27}$, whereas at 1000 K this increases to $1.37 \times 10^{-8}$.

At room temperature there are very few Schottky defects, even at 1000 K there are only about 1 or 2 defects per hundred million sites.

Depending on the value of $\Delta H$, a Schottky or Frenkel defect may be present. The lower $\Delta H$ dominates, but in some crystals it is possible that both types of defects may be present.

Increasing temperature increases defects, in agreement with the endothermic process and Le Chatelier’s principle.

### Compound $\Delta H (10^{-19}$ J) $\Delta H$ (eV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H$ (10$^{-19}$ J)</th>
<th>$\Delta H$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>10.57</td>
<td>6.60</td>
</tr>
<tr>
<td>CaO</td>
<td>9.77</td>
<td>6.10</td>
</tr>
<tr>
<td>LiF</td>
<td>3.75</td>
<td>2.34</td>
</tr>
<tr>
<td>LiCl</td>
<td>3.40</td>
<td>2.12</td>
</tr>
<tr>
<td>LiBr</td>
<td>2.88</td>
<td>1.80</td>
</tr>
<tr>
<td>LiI</td>
<td>2.08</td>
<td>1.30</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.69</td>
<td>2.30</td>
</tr>
<tr>
<td>KCl</td>
<td>3.62</td>
<td>2.26</td>
</tr>
<tr>
<td>UO$_2$</td>
<td>5.45</td>
<td>3.40</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>6.57</td>
<td>4.10</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>4.49</td>
<td>2.80</td>
</tr>
<tr>
<td>SrF$_2$</td>
<td>1.12</td>
<td>0.70</td>
</tr>
<tr>
<td>AgCl</td>
<td>2.56</td>
<td>1.60</td>
</tr>
<tr>
<td>AgBr</td>
<td>1.92</td>
<td>1.20</td>
</tr>
<tr>
<td>β-Agl</td>
<td>1.12</td>
<td>0.70</td>
</tr>
</tbody>
</table>

### Extrinsic defects

Doping with selected 'impurities' can introduce vacancies into a crystal.

- Consider incorporating CaCl$_2$ into NaCl, in which each Ca$^{2+}$ replaces two Na$^+$ and creates one cation vacancy.

### Defects and Ionic Conductivity in Solids

Defects make it possible for atoms or ions to move, through diffusion through the lattice or ionic conductivity (ions under the influence of an external electric field) through the structure.

Two possible mechanisms for the movement of ions through a lattice:

- **Vacancy mechanism**
- **Interstitial mechanism**
Ion Migration (Schottky defects)

Na\(^+\) ions move, but meet resistance in the crystal structure.

Ion Migration (Frenkel Defects)

The Frenkel defects in AgCl can migrate via two mechanisms.
The energy required to make the jump, $E_a$, is the activation energy.

**Ionic Conductivity**

Ionic Conductivity, $\sigma$, is defined the same as electrical conductivity:

$$\sigma = nZ\varepsilon \mu$$

where $n$ is the number of charge carriers per unit volume, $Z\varepsilon$ is the charge ($e = 1.602189 \times 10^{-19}$ C), and $\mu$ is the mobility, which is a measure of the drift velocity in a constant electric field.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity / (S m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic Conductors</td>
<td>Ionic crystals</td>
</tr>
<tr>
<td>Solid electrolytes</td>
<td>$10^{-1} \text{ to } 10^{3}$</td>
</tr>
<tr>
<td>Strong (liquid) electrolytes</td>
<td>$10^{-1} \text{ to } 10^{3}$</td>
</tr>
<tr>
<td>Electronic conductors</td>
<td>Metals</td>
</tr>
<tr>
<td></td>
<td>Semiconductors</td>
</tr>
<tr>
<td></td>
<td>Insulators</td>
</tr>
</tbody>
</table>
Ionic Conductivity

The temperature dependence of the mobility of the ions can be expressed by an Arrhenius equation.

\[ \mu \propto \exp\left(\frac{-E_a}{kT}\right) \quad \text{or} \quad \mu = \mu_0 \exp\left(\frac{-E_a}{kT}\right) \]

where \( \mu_0 \) is a proportionality constant known as the pre-exponential factor.

\( \mu_0 \) depends on the attempt frequency (frequency of vibration of the lattice \( 10^{12} - 10^{13} \) Hz), distance moved by ion, and the size of the external field.

If the external field is small (up to 300 V cm\(^{-1}\)), a temperature dependence of 1/T is present in the pre-exponential factor.

An expression for the variation of ionic conductivity:

\[ \sigma = \frac{\sigma_0}{T} \exp\left(\frac{-E_a}{T}\right) \]

The term \( \sigma_0 \) contains \( n \) and \( Z e \) as well as the attempt frequency and jump distance. Taking logs...

\[ \ln \sigma T = \ln \sigma_0 - \frac{E_a}{T} \]

Plotting \( \ln \sigma T \) vs 1/T should produce a straight line with a slope of \(-E_a\). 

\( \ln \sigma \) vs 1/T is also used.

Conductivities of Solid Electrolytes vs Temperature
Differences in slopes are evident, even in very pure crystals.

- At low temperatures extrinsic vacancies are most important.
  - The concentration of intrinsic vacancies are so small at low temperature that they may be ignored.
  - The number of vacancies will be essentially constant.
  - $\mu$ in the extrinsic region thus will only depend on the cation mobility due to extrinsic defects, with the temperature dependence:
    $$\mu = \mu_0 \exp\left(\frac{-E_a}{kT}\right)$$

At high temperatures the concentration of intrinsic defects has increased so that it is similar or greater than the concentration of extrinsic defects

$$n_i \approx N \exp\left(\frac{-\Delta H_s}{2kT}\right)$$

The conductivity in this intrinsic region on the left side of the plot:

$$\sigma = \frac{\sigma'}{T} \exp\left(\frac{-E_s}{2RT}\right) \exp\left(\frac{\Delta H_s}{2kT}\right)$$

A plot of $\ln\sigma T$ vs $1/T$ gives a larger value for the activation energy ($E_s$), because it depends on both the activation energy for the cation jump ($E_a$) and the enthalpy of formation of a Schottky defect. $E_s = E_a + 1/2\Delta H_s$

For a system with Frenkel defects, $E_F = E_a + 1/2\Delta H_F$

Activation energies typically lie in the range of 0.05 to 1.1 eV.

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**Solid Electrolytes**

Ionic conductivity of solids is important towards the development of solid state batteries.

- Primary batteries are not reversible and are discarded after use.
- Secondary or storage batteries are reversible and significant research is performed to improve properties of materials.
Fast ion conductors: α-AgI

α-AgI exists as two phases below 146°C

γ-AgI (zinc blende) and β-AgI (wurtzite), both \( \rightarrow \) ccp I-

above 146°C α-AgI has I- in body centered cubic arrangement.

The conductivity of α-AgI is very high, \( \sim 10^4 \) higher than γ-AgI & β-AgI.
There are many possible positions for the Ag\(^+\) to occupy, 6 are distorted octahedral, 12 are ~tetrahedral, and 24 are trigonal, giving 42 possible sites.

Structural determinations indicate the Ag\(^+\) ions are statistically distributed among the twelve tetrahedral sites.

There are five spare sites available per Ag\(^+\) atom.

Silver moves from site to site by jumping though a vacant trigonal site, changing the coordination from 4-3-4, the activation energy is very low, 0.05 eV.

Described as a molten sublattice of Ag\(^+\).

**Fast ion conductors: RbAg\(_4\)I\(_5\)**

The 146°C is higher than desired for many applications, so a search for other solids with high ionic conductivity resulted in RbAg\(_4\)I\(_5\).

- Has an ionic conductivity of 25 S/m and activation energy of 0.07 eV.
- The Rb\(^+\) and I\(^-\) form a rigid array while the Ag\(^+\) ions are randomly distributed over a network of tetrahedral sites.

A conducting solid electrolyte must have high ionic conductivity, but negligible electronic conductivity (otherwise a short circuit).

- A cell may be constructed with Ag and RbI\(_3\) electrodes.

- Cells constructed operate between -55 to +200°C, have long shelf life, and can withstand mechanical shock.

<table>
<thead>
<tr>
<th>Anion Structure</th>
<th>bcc</th>
<th>ccp</th>
<th>hcp</th>
<th>other</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Agl</td>
<td>α-Cul</td>
<td>β-CuBr</td>
<td>RbAg(_4)I(_5)</td>
<td></td>
</tr>
<tr>
<td>α-CuBr</td>
<td>α-Ag(_3)Te</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Ag(_2)S</td>
<td>α-Cu(_2)Se</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Ag(_2)Se</td>
<td>α-Ag(_2)Hgl</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- |
Fast ion conductors: oxygen ion conductors

Fluorite structure has some empty space that may enable an F⁻ ion to move into an interstitial site. Some fluorites (PbF₂) exhibit low ionic conductivity at room temperature, but increases to ~500 S/m at 500°C.

- Many oxides also adopt the fluorite structure (UO₂, ThO₂, CeO₂)
- Nernst found that mixed oxides of Y₂O₃ and ZrO₂ glowed white hot if an electrical current passed, which was attributed to conduction of oxide ions.
- These doped zirconia oxides were used for filaments in ‘glower’ electric lights.
- The cubic form of ZrO₂ (fluorite) is formed at high temperature or when doped with another element.
- Addition of either Y₂O₃ (yttria stabilized zirconia, YSZ) or CaO to ZrO₂

- If Ca²⁺ ions are located on Zr⁴⁺ sites, then compensating vacancies are created in the O²⁻ sublattice.
- Ca-doped ZrO₂ are very good fast-ion conductors of O²⁻ ions.
- Conductivity maximizes at relatively low concentrations of dopant, when the crystal lattice is distorted as little as possible.
- Two of the best oxygen ion conductors are ZrO₂ doped with Sc₂O₃, and CeO₂ doped with Gd₂O₃, and others based on CeO₂, ThO₂, HfO₂, and ZrO₂ are doped with other transition metals.
**Oxygen ion conductors: Other**

**Perovskite:**
Materials based on the perovskite lanthanum gallate, LaGaO$_3$, doped with Sr$^{2+}$ and Mg$^{2+}$, produce La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-d}$ (LSGM).

- Has similar conductivities to zirconias, but at a lower operating temperature.
- For a cathode material in a solid oxide fuel cell, a material is needed that can conduct both ions and electrons. The Sr$^{2+}$ doped LaMnO$_3$ (LSM) and LaCrO$_3$ (Sr) have both these properties.

**LAMOX:**
- Materials based on La$_3$Mo$_2$O$_9$ has high conductivity above 600°C, but tend to be susceptible to reduction by hydrogen.

**BIMEVOX:**
- Materials based on Bi$_2$O$_3$ have high conductivity above 600°C

**Apatite:**
- Structure based on La$_{10-x}$M$_6$O$_{26+y}$ (M = Si, Ge) conduct well at high temperatures.

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**Fast-Ion conductors: sodium ion conductors**

- β-alumina is a series of compounds that exhibit fast-ion conducting properties.
- Parent compound is sodium β-alumina, NaAl$_{11}$O$_{17}$
- General formula is M$_2$O-$n$X$_2$O$_3$, where $n$ can range from 5 to 11 and M is a monovalent cation (alkali metal)$^+$, Cu$^+$, Ag$^+$, NH$_4^+$, and X is a trivalent cation Al$^{3+}$, Ga$^{3+}$, or Fe$^{3+}$.
- High conductivity of the compound is related to the crystal structure.
- Close-packed layers of oxide ions, but in every fifth layer three-fourths of the oxygens are missing. The four close packed layers contain Al$^{3+}$ ions in both octahedral and tetrahedral holes. The Na$^+$ are found in the fifth oxide layer [B(ABCA) C (ACBA) B]. Na$^+$ ions move in the conduction plane.
NaZr$_2$(PO$_4$)$_3$ (NZP) consists of corner-linked ZrO$_6$ octahedra joined by PO$_4$ tetrahedra, each of which corner-shares to four octahedra.

- This arrangement creates a 3D system of channels with two types of vacant sites:
  - Type I – a single distorted octahedral site occupied by Na$^+$ ions in NZP.
  - Type II – a larger vacant site

- The structure type is very versatile and hundreds of compounds adopt it by varying the charge balancing 'A' cation with alkali or alkaline earth metals, the structural 'M' cation with transition metal, Ti, Zr, Nb, Cr, or Fe, and the P may be substituted with Si.

- The NASICON (Na SuperIonic Conductor) has a conductivity of 20 S/m at 300°C and has the formula Na$_3$Zr$_2$(PO$_4$)(SiO$_4$)$_2$ and has three out of the four vacant sites occupied by Na$^+$. 

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**Solid State Ionic Devices**

![Diagram of Solid State Ionic Devices]

**Batteries**

![Diagram of Batteries]

**Fuel Cells**

![Diagram of Fuel Cells]

**Electrochromic Devices**

![Diagram of Electrochromic Devices]
A battery is an electrochemical cell that produces an electric current at a constant voltage as a result of a chemical reaction.

- Ions travel through an electrolyte and are oxidized or reduced at the electrode.
  - Oxidation occurs at the anode.
  - Reduction occurs at the cathode.
- The solid electrolyte must have high conductivity of ions, but not electrons (electronic insulator).
- The electromotive force (emf), or voltage, produced by the cell under standard open circuit conditions is related to Gibb’s free energy.

\[ \Delta G^\circ = -nE^\circ F \]

where \( n \) is the number of electrons transferred in the reaction, \( E^\circ \) is the standard emf of the cell (voltage delivered under standard, zero-current conditions) and \( F \) is the Faraday constant (96485 C/mol or 96485 J/V).

- Energy stored in a battery is related to the energy generated by the cell reaction and the amount of material used.
- Typically expressed in watt-hours (current* voltage* discharge time)

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### Lithium batteries

**Energy density** (watt-hours/battery volume in L) or specific energy (watt-hours divided by battery weight in kg) is a more useful indicator in applications where size or weight is critical.

- LiI has relatively low ionic conductivity, but was used in heart pacemaker batteries in the early 1970’s, where a low current, small, long lasting, and generate no gases during discharge.

\[ \text{Anode A: } 2\text{Li(s)} \rightarrow 2\text{Li}^+(s) + 2e^- \quad \text{Cathode C: } \text{I}_2(s) + 2e^- \rightarrow 2\text{I}^-(s) \]

- LiI contains intrinsic Schottky defects and the small Li\textsuperscript{+} cations are able to pass through the solid electrolyte, while the electrons travel through the circuit to perform work.
Sony developed rechargeable lithium-ion batteries that are able to undergo many charge-discharge cycles.

- The lightweight batteries find use in many applications from mobile phones and laptop computers, etc.
- Driving reaction is that of Li with CoO\(_2\) to form an intercalation compound, Li\(_x\)CoO\(_2\) and anode is Li in graphitic carbon.

A \[ Li/C // Li^+ \text{ electrolyte // CoO}_2 \]

- Electrode reactions are:
  - **Anode A**: \( Li_xC_6(s) \rightarrow xLi^+ + 6C + xe^- \)
  - **Cathode C**: \( xLi^+ + CoO_2(s) + xe^- \rightarrow Li_xCoO_2(s) \)
Na\(^+\) conduction has been used in a high-temperature secondary battery, the sodium sulfur battery.

- Uses NASICON and β-alumina as the electrolyte.
- 110 Wh/kg, with lightweight Na and energetic rxn.
- Electrolyte separates molten sulfur/molten sodium

\[
\begin{align*}
\text{Anode A:} & \quad 2\text{Na(l)} \rightarrow 2\text{Na}^+ + 2e^- \\
\text{Cathode C:} & \quad 2\text{Na}^+ + 5\text{S(l)} + 2e^- \rightarrow \text{Na}_2\text{S}_5(l) \\
\text{Overall Reaction:} & \quad 2\text{Na(l)} + 5\text{S(l)} \rightarrow \text{Na}_2\text{S}_5(l)
\end{align*}
\]

- Reaction is completed when low polysulfides are formed, terminating with Na\(_2\)S\(_3\)

- Wind to battery project

**Sodium batteries**

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**Zebra batteries**

Uses β-alumina as a Na\(^+\) ion conductor:

- Nickel chloride or a mixture of ferrous and nickel chlorides are used as the cathode.
- Current flow is improved by adding a second liquid electrolyte, molten NaAlCl\(_4\) between the electrode and the β-alumina
- Overall cell reaction is 2Na + NiCl\(_2\) \rightarrow Ni + 2NaCl
- Has high specific energy > 100 Wh/kg and gives electric vehicles a range of up to 250 km.
- Fully rechargeable, safe, and need no maintenance to over 100,000 km
Fuel cells differ from conventional batteries in that the fuel is fed in externally to the electrodes.

• **Advantage:** cell can operate continuously as long as fuel is available, unlike a battery that must be discarded (primary) or recharged (secondary).

• The fuels used are usually hydrogen and oxygen (air), which react electrochemically to produce water, electricity and heat.

• **H**₂ is fed to the anode where it is oxidized to **H**⁺ ions and electrons.
  • Electrons travel through the external circuit and the **H**⁺ ions travel through the electrolyte to the cathode, where they react with **O**₂⁻.

• The reaction process is ‘green’ with byproducts of water and heat.

• The low temperature of the reaction means **NO**ₓ are avoided.

• Efficiency is up to about 50% or more, compared to 15-20% for ICE and 30% for diesel engines.

• Reduction of oxygen at the cathode is rather slow at low temperatures, therefore a Pt catalyst is incorporated into the carbon electrodes.
A  B  C
H₂(g)//Pt/C electrode// hydrogen electrolyte //Pt/C electrode//O₂(g)

- Electrode reactions are:
  Anode A: H₂(g) → 2H⁺ + 2e⁻
  Cathode C: 1/2O₂(g) + 2H⁺ +2e⁻ → H₂O

- The theoretical emf is E° = 1.229 V at 298K, but decreases to ~1 V at 500 K, so a compromise is needed between voltage and operating temperature.

- Hydrogen storage is difficult, as well as the transportation (heavy cylinders for transportation), and changeover of the current infrastructure.

- Production of very pure hydrogen is energy intensive, thus cheap sources of electricity must be found (solar, hydroelectric, nuclear) or through the use of reforming reactions from methane or methanol with steam to produce hydrogen and CO₂.

**Fuel Cells**

**Phosphoric Acid Fuel Cell (PAFC)**

- Anode reaction: H₂ → 2H⁺ + 2e⁻
- Cathode reaction: ½O₂ + 2H⁺ + 2e⁻ → H₂O

**Temperature: 160-220°C**

**Efficiency**

- Present: 40%
- Projected: 45%
**Alkaline Fuel Cell (AFC)**

Temperature: 60-90°C
Efficiency: present, 40%; projected, 50%

Anode reaction:

\[ \text{H}_2 + 2 \text{OH}^- \rightarrow \text{H}_2\text{O} + 2\text{e}^- \]

Cathode reaction:

\[ \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2 \text{OH}^- \]

Product: H\text{O} + waste heat

**Molten Carbonate Fuel Cell (MCFC)**

Temperature: 600-660°C
Efficiency: present, 45%; projected, 50-60%

Anode reaction:

\[ \text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^- \]

Cathode reaction:

\[ \frac{1}{2} \text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-} \]

Product: H\text{O} + waste heat
Direct Methanol Fuel Cell (DMFC)

Technical Specifications:
- Power: 0.50W (continuous)
- Voltage: 3.7 - 4.5V DC
- Ambient Temperature: 0°C to +40°C
- Fuel Consumption: 1.3 Methanol/Wh at continuous operation
- Weight: App. 8g (without fuel cartridge)
- Fuel Cartridges: M5, M10, M20
- Fuel: Methanol

Anode reaction: \(\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^-\)

Cathode reaction: \(\frac{3}{2} \text{O}_2 + 6 \text{H}^+ + 6 \text{e}^- \rightarrow 3 \text{H}_2\text{O}\)

Product: \(\text{H}_2\text{O}, \text{CO}_2\) + waste heat

Polymer Electrolyte Fuel Cell (PEFC)

Technical Specifications:
- Temperature: 50-85°C
- Efficiency:
  - Present: 43%
  - Projected: 50%

Anode reaction: \(\text{H}_2 \rightarrow 2 \text{H}^+ + 2\text{e}^-\)

Cathode reaction: \(\frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}\)

Product: \(\text{H}_2\text{O}\) + waste heat

http://www.udomi.de
SOFC's employ a ceramic oxide (ceria- or yttria-doped zirconia, Y$_2$O$_3$/ZrO$_2$), which becomes O$^{2-}$ conducting at very high temperature (800-1000°C) and requires heating, but at this temperature reforming and H$^+$ production can take place internally without Pt.

H$_2$(g)*/electrode*/ solid oxide electrolyte */ electrode*/O$_2$(g)

• Electrode reactions are:

  Anode A:  H$_2$(g) + O$^{2-}$ → H$_2$O + 2e$^-$
  Cathode C:  1/2O$_2$(g) + 2e$^-$ → O$^{2-}$

• The solid oxide electrolyte can withstand the extreme conditions of H$_2$ at the anode at 800°C. (many oxides would be reduced)

• Cathode materials must be able to conduct both oxide ions and electrons, and must similar thermal expansion coefficients as the electrolyte.
Proton Exchange Membrane Fuel Cells (PEM)

Proton Exchange Membrane Fuel Cells operate at ~80°C
- Electrolyte is a conducting polymer membrane (Nafion), which is a sulfonated fluoropolymer.
- The strongly acidic –SO₂OH group allows movement of H⁺, but not e⁻.
- Output voltage is ~1V at 80°C with a current flow of 0.5A/cm²
  - Ohmic losses reduce this to 0.5V
  - A membrane of 1 m² provides about 1 kW
- Cells are placed together to form a stack
- Large fuel cells are produced and can power banks, hospitals (250 kW)
- Medium cells (7 kW) can power a house and heat hot water. Fuel cells powered the Space Shuttle.

\[ \text{Anode A: } H_2(g) \rightarrow 2H^+ + 2e^- \]
\[ \text{Cathode C: } \frac{1}{2} O_2(g) + 2H^+ + 2e^- \rightarrow H_2O \]
\[ \text{Overall: } H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \]

Sensors: Oxygen meters and oxygen sensors

CSZ is used in O₂ detection, in oxygen meters and oxygen sensors.
- Gas pressures tend to equalize, and if $p' > p''$ oxygen ions pass through the stabilized zirconia.
- A potential difference, because the ions are charged, is formed, indicating the oxygen is present (in the sensor) and a measurement of the potential gives the oxygen pressure difference (in the oxygen meter).
Sensors: Oxygen meters and oxygen sensors

Oxygen gas is reduced to O\textsuperscript{2-} at the right-hand electrode (C). The oxide ions are able to pass through the doped zirconia and are oxidized to oxygen gas at the left-hand electrode (A).

- Electrode reactions are:
  
  **Anode A:** \( 2O\textsuperscript{2-} \rightarrow O\textsubscript{2}(p") + 4e^- \)
  
  **Cathode C:** \( O\textsubscript{2}(p') + 4e^- \rightarrow 2O\textsuperscript{2-} \)
  
  **Overall:** \( O\textsubscript{2}(p') \rightarrow O\textsubscript{2}(p") \)

Under standard conditions, the change in Gibb’s Free energy is related to the standard emf of the cell:

\[ \Delta G^o = -nE^oF \]

**Nernst equation** - allows calculation of the cell emf under nonstandard conditions, \( E \). Assume the cell reaction is given by a general equation: \( aA = bB + ... + ne \rightarrow xX yY + ... \)

\[ E = E^o - \frac{2.303RT}{nF} \log \left( \frac{a_x}{a_y} \right) \]

where the quantities \( a_x \) are the activities of the reactants and products.

Applying the Nernst equation to the cell reaction in an oxygen meter:

\[ E = E^o - \frac{2.303RT}{4F} \log \left( \frac{p_x}{p'} \right) \]

\( E^o \) is zero, since under standard conditions the oxygen pressure is equal.

- Typically the pressure of the oxygen on one side of the cell (\( p" \)) is set to be a known reference pressure, usually either pure oxygen at 1 atm or atmospheric oxygen pressure (~0.21 atm).

\[ E = E^o - \frac{2.303RT}{4F} \log \left( \frac{p'}{p_{ref}} \right) \]

- All of the quantities in the equation are known or can be measured, enabling a direct measure of the unknown oxygen pressure \( p' \).

- In order for a oxygen sensor of meter to operate, there must not be any electronic conduction through the electrolyte.

- Oxygen meters find use in detection of waste gases in chimneys, exhaust pipes, etc.

- Sensors for other gases operate using different electrolytes in the detection of H\textsubscript{2}, F\textsubscript{2}, Cl\textsubscript{2}, CO\textsubscript{2}, SO\textsubscript{x}, NO\textsubscript{x}. 
Electric current is applied to the cell, causing a movement of ions through the electrolyte and creating a colored compound in one of the electrodes.

Li⁺ ions flow from the anode, through the colorless electrolyte to form Li₃WO₃ at the cathode, changing it from colorless to deep blue.


The film used for the switchable mirror is made of an alloy of magnesium and one or more transition-metals.

Thin Ni-Mg films, on exposure to hydrogen gas or on reduction in alkaline electrolyte, the films become transparent. The transition is believed to result from formation of nickel magnesium hydride, Mg₂NiH₄.

http://eetd.lbl.gov/12m2/tms-mirrors.html
Crystals of alkali halides become brightly colored when exposed to X-rays. A color center is known as a Farbenzentrum (F-center).

Electron Spin Resonance (ESR) spectroscopy confirms the presence of unpaired electrons trapped at vacant lattice (anion site).

A H-center may also be formed by heating NaCl in Cl₂ gas, with the Cl⁻ ion occupying an anion site.
Impurity induced defects are extrinsic and maintain charge neutrality.

Color centers in NaCl may be formed by heating in the presence of Na vapor, becoming Na$_{x}$Cl, where the sodium atom occupies cation sites, creating anion vacancies. The sodium atoms oxidize to form a sodium cation with an electron at the anion vacancy.

• The resulting compound is known as a non-stoichiometric compound because the number of atomic components is no longer 1:1.

• Ionic compounds may also be non-stoichiometric when it contains an element with a variable valency, then a change in the number of ions of that element can be compensated with changes in ion charge.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Composition range</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_x$</td>
<td>[≈TiO] 0.65 $&lt;$ x $&lt;$ 1.25</td>
</tr>
<tr>
<td>V$_{O_x}$</td>
<td>[≈VO] 0.79 $&lt;$ x $&lt;$ 1.29</td>
</tr>
<tr>
<td>Mn$_{1-x}O$</td>
<td>0.849 $&lt;$ x $&lt;$ 1.000</td>
</tr>
<tr>
<td>Fe$_{1-x}O$</td>
<td>0.833 $&lt;$ x $&lt;$ 0.957</td>
</tr>
<tr>
<td>Co$_{1-x}O$</td>
<td>0.988 $&lt;$ x $&lt;$ 1.000</td>
</tr>
<tr>
<td>Ni$_{1-x}O$</td>
<td>0.999 $&lt;$ x $&lt;$ 1.000</td>
</tr>
<tr>
<td>Ce$_{1-x}O$</td>
<td>1.50 $&lt;$ x $&lt;$ 1.52</td>
</tr>
<tr>
<td>Zr$_{1-x}O$</td>
<td>1.700 $&lt;$ x $&lt;$ 2.004</td>
</tr>
<tr>
<td>U$_{1-x}O$</td>
<td>1.65 $&lt;$ x $&lt;$ 2.25</td>
</tr>
<tr>
<td>Li$_x$WO$_3$</td>
<td>0$&lt;$ x $&lt;$ 0.50</td>
</tr>
</tbody>
</table>

• Isolated point defects are not randomly located in non-stoichiometric compounds, but are dispersed in a regular pattern.

• Conventional XRD gives average structure, local structure may be investigated using high resolution electron microscopy (HREM) and direct lattice imaging.

Non-stoichiometry in Wustite (FeO)

Ferrous oxide, or wustite (FeO) has the NaCl structure type.

• Chemical analysis indicates it is non-stoichiometric and always deficient in iron. Stoichiometric FeO isn’t stable, and below 570°C disproportionates into α-Fe and Fe$_3$O$_4$.

• Iron deficiency may be accommodated in the structure on one of two ways:
  1. Iron vacancies, giving Fe$_{1-x}$O
  2. Excess of oxygen in interstitial positions, giving FeO$_{1+y}$
It is often found that non-stoichiometric compounds have a unit cell size that varies smoothly with composition but has symmetry that is unchanged, which is known as Vegard's Law.

<table>
<thead>
<tr>
<th>O:Fe ratio</th>
<th>Fe:O ratio</th>
<th>Lattice parameter (pm)</th>
<th>Observed density (g/cm³)</th>
<th>Interstitial O (g/cm³)</th>
<th>Fe Vacancies (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.058</td>
<td>0.945</td>
<td>430.1</td>
<td>5.728</td>
<td>6.075</td>
<td>5.742</td>
</tr>
<tr>
<td>1.075</td>
<td>0.930</td>
<td>429.2</td>
<td>5.658</td>
<td>6.136</td>
<td>5.706</td>
</tr>
<tr>
<td>1.087</td>
<td>0.920</td>
<td>428.5</td>
<td>5.624</td>
<td>6.181</td>
<td>5.687</td>
</tr>
<tr>
<td>1.099</td>
<td>0.910</td>
<td>428.2</td>
<td>5.613</td>
<td>6.210</td>
<td>5.652</td>
</tr>
</tbody>
</table>

Compensation for iron deficiency is energetically more favorable to oxidize Fe(II), requiring the oxidation of two Fe²⁺ to Fe³⁺ for every Fe²⁺ cation vacancy.

- In the case of excess metal, neighboring cations would be reduced.
- In the case of an Fe²⁺ vacancy, the two Fe³⁺ vacancies are determined to be neighboring as confirmed by Mossbauer spectroscopy.
- Some Fe³⁺ ions are found to be in a tetrahedral site.
- If the tetrahedral site is occupied, then the thirteen neighboring octahedral Fe²⁺ sites are empty.
- This type of defect is found for low values of x.
- At high values of x, the structure contains various types of defect clusters, one possibility is a Koch-Cohen cluster.
• A defect cluster is a region of the crystal where defects form an ordered structure.
  
• Surrounding the central defect unit cell, the other octahedral iron sites (Fe\textsubscript{oct}) are occupied, but may contain either Fe\textsuperscript{2+} or Fe\textsuperscript{3+}.
  
• Clusters sometimes referred to the ratio of cation vacancies to interstitial Fe\textsuperscript{3+} in tetrahedral holes (13:4).

Above 1127°C, a single oxygen-rich non-stoichiometric phase of UO\textsubscript{2} is found with formula UO\textsubscript{2} to UO\textsubscript{2.25} (U\textsubscript{4}O\textsubscript{9})
  
• Interstitial anions are present in the fluorite structure.
  
• Interstitial O’ causes O” displacement.
  
• A defect cluster, considered as two vacancies, one interstitial of one kind O’, and two of another O”, is called a 2:1:2 Willis cluster.
  
• The movement of the interstitial oxide O’ is along the direction towards the diagonal of the cube face (110) direction, whereas the O” is along cube diagonal (111)
  
• Can consider UO\textsubscript{2} as containing microdomains of U\textsubscript{4}O\textsubscript{9} structure within UO\textsubscript{2}. 
• Composition ranges from TiO$_{0.65}$ to TiO$_{1.25}$, with a stoichiometric 1:1 composition resembling the NaCl-type structure with vacancies in both the metal and oxygen sublattices: 1/6 of Ti and 1/6 of O are missing.

• Vacancies are randomly distributed above 900°C, but below are ordered.

• The structure appears stoichiometric, but contains defects on both the cation and anion sublattices.

• Note that every other atom along every third diagonal plane is missing.

• The new unit cell is monoclinic ($\beta \neq 90^\circ$)

• Vacancies permit sufficient contraction of the lattice to enable 3d orbitals on Ti to overlap, broadening the conduction band and allowing electronic conduction.

Titanium Monoxide (TiO)

• TiO$_{1.25}$ has all of the oxygens present and one in every five Ti missing.

• Ordering produces a superlattice with a different unit cell.

• Formula would be more correctly written as Ti$_{0.8}$O ($\text{Ti}_{1-x}$O) because this indicates the structure contains interstitial vacancies.
The simplest linear defect is a **dislocation** where there is a fault in the arrangement of atoms in a line through the crystal lattice.

Another linear defect is a **screw dislocation**. This occurs when a stress is applied to the crystal and the dislocation of the line of atoms is perpendicular to the stress.
**Antiphase domain:** the grain has the reverse structure from the surrounding structure.

There are also **planar defects** such as **grain boundaries**.

**Chemical twinning** (*planar defects*) contains unit cells mirrored about the twin plane through the crystal.
Non-stoichiometric compounds are found for the higher oxides of tungsten (WO$_{3-x}$), molybdenum (MoO$_{3-x}$), and titanium (TiO$_{2-x}$).

- In these systems a series of closely related compounds with similar formula exist (Mo$_n$O$_{3n-1}$, W$_n$O$_{3n-1}$, and W$_n$O$_{3n-2}$, and Ti$_n$O$_{2n-1}$, where $n$ can take values of 4 and above). The resulting series of oxides is known as a homologous series.

- These compounds have regions of corner-sharing octahedra separated from each other by regions of a different structure known as a crystallographic shear plane.

- The different members of a homologous series are determined by the fixed spacing between the crystallographic shear planes.

- Above 900°C, the WO$_3$ structure is that of ReO$_3$, which has [WO$_6$] octahedra sharing corners with any octahedron lined to four others in the same layer.

- Non-stoichiometry is WO$_{3-x}$ is achieved by some of the octahedra in this structure changing from corner-sharing to edge-sharing.

- Shearing occurs at regular intervals and creates groups of four octahedra which share edges.

- Direction of maximum density of edge sharing groups in the CS plane.

**Crystallographic Shear Planes**

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**WO$_3$**

**WO$_{3-x}$**

= o W o
The four octahedra consist of four W atoms and 18 O atoms.

- 14 of the O are linked to other octahedra and 4 O are involved in edge sharing within the group.
- The overall stoichiometry is given by $4W + (14*1/2)O + 4O = W_4O_{11}$
- If groups of $W_4O_{11}$ are interspersed throughout the $WO_3$ structure, the groups can be written as $WO_{3-x}$.
  - $W_4O_{11} + WO_3 = W_5O_{14}$
  - $W_4O_{11} + 2WO_3 = W_6O_{17}$
  - $W_4O_{11} + 3WO_3 = W_7O_{20}$
  - $W_4O_{11} + 4WO_3 = W_8O_{23}$
- Simplifies to $W_nO_{3n-1}$
The term bronze is applied to metallic oxides that have a deep color (yellow to red or deep purple), metallic luster, and are metallic or semiconducting.

- Color depends on $x$ in Na$_x$WO$_3$.
- Structure is a 3d network of channels throughout the structure, with alkali metals in the channels.
- Three main types of structures:
  1. Cubic, 2. Tetragonal, 3. Hexagonal
- Charge compensation occurs with the M$^+$ presence, reducing the metal M$^{5+}$.
- In the case of K, stability lies in the range of K$_{0.19}$WO$_3$ to K$_{0.33}$WO$_3$, below 0.19 the structure has WO$_3$ intergrown with the hexagonal structure in a regular fashion.
- Layers of hexagonal structure 1 or 2 tunnels wide.
(2.) Planar Intergrowths: Tungsten Bronze

Electron micrograph of intergrowth Ba$_x$WO$_3$
Three-Dimensional Defects: Block Structures

In O-deficient Nb$_2$O$_5$, and mixed oxides of Nb and Ti, and Nb and W, the crystallographic shear planes occur in two sets at right angles to each other.

- Intervening regions of perfect structure change from infinite sheets to infinite columns or blocks, which are known as double shear or block structures.
- Characterized by the cross sectional size of the blocks.
- May also have blocks of two or three different sizes arranged in an ordered fashion, such as the 4x4 and 3x4 blocks in W$_4$Nb$_{26}$O$_{77}$.

High-resolution electron micrograph of W$_4$Nb$_{26}$O$_{77}$

Three-Dimensional Defects: Pentagonal Columns

- Structure consists of a pentagonal ring of five [MO$_6$] octahedra, which when stacked form a pentagonal column with alternating M and O atoms.
- The pentagonal columns fit inside an ReO$_3$ type structure in an ordered way and, depending on the spacing, form a homologous series.
- One example is the Mo$_5$O$_{14}$ structure.
Three-Dimensional Defects: Infinitely Adaptive Structures

- A large number of compounds form in the Ta$_2$O$_5$-WO$_3$ system, built from fitting together pentagonal columns.
- Structure have a wavelike skeleton of pentagonal columns.
- As the composition varies, the 'wavelength' of the backbone changes, giving rise to a huge number of possible ordered structures, known as infinitely adaptive structures.

Electronic Properties of Non-stoichiometric Oxides

Four basic types of compounds are non-stoichiometric:

**Metal excess (reduced metal)**
- Type A: anion vacancies present $\rightarrow$ formula MO$_{1-x}$ (e.g. TiO, VO, ZrS)
- Type B: interstitial cations $\rightarrow$ formula M$_{1+x}$O (e.g. CdO, ZnO)

**Metal deficiency (oxidized metal)**
- Type C: interstitial anions $\rightarrow$ formula MO$_{1+x}$
- Type D: cation vacancies $\rightarrow$ M$_{1-x}$O (e.g. TiO, VO, MnO, FeO, CoO)
**Type A oxides:** Compensate for metal excess with anion vacancies. Two electrons have to be introduced for each anion vacancy, which may be trapped at the vacant anion site. More likely to find electrons associated with the reduction of nearby metal cations from \( \text{M}^{2+} \) to \( \text{M}^+ \).

**Type B oxides:** Have a metal excess incorporated into the lattice in interstitial positions. Most likely that an interstitial atom is ionized, reducing nearby metal cations from \( \text{M}^{2+} \) to \( \text{M}^+ \).

**Type C oxides:** Compensate for the lack of metal with interstitial anions. Charge balance is maintained by creation of two \( \text{M}^{3+} \) cations for each interstitial anion \( (\text{O}^2-) \).

**Conductivity:**

(i) depends on d-orbital overlap – the bigger the overlap the greater the band width and electrons in the band are delocalized over the whole structure.

(ii) interelectronic repulsion tends to keep electrons localized on individual atoms.
**TiO and VO are metallic conductors** – have good overlap between d-orbitals (forming a d-electron band), partly because Ti and V are early in the transition series and the d orbitals have not suffered contraction due to increase nuclear charge as is later in the series.

-TiO also has 1/6 of the Ti and O missing from NaCl structure type, leading to a contraction of the structure and better d overlap.

**MnO, FeO, CoO, and NiO are insulators** – the d-orbitals are too contracted to overlap much, with typical band width 1 eV, and the overlap is not sufficient to overcome the localizing influence of interelectronic repulsions. Gives rise to magnetic properties.

Non-stoichiometric oxides, types A and B metal excess monoxides, have extra electrons to compensate for excess metal in the structure. These electrons can be free to move through the lattice and are not necessarily bound to a particular atom.

-thermal energy is enough to make the electrons move and conductivity increases with temperature (like a semiconductor).

Compounds of type A and B would produce **n-type semiconductors** because the conduction is produced by electrons.

-Consider the conduction electrons (or holes) as localized, or trapped, at atoms or defects instead of delocalized in bands.

-Conduction occurs by jumping or hopping from one site to another under the influence of an electric field.

  -Energetically, electron ‘jumps’ between two valence states (e.g. Zn\(^+\) and Zn\(^{2+}\)), it doesn’t take much energy.

  -These are called **hopping semiconductors** and can be described in the same way as ionic conduction.

- The mobility (\(\mu\)) for a charge carrier (electron or positive hole), is an activated process.

  \[ \mu \text{ is proportional to } e^{-E_a/kT} \]

where \(E_a\) is the activation energy of the hop (0.1 to 0.5 eV).

The hopping conductivity is \(\sigma = ne\mu\)

where \(n\) is the number of mobile charge carriers per unit volume and \(e\) is the electronic charge. \(n\) doesn’t depend on temperature, only on composition.
Compounds of type C and D monoxides have M$^{3+}$ ions, which can be regarded as a positive hole compared to the M$^{2+}$ cation.

• If sufficient energy is available, conduction can be thought to occur via the positive hole hopping to another M$^{2+}$ cation, giving rise to p-type electronic conductivity.
• This type of conductivity is found for MnO, CoO, NiO, and FeO

Non-stoichiometric oxides cover the entire range from metal to insulator.
• Others, such as TiO$_2$ and WO$_3$ require a different description.
• Each structure needs to be examined individually in terms of conductivity.

Doping compounds with an impurity extends the range of properties:

\[
0.5x \text{ Li}_2\text{O} + (1-x)\text{NiO} + 1/4x \text{ O}_2 \rightarrow \text{Li}_x\text{Ni}_{1-x}\text{O}
\]

where Ni$^{2+}$ is oxidized to Ni$^{3+}$, creating a high concentration of positive holes located at Ni cations. This process is known as valence induction. In greatly increase the conductivity range of NiO – at high Li concentration the conductivity approaches that of a metal.