ESP5403 Nanomaterials for Energy Systems

Mixed Conductors and Defect Chemistry

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1

Mixed Conductors

Mixed ionic–electronic conductors (MIECs) are materials that conduct both ions (σ_i) and electronic (σ_e) charge carriers (electrons and/or holes).

It is customary to limit the use of the name MIEC to those materials in which σ_i and σ_e do not differ by more than 2 orders of magnitude

It is also customary to use the term MIEC if σ_i and σ_e are not too low (σ_i, $\sigma_e \geq 10^{-5}$ S/cm)

Examples:
- $CeO_{2-\delta}$ - conducts both oxygen ions and electrons
- $Ag_{2+\delta}S$ with $10^{-3} < \delta < 2.5*10^{-3}$ – diffusion of silver

- $YBa_2Cu_3O_{6+\delta}$ – diffusion of oxygen

2

Ionic transport in MIECs

For ionic conduction in solids to occur, ions have to move through a rather dense matrix (whether crystalline or amorphous) consisting of ionic species of comparable size.

To enable this, three conditions must be fulfilled:
a) an empty site exists in the "forward" direction, into which a conducting ion can move;
b) the propagation of the ion from site to site is not impeded;
c) there is a continuous path of sites, extending from one side of the sample to the other side which fulfil conditions (a) and (b).

Ion transport occurs normally via interstitial sites or by hopping into a vacant site (vacancy motion) or a more complex combination based on interstitial and vacant sites.

These ionic defects (interstitials and vacancies) can be formed in three ways:
a) by thermal excitation: Frenkel pairs of an interstitial and a corresponding vacancy
b) by change of stoichiometry: e.g. $CeO_{2-\delta}$ - change of stoichiometry introduces oxygen vacancies into ceria
c) by doping: formation of mobile interstitial donors as in Li-doped Ge and Li-doped Si. introduction of mobile vacancies as in Gd_2O_3-doped CeO_2, where each pair of Gd cations substituting for a pair of Ce cations introduces an oxygen vacancy on the anion sublattice. These vacancies are mobile at elevated temperatures.

3

Electronic/hole transport in MIECs

Electronic (electron/hole) conductivity occurs via delocalized states in the conduction/valence band (in chemistry, **delocalized electrons** are electrons in a molecule, ion or solid that are not associated with a single atom or a covalent bond).

The electronic conductivity is generated in three ways:
a) thermal excitation,
b) deviation from stoichiometry,
c) doping (except in stoichiometric metals where free electrons are present anyway).

Though, formally, these are the same three ways as are used to generate mobile ionic defects, the mechanisms are quite different:

a) Thermal excitation generates an electron hole pair across the band gap.
b) Deviation from stoichiometry introduces native defects that may act as donors or acceptors. For example, an oxygen vacancy acts as a donor, an oxygen interstitial as an acceptor.
c) Doping may introduce donors or acceptors. Electronic conduction by doping may require also thermal excitation if the donor (acceptor) electronic levels are not degenerate with or above the conduction band (or: degenerate with or below the valence band).

4

Defects in ionic crystal and oxides. Kröger-Vink Notation

Introduction of a concentration α of vacancies to Na^+ sites (or the same concentration of Cl^- interstitials) creates net charge of $-q\alpha N$ in a crystal with N lattice sites → very high energy → $Na_{1-\alpha}Cl$ cannot exist

pure ionic crystals must be perfectly stoichiometric (?)

introduction of impurities with different valence and electronegativity than the host ions can require additional point defects to charge balance
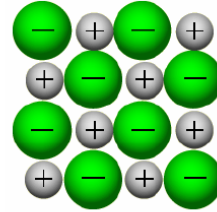
The concentration of vacancies can be much higher than required by *thermal* equilibrium - electrochemical equilibrium must be maintained. How to incorporate point defects into chemical reaction equations?

Kröger-Vink Notation: X_Y^Z

X – nature of species located on a site: element symbol for an atom, V for vacancy

Y – type of the site occupied by X: (i for an interstitial, element symbol for site normally occupied by this element)

Z – charge relative to the normal ion charge on the site
- ′ negative relative charge
- • positive relative charge
- ˣ zero relative charge (ˣ is often omitted)

5

Kröger-Vink Notation X_Y^Z

Examples:

interstitial Ag ion in AgCl:	$Ag_i^\bullet$
vacancy on a Ag site in AgCl:	V_{Ag}'
Ca^{2+} ion on a Na site in NaCl:	$Ca_{Na}^\bullet$
vacancy on an O site in Al_2O_3:	$V_O^{\bullet\bullet}$
Cu^+ on a Cu^{2+} site CuO:	Cu_{Cu}'

In a generic discussion of defect reactions, M and X are often used:

M - atom of electropositive element
X - atom of electronegative element

6

3

Site, mass, and charge balance

Formation and annihilation of point defects in ionic crystals must satisfy the following 3 rules:

1. Site balance

– Ratios of regular lattice sites must be conserved, i.e., fixed proportion of M and X sites must be created regardless of whether they are occupied or not. Total number of sites may change, but the ratio must remain constant.

Example: Al_2O_3: by oxidation of aluminum create $3O_O$ then $2Al_{Al}$ must also be created, although they may be vacant.
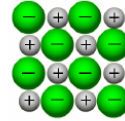
2. Mass balance

– Total number of atoms of each species on right and left side of defect formation reaction must be equal

– Vacancies and electronic defects do not affect mass balance

3. Charge balance (electroneutrality)

– Compounds are assumed to remain neutral

Any charge inbalance, *global* or *local*, leads to high electrostatic energy that exceed any other contributions to the Gibbs free energy, making the charged state to be strongly nonequilibrium one.

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7

Frenkel defects

Frenkel defect (Frenkel pair) = vacancy + interstitial in close proximity
first discussed in 1926 by Frenkel for AgCl
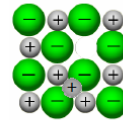
two types of Frenkel defects:

• cation Frenkel pair: cation vacancy + cation interstitial

• anion Frenkel pair: anion vacancy + anion interstitial

Typically, the enthalpies of formation are very different for the two types and, in a given crystal, one type of Frenkel defect is prevalent.

formation reaction for a cation Frenkel pair in AgCl: $Ag_{Ag}^x \leftrightarrow Ag_i^\bullet + V_{Ag}^{'}$

compound	reaction	ΔH_{j_f}, eV
AgBr	$Ag_{Ag}^x \leftrightarrow Ag_i^\bullet + V_{Ag}^{'}$	1.1
CaF$_2$	$F_F^x \leftrightarrow V_F^\bullet + F_i^{'}$	2.3-2.8
	$Ca_{Ca}^x \leftrightarrow Ca_i^{\bullet\bullet} + V_{Ca}^{''}$	7
Li$_2$O	$Li_{Li}^x \leftrightarrow Li_i^\bullet + V_{Li}^{'}$	2.3
TiO$_2$	$O_O^x \leftrightarrow V_O^{\bullet\bullet} + O_i^{''}$	8.7
	$Ti_{Ti}^x \leftrightarrow Ti_i^{\bullet\bullet\bullet\bullet} + V_{Ti}^{''''}$	12
UO$_2$	$O_O^x \leftrightarrow V_O^{\bullet\bullet} + O_i^{''}$	3.0
	$U_U^x \leftrightarrow U_i^{\bullet\bullet\bullet\bullet} + V_U^{''''}$	9.5
ZnO	$O_O^x \leftrightarrow V_O^{\bullet\bullet} + O_i^{''}$	2.5

this reaction satisfies the mass, charge, and site balance
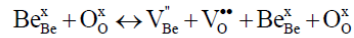
$$n^i = n^v = n^{FP}$$
(Frenkel pair)

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8

4

Schottky defects

Schottky defect = cation vacancy + anion vacancy in close proximity

formation reaction for a Schottky defect in BeO:

$$Be_{Be}^x + O_O^x \leftrightarrow V_{Be}^{''} + V_O^{\bullet\bullet} + Be_{Be}^x + O_O^x$$

compound	Schottky defect	ΔH_s , eV
α-Al_2O_3	$2V_{Al}^{'''} + 3V_o^{\bullet\bullet}$	26
CaF_2	$V_{Ca}^{''} + 2V_F^{\bullet}$	5.5
BeO	$V_{Be}^{''} + V_O^{\bullet\bullet}$	6
TiO_2	$V_{Ti}^{''''} + 2V_O^{\bullet\bullet}$	5.2
UO_2	$V_U^{''''} + 2V_O^{\bullet\bullet}$	6.4
NaCl	$V_{Na}^{'} + V_{Cl}^{\bullet}$	2.2-2.4
KCl	$V_K^{'} + V_{Cl}^{\bullet}$	2.6

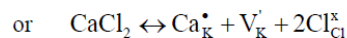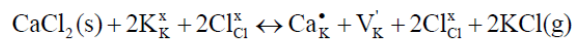} relative low $\Delta H_s \rightarrow$ Schottky defects dominate

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9

Extrinsic point defects in ionic crystals - impurities

Introduction of impurities may require simultaneous introduction of additional defects, e.g., in addition to the thermally-induced (intrinsic) vacancies, some additional *extrinsic vacancies* may be induced by impurity ions with valence different from the one of the ions in the host crystal.

Let's consider incorporation of $CaCl_2$ to KCl crystal as a substitutional impurity:

$$CaCl_2(s) + 2K_K^x + 2Cl_{Cl}^x \leftrightarrow Ca_K^{\bullet} + V_K^{'} + 2Cl_{Cl}^x + 2KCl(g)$$

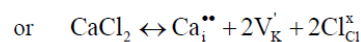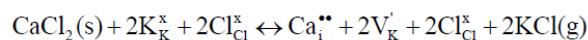$$\text{or} \quad CaCl_2 \leftrightarrow Ca_K^{\bullet} + V_K^{'} + 2Cl_{Cl}^x$$

Site balance: the 1:1 ratio of K and Cl sites must be maintained. Two Cl anions occupy the existing Cl sites $\rightarrow$ two cation sites must be created. One of the cation sites is occupied by Ca^{2+} and one is left vacant.

Mass balance: the numbers of atoms of each species on both sides of the equation are equal.

Charge balance: placing Ca^{2+} on a K^+ gives a net charge of +1 that has to be compensated by a vacancy.

If Ca^{2+} occupies an interstitial site, the equation has to be modified:

$$CaCl_2(s) + 2K_K^x + 2Cl_{Cl}^x \leftrightarrow Ca_i^{\bullet\bullet} + 2V_K^{'} + 2Cl_{Cl}^x + 2KCl(g)$$

$$\text{or} \quad CaCl_2 \leftrightarrow Ca_i^{\bullet\bullet} + 2V_K^{'} + 2Cl_{Cl}^x$$

10

5

Extrinsic point defects in ionic crystals - impurities

Different schemes of impurity incorporation can be sometimes distinguished from experimental measurements of the effect of impurity concentration on material density.
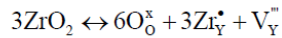
Let's consider incorporation of ZrO_2 to Y_2O_3 crystal

Two simplest options:

(1) Zr^{4+} fully occupy Y sites and anion defects take care of the charge balance

$$2ZrO_2 \leftrightarrow 2Zr_Y^{\bullet} + 3O_O^x + O_i''$$
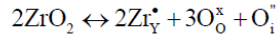
(2) O^{2-} fully occupy O sites and cation defects take care of the charge balance

$$3ZrO_2 \leftrightarrow 6O_O^x + 3Zr_Y^{\bullet} + V_Y'''$$

Experimental observation that density of Y_2O_3 increases with addition of ZrO_2 is in favor of option (1), since appearance of vacancies would decrease density and Zr has slightly higher atomic mass and smaller ionic radius than Y.

In the battery industry, many types of mixed ionic/electronic conductors (MIECs) have been intensively used for the cathode/anode materials.

$LiCoO_2$ spinel is most famous cathode materials of lithium ion secondary battery, which is the largest commercial application for solid ionic materials. This oxide conducts reversible Li insertion/desertion for the discharge/charge processes via coupled with Co redox due to the excellent Li^+ ion electron mixed conductivity, and the Li^+ ion conductivity reaches to 5.0×10^{-6} S/cm even at room temperature.

Recently, $LiMn_{1.5}Ni_{0.5}O_4$ has also attracted much attention as an alternative cathode because of the superior Li^+ ion conductivity at room temperature

Summary of mixed conductors and their application at room temperature

| Mobile ion carrier	MIECs	Crystalline structure	Operating temperature	Conductivity at 25°C / S cm^{-1}	Applications
Li$^+$	LiCoO$_2$	Spinel	rt	5.0×10^{-6}	Cathode of Li battery
	LiMn$_{1.5}$Ni$_{0.5}$O$_4$	Spinel	rt	2.0×10^{-7}	Cathode of Li battery
	LiFePO$_4$	Alluaudite	rt	5.0×10^{-5}	Anode of Li battery
H$^+$	Ni/BaCe$_{1-x}$Y$_x$O$_2$	Perovskite	$T > 700°C$	-	Dense separation membrane Fuel cell anode
O^{2-}	La$_{0.5}$Sr$_{0.5}$CrO$_3$	Perovskite	$T > 500°C$	-	Dense separation membrane
	La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$	Perovskite	$T > 800°C$	1.0×10^{-2}	Fuel cell cathode
	Sm$_{0.5}$Sr$_{0.5}$CoO$_3$	Perovskite	$T > 500°C$	-	Fuel cell cathode
	BiCuVO$_x$	Fluorite	$T > 300°C$	1.0×10^{-3}	Fuel cell cathode
	TiO$_x$, TaO$_x$ thin films	Amorphous	rt	-	Memristive switching
I$^-$	CH$_3$NH$_3$PbI$_3$	perovskite	rt	1.1×10^{-2}	Dye for solar cells

Non-stoichiometry and Oxygen Incorporation
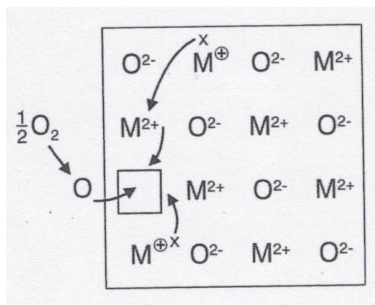
Oxygen incorporation resulting from the jump of an adsorbed oxygen into a vacant site with uptake of two electrons.

In n-type conducting SnO$_{2-\delta}$ (where $\delta \sim 0.1$- 0.5) an increase in oxygen partial pressure of the surroundings leads to drastic reduction in conductivity, according to the equation given below:

$$\frac{1}{2}O_2 + V_O^{\cdot\cdot} + 2e' \rightleftharpoons O_O$$
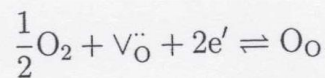
In this case oxygen introduced occupies oxygen vacancies in the lattice. It is incorporated in the form of O^{2-}, and electrons are required for this; these are available in SnO$_2$ in the form of conduction electrons. In other words, we may state that reduced Sn states (Sn^{m+}, m<4) are oxidized and thus annihilated.

If oxygen incorporated in La$_2$CuO$_4$, there are almost no excess electrons in the material, the incorporation of oxygen is associated with the consumption of bonding electrons. Holes are then created in the valance bond and p-type conductivity increases.