2. Electronic and ionic conductivity

Learning subject

1. Classes of conductors
2. Mobility and transport number
3. Conductivity

Learning objective

1. To identify electronic and ionic conductors
2. Understanding concepts of mobility and transport number
3. Understanding the concept of conductivity

Heith B. Oldham, Jan C. Myland, Allan M. Bond, *Electrochemical Science & Technology: Fundamentals & Applications*, Wiley, 2013. (e-book, SNU Library)

1. Classes of conductors

Materials 1.Conductors Electronic conductors

Ionic conductors

2. Insulators

Conductors: metals

Insulators: plastics, ceramics, gases

No clear cut distinction between conductor and insulator

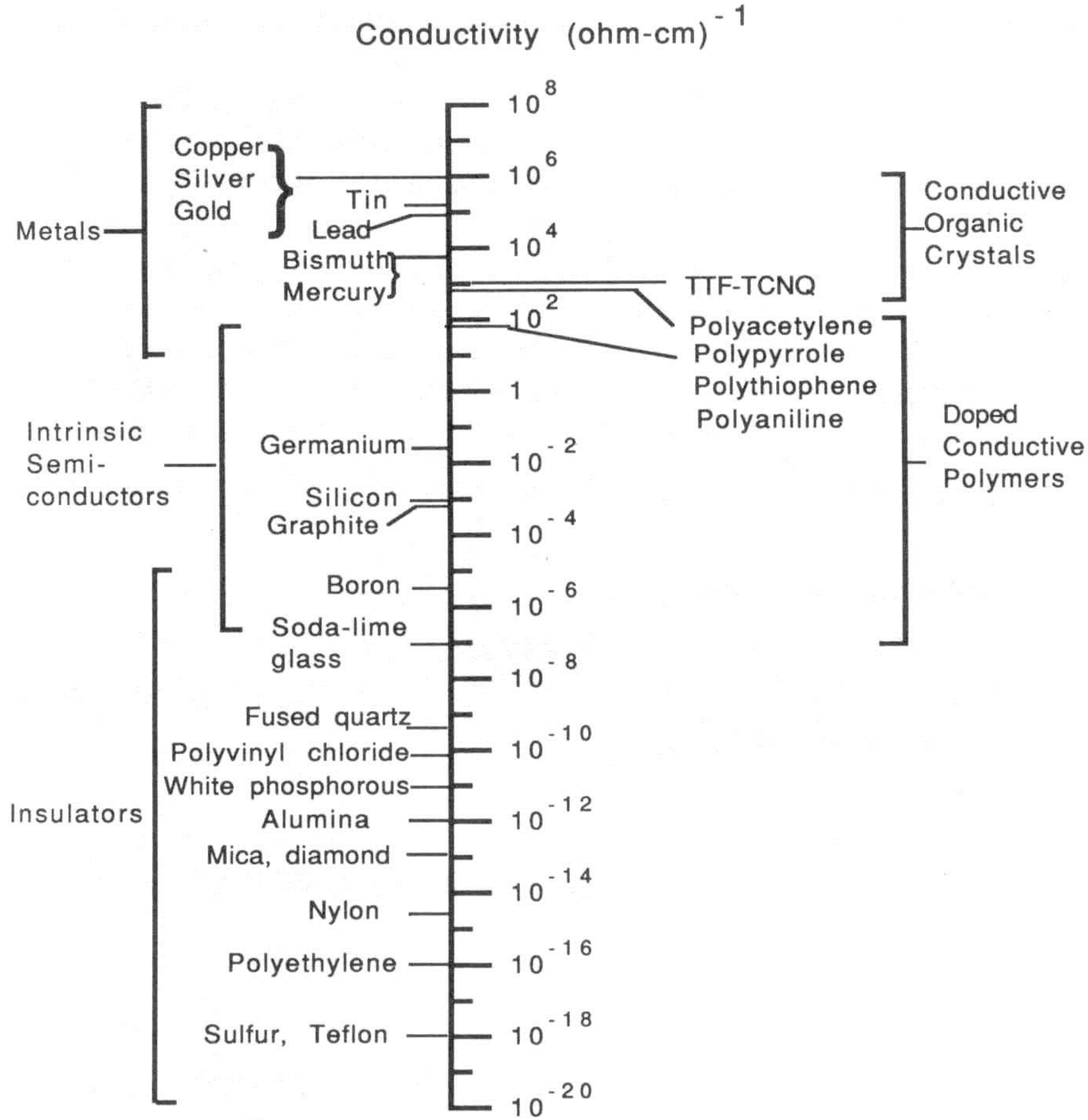
Typical value of electrical conductivity

	Material	κ/Sm^{-1}
Ionic conductors	Ionic crystals Solid electrolytes Strong(liquid) electrolytes	$10^{-16} – 10^{-2}$ $10^{-1} – 10^{3}$ $10^{-1} – 10^{3}$
Electronic conductors	Metals Semiconductors Insulators	$10^{3} – 10^{7}$ $10^{-3} – 10^{4}$ $<10^{-10}$

S/m $\rightarrow$ x10^{-2} for S/cm

Electrical conductivity of various materials (most at 298 K)

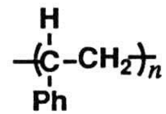
Material	κ/Sm^{-1}	Charge carriers
Superconductors (low temp)	∞	Electron pairs
Ag	6.3×10^7	Electrons
Cu	6.0×10^7	Electrons
Hg	1.0×10^6	Electrons
C (graphite)	4×10^4	Pi electrons
Doped polypyrrole	6×10^3	Pi electrons
Molten KCl (at 1043 K)	217	K^+ and Cl^-
5.2 M H_2SO_4 (battery acid)	82	H^+ and HSO_4^-
Seawater	5.2	Cations & anions
Ge	2.2	Electrons and holes
0.1 M KCl	1.3	K^+ and Cl^-
H2O	5.7×10^{-6}	H^+ and OH^-
Typical glass	3×10^{-10}	Univalent cations
Teflon, $(CF_2)n$	10^{-15}	?
Vacuum & most gases	0	



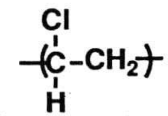
Conductivity (ohm-cm)$^{-1}$
10^{8}
10^{6}
10^{4}
10^{2}
1
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
10^{-14}
10^{-16}
10^{-18}
10^{-20}
Metals
Copper
Silver
Gold
Tin
Lead
Bismuth
Mercury
Intrinsic Semi-conductors
Germanium
Silicon
Graphite
Boron
Soda-lime glass
Insulators
Fused quartz
Polyvinyl chloride
White phosphorous
Alumina
Mica, diamond
Nylon
Polyethylene
Sulfur, Teflon
Conductive Organic Crystals
TTF-TCNQ
Polyacetylene
Polypyrrole
Polythiophene
Polyaniline
Doped Conductive Polymers

Inert

polyethylene

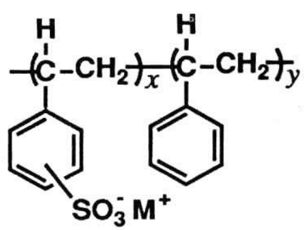


polystyrene

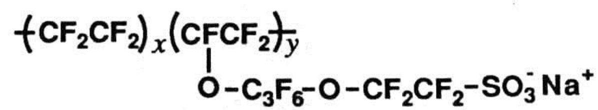


poly(vinylchloride)

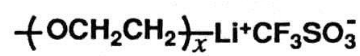
Ion exchange (ionic conductors)



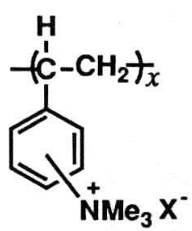
polystyrene sulfonate



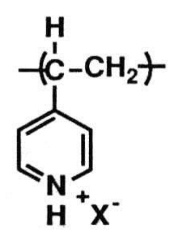
Nafion



polyethylene oxide

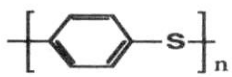
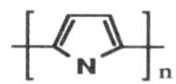
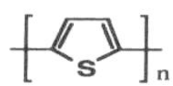
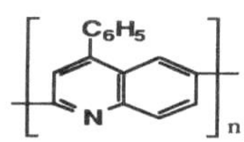
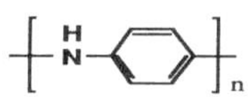


quaternized polystyrene



polyvinylpyridinium

Electronically conductive polymers

polymer	structure	typical methods of doping	typical conductivity $(\text{ohm-cm})^{-1}$
polyacetylene		electrochemical, chemical (AsF_5, I_2, Li, K)	500 (2000 for highly-oriented films)
polyphenylene		chemical (AsF_5, Li, K)	500
poly(phenylene sulfide)		chemical (AsF_5)	1
polypyrrole		electrochemical	600
polythiophene		electrochemical	100
poly(phenylquinone)		electrochemical, chemical (sodium naphthalide)	50
polyaniline		electrochemical	500

Measurement of electrical conductivity

1. Four terminal method: κ calculation from measured I, $\Delta\phi$, A and x

2. a.c. impedance method

The nature of the charge carriers

1) Electronic conductors: mobile electrons; metals, some inorganic oxides and sulfides (e.g., PbO_2 and Ag_2S which are slightly non-stoichiometric), semiconductors (n-type: electrons, p-type: holes, intrinsic: both), conducting polymer (pi-electrons), graphite(pi-electrons), organic metals (organic salts, e.g., TTF-TCNQ(tetrathiafulvalene tetracyanoquinodimethane, pi-electrons)

• Metals: shared valence electrons with all atoms in solid (delocalized electrons) $\rightarrow$ high electric and thermal conductivity

cf: insulator vs. conductor: valence band completely filled vs. partially filled e.g., Diamond (insulator); sp^3 orbital (completely filled valence band), E_g: 5.6 eV

Na (alkali metal); 11 electrons (10 filled 1s & 2p, 1 valence electron 3s (half filled → electric conduction using unfilled part of VB)

Alkaline earth metal (divalent, 12 e's) → good conductors because their valence band overlaps another band

Conductivity of metal increases as temperature lowered or impurities reduced since low resistance

• Semiconductors: E_g is smaller than insulator (1 ~ 2 eV; relatively small excitation energy, cf) 1eV = 12000 K = 1240 nm (1.2 μm (IR)))

Conductivity of semiconductors increases as temperature & impurity concentration increased.

• Semimetals; between metals & semiconductors, e.g., graphite $\rightarrow$ planar sheet of hexagons with weak van der Waals forces (2-dimensional molecule), $E_g = 0$ (top energy level of pi(π)-bonding orbitals (the valence band) is at the same level of that of the anti-bonding orbital

• Conducting polymer: π-electrons

2) <u>Ionic conductors</u>: motion of anions and/or cations; solutions of electrolytes (salts, acids and bases) in water and other liquids, molten salts, solid ionic conductors (solid electrolyte)(O^{2-} in ZrO_2 at high temperature, Ag^+ in $RbAg_4I_5$ at room temperature, fluoride ion holes in EuF_2 doped LaF_3)

3) <u>Electronic & ionic conductors</u>; plasmas (hot gases, positive ions and free electrons), sodium metal in liquid ammonia(Na^+ cation and solvated electrons), hydrogen dissolved in Pd metal(hydrogen ions(protons) and electrons)

- conductors
  - electronic
    - metals
    - some inorganic oxides & sulfides
    - semiconductors
      - n-type
      - intrinsic
      - p-type
    - organic metals
    - conducting polymers
  - mixed
    - plasmas
    - some solids & solutions
  - ionic
    - solutions of electrolytes
    - molten salts
    - solid ionic conductors
    - doped crystals

2. Mobility and transport number

<u>Mobilities</u>: conduction from the standpoint of the charge carriers

Electric current = rate at which charge crosses any plane = [number of carriers per unit volume][cross sectional area][charge on each carrier][average carrier speed]

$$I = dq/dt = (N_A c_i)(A)(q_i)(\nu_i)$$

i: particular charge carrier, c_i; concentration, q_i; charge, ν_i; average velocity,
N_A; Avogadro's constant (6.0220×10^{23} mol^{-1}), A; area
z_i; charge number = q_i/q_e where q_e (1.6022×10^{-19} C),
e.g., electrons:-1, Mg^{2+}; +2

$$\nu_i \propto f_i \propto X \propto d\phi/dx$$

f_i; force exerted on the charge carrier, X; electric field strength

mobility of the carrier, u_i ($m^2s^{-1}V^{-1}$ unit) = velocity to field ratio (ν_i / X)

$$\nu_i = \pm u_i X = -(z_i/|z_i|)u_i d\phi/dx$$

$|z_i|$: absolute value of the charge number

u_{e-} of electrons: 6.7 x 10^{-3} $m^2s^{-1}V^{-1}$ for Ag, less mobile in other metals
mobility of ions in aqueous solution: smaller than the factor of 10^5 (factor 10^5 slower); $u_{cu2+}{}^{o}$ = 5.9 x 10^{-8} $m^2s^{-1}V^{-1}$ in extremely diluted solution

Current I,

$$I = -A N_A q_e |z_i| u_i c_i d\phi/dx$$

Faraday constant

$$F = N_A q_e = (6.02 \text{ x } 10^{23} \text{ mol}^{-1})(1.6022 \text{ x } 10^{-19} \text{ C}) = 96485 \text{ Cmol}^{-1}$$

is numerically equal to the charge carried by one mole of univalent cations.
(F is large. Small amount of chemicals $\longrightarrow$ higher electricity)

If there are several kind of charge carriers,

$$I = -AF d\phi/dx \Sigma |z_i| u_i c_i$$

$$i = -F d\phi/dx \Sigma |z_i| u_i c_i$$

Transport number t_i; the fraction of the total current carried by one particular charge carrier

$$t_i = (|z_i|u_i c_i)/\Sigma(|z_i|u_i c_i)$$

From $i = \kappa X = -\kappa d\phi/dx$,

conductivity κ

$$\kappa = F\Sigma|z_i|u_i c_i$$

molar ionic conductivity (λ_i); Fu_i

Ion mobilities at extreme dilution in aqueous solution at 298 K

Ion	$u^o/m^2s^{-1}V^{-1}$
H^+	362.5×10^{-9}
K^+	76.2×10^{-9}
Ag^+	64.2×10^{-9}
Cu^{2+}	58.6×10^{-9}
Na^+	51.9×10^{-9}
Li^+	40.1×10^{-9}
OH^-	204.8×10^{-9}
SO_4^{2-}	82.7×10^{-9}
Cl^-	79.1×10^{-9}
ClO_4^-	69.8×10^{-9}
$C_6H_5COO^-$	33.5×10^{-9}

cf. u_{e-} of electrons: $6.7 \times 10^{-3}\ m^2s^{-1}V^{-1}$ for Ag

Capacitance

parallel conducting plate separated by a narrow gap containing air or insulator

$$\int I dt = Q \propto \Delta E$$

$$\mathbf{Q = -C\Delta E}$$

C; capacitance (unit; farads (F) = C/V)

$$\mathbf{C = -Q/\Delta E = \varepsilon A/L}$$

A;cross-section area of the gap, L; width, ε; permittivity of the insulator

• Relative permittivity (ε_r) or dielectric constant

air: ~ 1

water: 78 → Coulomb interaction energy is reduced by two orders of magnitudes from its vacuum value

polar molecules: $\varepsilon_r \uparrow$

refractive index: $n_r = \varepsilon_r^{1/2}$ at the frequency

Capacitor; —| |— ; current integrator

Permittivity of various materials

Material	10^{12} ε/Fm^{-1}	Material	10^{12} ε/Fm^{-1}
vacuum (ε_0)	8.85419	Neoprene	58
N_2(g)	8.85905	ClC_2H_4Cl(l)	91.7
Teflon(s), $(CF_2)_n$	18	CH_3OH(l)	288.9
CCl_4(l)	19.7	$C_6H_5NO_2$(l)	308.3
Polyethene (s)	20	CH_3CN(l)	332
Mylar (s)	28	H_2O(l)	695.4
SiO_2(s)	38.1	$HCONH_2$(l)	933
Typical glass (s)	44	TiO_2(s)	≤1500
C_6H_5Cl(l)	49.8	$BaTiO_3$(s)	≤110000

$\varepsilon/\varepsilon_0$; relative permittivity or dielectric constant

mylar; poly(ethylene glycol terephthalate), $(CH_2OOCC_6H_4COOCH_2)_n$

Liquid > solid: large capacitance in electrochemical capacitor (supercapacitor)

3. Conductivity

Electricity flows either by electron motion or ion motion

In both cases,

the intensity of the flow (= current density) $\propto$ electric field strength

$$i = \kappa X = -\kappa d\phi/dx$$

conductivity κ

$$\kappa = F\Sigma|z_i|u_i c_i$$

determined by the concentration of charge carriers and their mobilities

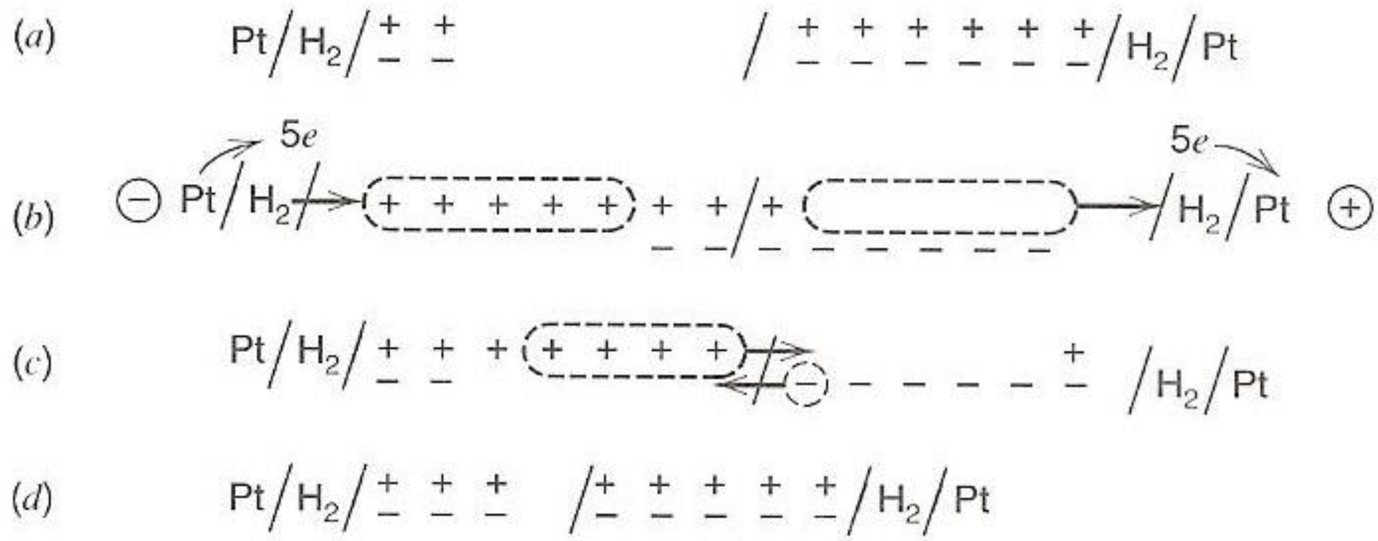
one form of Ohm's law

$$\Delta E = -RI$$

potential difference across resistor to the current flowing through it

Resistor: dissipate energy

Capacitor: store energy



Transference number (or transport number)

The fraction of the current carried by H^+ and Cl^-: t_+ and t_-

$$t_+ + t_- = 1$$

$$\sum t_i = 1$$

e.g., Figure above: $t_+ = 0.8$, $t_- = 0.2$

Conductance ($S = \Omega^{-1}$), $L = \kappa A/l$

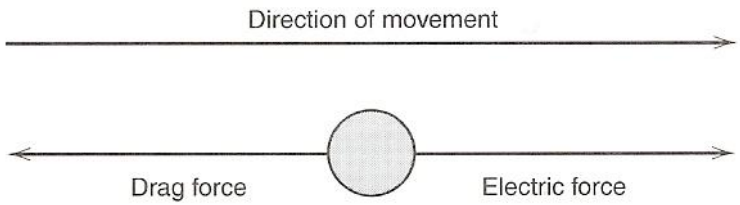
conductivity (κ, Scm^{-1}): contribution from all ionic species

$\propto$ ion conc, charge magnitude ($|z_i|$), index of migration velocity (u_i)

Mobility (u_i): limiting velocity of the ion in an electric field of unit strength

unit: $cm^2V^{-1}s^{-1}$ (cm/s per V/cm)

electric field, E → electric force → counterbalance with frictional drag → terminal velocity



Electric force = $|z_i|eE$ e: electronic charge

Frictional drag (Stokes law) = $6\pi\eta rv$

η :viscosity of medium, r: ion radius, v: velocity

When the terminal velocity is reached:

$$u_i = v/E = |z_i|e/\ 6\pi\eta r$$

Conductivity

$$\kappa = F\sum|z_i|u_iC_i$$

Transference number for species i = conductivity by i /total conductivity

$$t_i = |z_i|u_iC_i/\sum|z_j|u_jC_j$$

For pure electrolytes (e.g., KCl, $CaCl_2$, HNO_3) → equivalent conductivity (Λ)

$$\Lambda = \kappa/C_{eq} \qquad \text{(conductivity per unit concentration of charge)}$$

C_{eq}: concentration of + (or -) charges = $C|z|$

$$\Lambda = F(u_+ + u_-) = \lambda_+ + \lambda_-$$

equivalent ion conductivity, $\lambda_i = Fu_i$

$$t_i = \lambda_i/\Lambda = u_i/(u_+ + u_-)$$

- Table: t_+ → individual ionic conductivities, λ_i
- λ_i, t_i depend on concentration of pure electrolyte because interactions between ions tend to alter mobilities

→ Table : λ_{0i} (extrapolated to infinite dilution) → calculate t_i

For pure electrolyte: $t_i = \lambda_i/\Lambda$

$$t_i = |z_i|C_i\lambda_i/\sum|z_j|C_j\lambda_j$$

Electrolyte	Concentration, C_{eq} [b]			
	0.01	0.05	0.1	0.2
HCl	0.8251	0.8292	0.8314	0.8337
NaCl	0.3918	0.3876	0.3854	0.3821
KCl	0.4902	0.4899	0.4898	0.4894
NH_4Cl	0.4907	0.4905	0.4907	0.4911
KNO_3	0.5084	0.5093	0.5103	0.5120
Na_2SO_4	0.3848	0.3829	0.3828	0.3828
K_2SO_4	0.4829	0.4870	0.4890	0.4910

Ion	λ_0, $cm^2\ \Omega^{-1}\ equiv^{-1}$ [a]	u, $cm^2\ sec^{-1}\ V^{-1}$ [b]
H^+	349.82	3.625×10^{-3}
K^+	73.52	7.619×10^{-4}
Na^+	50.11	5.193×10^{-4}
Li^+	38.69	4.010×10^{-4}
NH_4^+	73.4	7.61×10^{-4}
$\frac{1}{2}Ca^{2+}$	59.50	6.166×10^{-4}
OH^-	198	2.05×10^{-3}
Cl^-	76.34	7.912×10^{-4}
Br^-	78.4	8.13×10^{-4}
I^-	76.85	7.96×10^{-4}
NO_3^-	71.44	7.404×10^{-4}
OAc^-	40.9	4.24×10^{-4}
ClO_4^-	68.0	7.05×10^{-4}
$\frac{1}{2}SO_4^{2-}$	79.8	8.27×10^{-4}
HCO_3^-	44.48	4.610×10^{-4}
$\frac{1}{3}Fe(CN)_6^{3-}$	101.0	1.047×10^{-3}
$\frac{1}{4}Fe(CN)_6^{4-}$	110.5	1.145×10^{-3}