Ion and Electron Transport

Jong Hak Kim
Chemical & Biomolecular Engineering
Yonsei University
Polymer Electrolytes (PEs)

- **Newest solid ionics:** generation, storage, distribution
  - Applications to electrochemical devices
  - Synthesis of new polymer electrolytes
  - Physical studies of their structure & charge transport
  - Theoretical modeling of charge transport processes

- **Charge transport mechanisms**
  - Inorganic: ion “hopping mechanism”
  - PEs: local motion of polymer (*segmental motion*) in the vicinity of ion

- **Two Types**
  - polymer/salt complex: coordination P + salt (PEO/LiClO₄)
  - polyelectrolytes: covalently attached charged group
Solid Ionics

- **Crystalline solid electrolytes**
  - $H^+$, $Li^+$, $Na^+$, $K^+$, $Ag^+$, $F^-$, $O_2^-$, & di- or trivalent ions conductors
  - (i) high concentration of mobile ions
  - (ii) low $E_a$ for ionic motion from site to site
  - conductivity: hopping mechanism along channels
  - crystal structure: 1-, 2-, 3-D network of channels

- **Glass electrolytes**: amorphous solid conductors

- **Molten electrolytes**
  - molten salts or mixtures high conductivities (> 1 S/cm)
  - e.g., LiCl-KCl eutectic (m.p. 355 °C < LiCl at 613 °C)
  - high operation T & corrosion
Polymer electrolytes
- good interfacial contacts with electrode (not brittle)
- Conductivity (by 100 - 1000) < Liq. or ceramic electrolytes
- thin film configuration compensate for the lower values

Conductivity vs. temperature for some of the first studied polymer electrolytes. PESc = poly(ethylene succinate), PEO = poly(ethylene oxide), PPO = poly(propylene oxide), PEI = poly(ethylene imine), MEEP = poly(bis(methoxyethoxyethoxy)phosphazene)
Properties of polymer electrolyte

- adequate conductivity for practical purposes
- low electronic conductivity
- good mechanical properties
- high chemical, electrochemical and photochemical stability
- ease of processing
Fundamentals of polymer electrolyte

1. **Solvent free system**: polymer + salts

2. **Gel electrolyte**: (salt + polar liquid) + inactive polymer

3. **Plasticized electrolyte**: (salt + polymer) + liquid with high dielectric constant

4. **Ionic rubber**: (low T molten salt + liquid) + high $M_w$ polymer

5. **Membrane ionomer**
   - $H^+$ conducting polyelectrolyte, e.g. Nafion. (with plasticizer)
Thermodynamics of salt dissolution

● Salt dissolution: Reduction in $\Delta G$ of the system at constant $T$ & $P$

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

● Overall $\Delta S$ on dissolution
  (+): break up of crystal lattice and the subsequent disordering of ions
  (−): stiffening of chains due to coordination

● Major $\Delta H$ on dissolution
  (+): the lattice energy of salt
  (−): cation solvation
Polymer solvent

- capable of strongly coordinating cations
- polyethers, polyesters, polyimines, polythiols

- **High Mw PEO**
  - poor conductors in crystalline
  - amorphous; loss of mechanical stability

- **Atactic PPO**
  - amorphous due to random arrangement of methyl group

- **Random polyethers**
  \((-\text{OCH}_2\text{CH}_2)_m\text{-OCH}_2\text{-})_n\): amorphous, dimethyl siloxy units

- **Comb, branched copolymers**
  - flexibility of the system & conductivity

- **Networks**
  - higher ionic conductivity & dimensional stability by crosslinking
Host Polymers

Rubbery & Amorphous

- **Poly(ethylene oxide) (PEO)**
  - at $T < 60 \, ^\circ\text{C}$, presence of crystalline part $\rightarrow$ reduce conductivity

- **Atactic poly(propylene oxide), PPO**
  - random arrangement of $\text{CH}_3$
    $\rightarrow$ prevent the order necessary for crystallization
    $\rightarrow$ not best electrolyte (due to steric hindrance of side group)
    1) limits the segmental motion
    2) reduces polymer-cation interaction
● **Poly (methylene oxide), (CH₂O)_n**
  - superficially good due its high conc. polar groups
  - but not good in practice since hard with high cohesive energy

● **Amorphous PEO**
  - Randomly variable length segments of PEO joined by methylene oxide units
  - CH₂O units **break up the regular helical pattern and suppress crystallization**

Fig. 5.13 Methoxy linked poly(ethylene oxide).

● **PEO w/ DMS units**
  - to produce an amorphous polymer

Dimethyl siloxy linked poly(ethylene oxide)
**Comb polymers**
- short chain polyethers attached to polyphosphazene or polysiloxane
- excellent hosts for salts due to high flexibility of backbone

**Branched & Network polymer ionics**
- Microscopically, crosslinking degree must not be so great as to make the local polymer segments rigid, thereby increasing $T_g$
- Strategy: chemical or irradiation crosslinking
Additives

○ Small polar molecules
  - improvement in conductivity
    i) plasticize polymer $\rightarrow$ high flexibility & segmental motion
    ii) solvate ions $\rightarrow$ reduce ion-ion interactions
  - e.g., propylene carbonate (PC)
    $(\text{polymer} + \text{LiClO}_4) + \text{PC} \rightarrow$ high conductivities $(1.7 \times 10^{-3}$ at $20 \, ^\circ\text{C})$

○ Small chelating agents
  - short chain poly(ethylene glycol), cyclic polyethers
  - break up ion-ion interactions
### Other Polymer Hosts

Some coordinating polymers which have been used as solid solvents for polymer electrolytes

<table>
<thead>
<tr>
<th>Name</th>
<th>Monomer unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(propylene oxide)$^a$</td>
<td>$[CH_2CH(CH_3)O]_n$</td>
</tr>
<tr>
<td>Poly(ethylenimine)$^b$</td>
<td>$(CH_2CH_2NH)_n$</td>
</tr>
<tr>
<td>Poly(alkylene sulfides)$^c$</td>
<td>$[(CH_2)_pS]_n$</td>
</tr>
<tr>
<td>Poly(ethylene succinate)$^d$</td>
<td>$[OCH_2CH_2O(C(O)CH_2CH_2C(O))]_n$</td>
</tr>
<tr>
<td>Poly($N$-methylaziridine)$^e$</td>
<td>$[CH_2CH_2N(CH_3)]_n$</td>
</tr>
<tr>
<td>Poly(epichlorohydrin)$^f$</td>
<td>$[OCH_2CH(CH_2Cl)]_n$</td>
</tr>
<tr>
<td>Poly(vinyl acetate)$^g$</td>
<td>${CH_2CH[OC(O)CH_3]}_n$</td>
</tr>
<tr>
<td>Poly[bis(methoxyethoxyethoxy) phosphazene]$^h$</td>
<td>${NP[O(CH_2CH_2O)<em>{2}CH_3]</em>{2}}_n$</td>
</tr>
<tr>
<td>Oxymethylene-linked poly(oxyethylene)$^i$</td>
<td>$[(CH_2CH_2O)_{m}CH_2O]_n$</td>
</tr>
</tbody>
</table>
Salts

● **Polyatomic anions w/ monovalent charge**
  - weak anion solvation
  - e.g., water soluble LiF (strong solvation of F by water)
    \[ \text{LiF insoluble in PEO but LiClO}_4 \text{ soluble} \]

● **Large, polarizable, monovalent anions low lattice E**
  - better dissolution
  - \( \text{ClO}_4^-, \text{CF}_3\text{SO}_3^-, (\text{CF}_3\text{SO}_2)_2\text{N}^-, (\text{CF}_3\text{SO}_2)_3\text{C}^-, \text{AsF}_6^-, \text{PF}_6^- \)
  - I\(^-\) & Br\(^-\) (but Cl\(^-\), F\(^-\) poor solubility)

● **Solvation H depends on cation-polymer interaction**
  - dissolution occurs if atoms which are capable of coordinating the cations are available on the polymer chains
Weaker solvation of \((-\text{CH}_2\text{-O})_n\) & \((-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-O})_n\)
- the chains wrap around cation without excess strain
  → right spacing of \((-\text{CH}_2\text{-CH}_2\text{-O})_n\) unit
- other coordination groups: -NR-, -NH- and -S-

Hard/soft acid base theory (HSAB)
  → HA prefer HB and SA do SB; e.g., polyether vs Li$^+$

1) hard/soft acids
   (a) hard: small cations w/ no valence electrons, e.g., Na$^+$, Li$^+$
   (b) soft: larger cations w/ several valence electrons, e.g. Hg$_2^+$

2) hard/soft bases
   (a) hard: non-polarizable ligand of high electronegativity (-O-)
   (b) soft: more polarizable groups, e.g., thio group
  → -O- > -NH- > -S-
Polyelectrolytes
- polymeric backbones with covalently bonded ionizing groups
- Common functional group: $\text{SO}_3^-, \text{COO}^-, \text{NH}_3^+, =\text{NH}_2^+$

Gel electrolytes
- as alternatives to solvent-free systems $\rightarrow$ higher ionic conductivities
- Formed by dissolving salt in polar liquid and adding polymer network to give the material mechanical stability
- Two methods to achieve macroscopic immobilization of solvent
  1) increase the viscosity of liq. electrolyte by adding soluble polymer, e.g., PEO, PMMA, PAN until gel consistency is achieved
  2) load the liq. electrolyte into microporous matrix, e.g., porous polyethylene
• **Low molecular solvents**
  - propylene carbonate (PC), ethylene carbonate (EC), N,N-dimethyl formamide (DMF), γ-butyrolactone (GBL)
  - high dielectric constant, high B.P.
  - increase salt dissociation
  - low viscosity → high ionic mobility

• **Polymeric materials**: PAN, PVDF, PVC, PMMA

• **Bellcore (USA) Co.**
  - commercially available gel electrolyte (for Li battery)
  - P(VDF-co-HFP) electrolyte + Lisalt + carbonate esters
  - HFP → decrease crystallinity of PVDF & enhance liquid adsorption
  - Hybrid electrolytes: porous polymer + organic solvent
Mechanisms of ion conduction

- ‘dry’ polymer electrolyte: polymer itself is immobile (macroscopically)

→ by the semi-random motion of short polymer segments

*Representation of cation motion in a polymer electrolyte (a) assisted by polymer chain motion only; (b) taking account of ionic cluster contributions*
**Mechanism of Ion transport**

**Solvent & ion transport**

- In low $M_W$; move together w/ their coordinated solvent

- If $M_W > 3200$ g/mol, $M_W$ has no significant effect on cation mobility.
• For high $M_w$,
  - chain diffusion is small and makes little contribution for ion transport
  - motion of ions is strongly dependent on *segmental motion* of the polymer host

● **Dynamic bond percolation theory (DBP)**
  - Microscopic model $\rightarrow$ conductivity due to combination of ion/polymer cooperative motion with the occasional independent ion movement.
  - Time scale for the latter is much shorter than for polymer relaxation, different cation and anion motions.

• cation $\rightarrow$ *making and breaking of coordinate bonds* with motion between coordinating sites

• anion $\rightarrow$ hopping between *occupied site and void*
Macroscopic approach

- **Empirical relationship**: conductivity vs. temperature
  - Crystalline: the classical Arrhenius relation
    \[ \sigma = \sigma_0 \exp \left[ -\frac{E_a}{k_B T} \right] \]
  - Amorphous: the Vogel-Tamman-Fulcher (VTF) equation
    \[ \sigma = \sigma_0 \exp \left[ -\frac{B}{(T-T_0)} \right] \]

- **Free volume-based models**:
  - redistribution of free volume within the system

- **Configurational entropy model**
  - based on entropy, not volume
  - group cooperative rearrangements of polymer chains rather than a void-to-void jumping mechanism
Morphology

● General techniques to characterize structure and morphology
  - optical microscopy, DSC, NMR, XRD

● Phase diagrams

Phase diagram of the PEO–LiClO$_4$ system. The vertical boundaries indicate the formation of 6:1, 3:1, 2:1 and 1:1 crystalline complexes.
Preparative Techniques

- Solvent-free electrolyte film

1) Solvent casting
   casting $\rightarrow$ solvent evap. $\rightarrow$ heating under vacuum

2) Hot pressing method
   - grinding polymer & salt at liquid $N_2$ Temp. $\rightarrow$ hot pressed
     ; totally solvent free

- Gel electrolyte film: importance of polymer matrix
Suitable polymer electrolytes

- **Minimum requirements**
  - ionic conductivity: $10^{-2} - 10^{-3}$ S cm$^{-1}$ ideal at RT
    (min. $10^{-5}$ S cm$^{-1}$ for practical use)
  - electrochemical stability in a voltage window-compatibility:
    chemically & electrochemically compatible with electrodes
  - Thermal stability
  - Mechanical stability
  - Availability: available & inexpensive

- **Electrode-electrolyte interface**
  - different interfacial processes, e.g., electron transfer mechanisms
**Lithium anode**

- Li/PEO $\rightarrow$ **thin layer of third phase** formed b/w two bulk phases

- passive layer composition: **LiF** (for LiCF$_3$SO$_3$) or **Li$_2$O** (for LiClO$_4$)

- inhomogeneous $\rightarrow$ **low ionic conductivity**
**Intercalation cathode**

- provide a mechanism for reversible and kinetically fast solid-state electrochemical reactions
- Li secondary battery, electrochromics, sensors, solar cells

\[ MX_n + aLi^+ + ae^- \rightarrow Li_aMX_n \]

- e.g., \( V_2O_5/PEO \) electrolytes with \( LiClO_4 \)
- two semicircle in a.c. impedance
  - high frequency semicircle; ionically conducting surface layer that grows on the \( V_2O_5 \)
  - low frequency semicircle; charge transfer between surface layer and the electrode
- total interfacial resistance; many times greater than bulk resistance
  - minimize !!
**Nanocomposite polymer electrolytes (Mixed phase)**

- ceramic or glassy electrolytes vs. polymer electrolytes
  - higher conductivity, better thermodynamic stability

- polymer vs. ceramic/glassy electrolytes
  - flexible, superior interfacial contacts
  - processed as thin large area films

- mixed phase PEs-ceramics of nanometer grain size
  ⇒ nanocomposites

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Polymer electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_3$N</td>
<td>PEO–LiCF$_3$SO$_3$</td>
</tr>
<tr>
<td>γ-LiAlO$_2$</td>
<td>PEO–LiClO$_4$</td>
</tr>
<tr>
<td>α-LiAlO$_2$</td>
<td>PEO–LiClO$_4$</td>
</tr>
<tr>
<td>NASICON</td>
<td>PEO–NaI</td>
</tr>
<tr>
<td>α-Al$_2$O$_3$</td>
<td>PEO–LiClO$_4$</td>
</tr>
<tr>
<td>β”-Al$_2$O$_3$</td>
<td>PEO–NaI</td>
</tr>
<tr>
<td>θ-Al$_2$O$_3$</td>
<td>PEO–NaI</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>Zeolite, [(Al$_2$O$<em>3$)$</em>{12}$(SiO$<em>2$)$</em>{12}$]</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>1.2Li$_2$S·1.6LiI·B$_2$S$_3$</td>
<td>Polyethylene</td>
</tr>
</tbody>
</table>
• Conductivity: a beneficial effect of ceramic additives
• Interfacial properties: Improved stability by nanocomposite
  - resistance of interfacial passivation layer

*Variation of interfacial resistance at 70°C under open circuit conditions.*
(●) Li|PEO₈LiBF₄|Li; (□) Li|PEO₈LiBF₄ + 10 wt.% nanosize Al₂O₃|Li; (○) Li|PEO₈LiBF₄ + 20 wt.% nanosize Al₂O₃|Li; (■) Li|PEO₈LiBF₄ + 20 wt.% microsize Al₂O₃|Li
• Why ceramic or glass powder render the interface more stable?

1) Reactivity
   - formation of conducting product (Li$_3$N) to facilitate ion transport

2) Shielding effect
   - ceramic/glass reduce the contact between Li and polymer

*Schematic diagrams of the lithium–composite-electrolyte interface. The smaller particles are able to cover a greater surface area, minimizing the area of lithium electrode exposed to species that give rise to passivation.*
Proton Conducting Membrane

- Thickness: 50~175 μm, equivalent weight: 1,100 mEq/g
- High oxygen solubility, high proton conductivity, low density, high chemical and thermal stability, high water solubility
- H2SO4 solution as pretreatment

**Problem**

- Low water content => low proton conductivity
  - High content => flooding in electrode => inefficient reaction
- Methanol crossover in DMFC
- High cost
Production Company for Membrane

- US: Du Pont (Nafion), Dow Chemical (XUS), W.L. Gore & Associate (Gore-Select)
- Canada: Ballard Advanced Materials (BAM3G)
- Japan: Asahi Chemical (Aciplex), Asahi Glass (Flemion), Chlorine Engineer (Product ‘c’),
- German: Hoechst

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Equivalent weight (g/mol SO₃⁻)</th>
<th>Thickness, dry(μm)</th>
<th>Water content(%)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XUS</td>
<td>800</td>
<td>125</td>
<td>54</td>
<td>0.114</td>
</tr>
<tr>
<td>Aciplex-S</td>
<td>1000</td>
<td>120</td>
<td>43</td>
<td>0.108</td>
</tr>
<tr>
<td>Nafion 115</td>
<td>1100</td>
<td>130</td>
<td>34</td>
<td>0.059</td>
</tr>
<tr>
<td>Gore-Select</td>
<td>1100</td>
<td>20</td>
<td>32</td>
<td>0.053</td>
</tr>
<tr>
<td>Flemion</td>
<td>900</td>
<td>50, 80</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
- **Aciplex, Dow membrane**
  - Short side chain
  - High ratio of SO3H/CF2
  - High specific conductivity

- **Gore-Select**
  - Fine mesh PTFE support impregnated with Nafion
  - high mechanical stability ~ 10μm
Conducting Mechanisms

- Polar ionic groups tend to cluster together, away from nonpolar backbones.

- Reversible crosslinker: when heated, ionic groups lose their attraction, chains move around freely.

Grotthus mechanism vs. vehicle mechanism.
Sulfonated Aromatic Polymers

- Poly(styrene) (PS)
- Polysulfone (PSf)
- Poly(ether ether ketone) (PEEK)
- Poly(benz imidazole) (PBI)
- Poly(ether sulfone) (PES)
- Poly(phenylene sulfide) (PPS)
Polymer electrodes: conjugated polymer

*Polyacetylene*

• \((\text{CH})_x\); room T conductivity;
  
  \(10^{-5} \text{ Scm}^{-1}\) for *trans*, \(10^{-9} \text{ Scm}^{-1}\) for *cis*
● Exposure to oxidizing or reducing agents
  → increase several orders of conductivity
  e.g., exposure to halogens: poor conductor approaching that of metals
Doping process

- p-doping process
  - exposure to oxidizing agent (X)
  - formation of positively charged polymer complex & reduction of X

\[
(CH)_x \rightarrow [(CH^{y+})]_x + (xy)e^- \\
(xy)X + (xy)e^- \rightarrow (xy)X^-
\]

with total reaction

\[
(CH)_x + (xy)X \rightarrow [(CH^{y+})]_x + (xy)X^- \rightarrow [(CH^{y+})X_y^-]_x
\]

where \(X^- = \text{I}^-, \text{Br}^-\ldots\)

\(X^- \rightarrow \text{dopant counter anion}\)

\(y \rightarrow \text{ratio b/w dopant ion and repeating unit (doping level)}\)
n-doping process

- exposure to reducing agent (M)
- formation of negatively charged polymer complex & oxidation of M

\[(CH)_x + (xy)e^{-} \rightarrow [(CH^{y-})]_x \]
\[(xy)M \rightarrow (xy)M^{+} + (xy)e^{-}\]

with total reaction

\[(CH)_x + (xy)M \rightarrow [(CH^{y-})]_x + (xy)M^{+} \rightarrow [M_y^{+}(CH^{y-})]_x\]

where \(M^{+} = Na^{+}, Li^{+}... \) → dopant counter cation
● **Heterocyclic polymers**
  - polypyrrole & polythiophene

![Chemical structures of polypyrrole and polythiophene](image)

● **Polyacetylene**
  - degenerate ground state; two geometric structures with same energy and different sequence single-double bonds

![Chemical structures of polyacetylene](image)
**Polyaniline**

- prepared electrochemically, by oxidation of aniline in acid media

![Polyaniline structure](image)

**Polythiophene and its derivatives**

![Polythiophene structure](image)
Mechanism of doping processes

- **Two contributions**
  - Intrachain transport: average conjugation length of chains
  - Interchain transport: regularity of polymer structure
    (conductivity increases by ordering of structure)

- **Methods for monitoring the doping processes**
  - Optical absorption: intergap transition changes absorption
  - in situ spectroelectrochemical cell measurement
- **Microbalance** (QCM, quartz crystal)

- **Cyclic voltammetry & a.c. impedance**
  
e.g., CV of \((\text{CH})_x\) in \(\text{LiClO}_4\)-PC:
  
anodic (doping) & cathodic (undoping) peaks
  
→ reversible process, two structural sites, long tail: diffusion controlled kinetics
Application of polymer electrode

● Batteries; lithium/polypyrrole batteries

\[ \text{Li} / \text{LiClO}_4\cdot\text{PC} / (C_4H_5N)_v \]

Characterized by the following electrochemical process:

\[
(C_4H_5N)_v + (xy)\text{LiClO}_4 \xleftrightarrow{\text{charge}} (C_4H_5N^{3+})(\text{ClO}_4^-)_{xy} + (xy)\text{Li} \]

\[
(C_4H_5N)_v + (xy)\text{LiClO}_4 \xleftrightarrow{\text{discharge}} (C_4H_5N^{3+})(\text{ClO}_4^-)_{xy} + (xy)\text{Li} 
\]

● Optical display (electrochromic device)

\[ \text{Li} / \text{LiClO}_4\cdot\text{PC} / [C_5H_7S]_v, \text{ITO, glass} \]

Display is a battery with a color change.

Electro-chemical process:

\[
[C_5H_7S]_v + (xy)\text{LiClO}_4 \xleftrightarrow{\text{doping}} [(C_5H_7S^{7+})(\text{ClO}_4^-)_{xy}]_v + (xy)\text{Li} 
\]

\[
[C_5H_7S]_v + (xy)\text{LiClO}_4 \xleftrightarrow{\text{undoping}} [(C_5H_7S^{7+})(\text{ClO}_4^-)_{xy}]_v + (xy)\text{Li} 
\]

(red)          (blue)