Polymer Electrolytes

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

● **Newest solid ionics**: for E 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 the ion

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

● Crystalline solid electrolytes
  - $\text{H}^+$, $\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, $\text{Ag}^+$, $\text{F}^-$, $\text{O}_2^-$, & di- or trivalent ions conductors
  - (i) a high concentration of mobile ions, (ii) a low activation energy for ionic motion from site to site
  - conductivity: hopping mechanism along channels
  - in crystal structure: 1-, 2-, 3-D network of channels

● Glass electrolytes: amorphous solid conductors

● Molten electrolytes
  - molten salts or mixtures high conductivities (> 1 Scm$^{-1}$)
  - e.g., LiCl-KCl eutectic (m.p. 355 °C < LiCl at 613 °C)
  - Drawback: high operation T & corrosion
Polymeric electrolytes
- **good interfacial contacts** with electrode materials (not brittle)
- Conductivity (by 100~1000) < than Liq. or ceramic electrolytes
- thin film configuration compensate for the lower values

*Conductivity vs. temperature for some of the first studied polymer electrolytes.\(\text{PESc} = \text{poly(ethylene succinate)}, \ \text{PEO} = \text{poly(ethylene oxide)}, \ \text{PPO} = \text{poly(propylene oxide)}, \ \text{PEI} = \text{poly(ethylene imine)}, \ \text{MEEP} = \text{poly(bis(methoxyethoxyethoxy)phosphazene)}\)*
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 (liquid) free system**: ionically conducting phase is formed by dissolving salts in polymer.

2. **Gel electrolyte**: formed by dissolving salt in polar liquid and adding inactive polymeric material.

3. **Plasticized electrolyte**: essentially a gel electrolyte but is usually associated with the addition of small amounts of a high dielectric constant solvent to enhance its conductivity.

4. **Ionic rubber**: a liquid electrolyte comprising a low temperature molten salt mixture, reduced to a rubbery condition by addition of a small amount of high $M_w$ polymer.

5. **Memb ionomer**, $H^+$ conducting polyelectrolyte, comprising fluorocarbon backbone to which sulfonic acid are bonded chemically. e.g. Nafion. (with plasticizer)
Thermodynamics of salt dissolution

● Dissolution of salts → reduction in $\Delta G$ of the system at constant $T$ & $P$ → consider $\Delta H$, $\Delta S$

$$\Delta G = \Delta H - T\Delta S$$

● Overall entropy change on dissolution
  (+) : due to the break up of crystal lattice and the subsequent disordering of ions in the system
  (−) : caused by the stiffening of chains as they coordinate to cations

● Major enthalpy changes on dissolution
  (+) : due to the lattice energy of the salt
  (−) : due to cation solvation
**Polymer solvents**

- A polymer that is capable of strongly coordinating cations
- polyethers, polyester, polyimines, polythiols
- have strong coordinating groups to dissolve salts easily
- **High Mw PEO-based polymer electrolytes**
  - poor conductors in crystalline
  - amorphous; loss of mechanical stability

- **Atactic PPO**
  - amorphous since random arrangement of methyl group

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

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

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

Rubbery & Amorphous

- **PEO**
  - $T < 60 \, ^\circ \text{C}$, presence of crystalline part $\rightarrow$ reduce conductivity

- **Atactic poly(propylene oxide), PPO**
  - random arrangement of CH$_3$ along the chain
    $\rightarrow$ prevent the order necessary for crystallization of polymer
    $\rightarrow$ *not best electrolyte* (∴ steric hindrance of CH$_3$ side group)
    1) limits the segmental motion
    2) reduces polymer-cation interaction

![PEO and PPO chemical structures](image)
• **Poly (methylene oxide), \((\text{CH}_2\text{O})_n\)**
  - superficially good because of its high conc. polar groups
  - but not good in practice since hard with high cohesive energy

• **Amorphous poly(ethylene oxide), PEO**
  - consists of medium but randomly-variable length segments of PEO joined by methylene oxide units
  → methylene oxide units break up the regular helical pattern of PEO and suppress crystallization

\[
\begin{array}{c}
\text{\(\big(\text{C}_2\text{H}_4\text{O}\big)\)}_n \text{CH}_2 \text{O}\_m \\
\text{Methoxy linked poly(ethylene oxide).}
\end{array}
\]

• **PEO with DMS units**
  - introduced btn. PEO units to produce an amorphous polymer

\[
\begin{array}{c}
\text{\(\big(\text{C}_2\text{H}_4\text{O}\big)\)}_n \text{CH}_2 \text{O}\_m \\
\text{Dimethyl siloxy linked poly(ethylene oxide).}
\end{array}
\]
● **Amorphous comb polymers**
  - short chain polyethers attached to a polyphosphazene or a polysiloxane backbone
  - excellent hosts for alkali metal salts since high flexibility of PN backbone to promote ion transport

![Chemical structures of MEEP (poly(bis-(methoxyethoxyethoxy)phosphazene)) and SiO₅ structure](image)

● **Branched & Network polymer ionics**
  - at a microscopic level, the degree of crosslinking must not be so great as to make the local polymer segments rigid, thereby increasing $T_g$ and reducing ion transport
  - chemical crosslinking strategy → chemical or irradiation crosslinking
● Additives: small polar molecules into PEs
  - improvement in conductivity
    i) plasticize polymer → high flexibility & segmental motion
    ii) solvate cation (or anion) → reduce ion-ion interactions

  - e.g., propylene carbonate
    poly(acrylonitrile) & poly(vinyl pyrrolidone) + LiClO₄ + PC
    → high conductivities (1.7 x 10⁻³ at 20 °C)

● Additives: 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>([\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_n)</td>
</tr>
<tr>
<td>Poly(ethylenimine)(^b)</td>
<td>((\text{CH}_2\text{CH}_2\text{NH})_n)</td>
</tr>
<tr>
<td>Poly(alkylene sulfides)(^c)</td>
<td>([\text{(CH}_2\text{)}_p\text{S}]_n)</td>
</tr>
<tr>
<td>Poly(ethylene succinate)(^d)</td>
<td>([\text{OCH}_2\text{CH}_2\text{OC(O)}\text{CH}_2\text{CH}_2\text{C(O)}]_n)</td>
</tr>
<tr>
<td>Poly((N)-methylaziridine)(^e)</td>
<td>([\text{CH}_2\text{CH}_2\text{N(CH}_3)]_n)</td>
</tr>
<tr>
<td>Poly(epichlorohydrin)(^f)</td>
<td>([\text{OCH}_2\text{CH(CH}_2\text{Cl)]}_n)</td>
</tr>
<tr>
<td>Poly(vinyl acetate)(^g)</td>
<td>{\text{CH}_2\text{CH}[\text{OC(O)CH}_3]}_n</td>
</tr>
<tr>
<td>Poly[bis(methoxyethoxyethoxy) phosphazene]^h</td>
<td>{\text{NP}[\text{O(CH}_2\text{CH}_2\text{O})_2\text{CH}_3]_2}_n</td>
</tr>
<tr>
<td>Oxymethylene-linked poly(oxyethylene)(^i)</td>
<td>([\text{(CH}_2\text{CH}_2\text{O})_m\text{CH}_2\text{O}]_n)</td>
</tr>
</tbody>
</table>
**Salts**

- **Polyatomic anions with monovalent charge** are the best candidates (∵ weak anion solvation).
  - e.g., water soluble LiF (strong solvation of F by water)
    - → LiF insoluble in PEO
    - → LiClO₄ highly soluble in PEO

- **Large, polarizable, monovalent anions low lattice E**
  - → better dissolution
    - → ClO₄⁻, CF₃SO₃⁻, (CF₃SO₂)₂N⁻, (CF₃SO₂)₃C⁻, AsF₆⁻, PF₆⁻
    - → I⁻ & Br⁻ (but Cl⁻, F⁻ poor solubility)

- **Solvation H of salt depends on cation-polymer interaction**
  - → dissolution only 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–

Interaction strength btn. cation and coordinating group
classified according to 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 with no valence electrons,
      e.g., alkali, alkaline earth ions, Mg\(^{2+}\)
   (b) soft: larger cations with several valence electrons, Hg\(^{2+}\)

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

**Gel electrolytes**
- Great interest commercially as alternative to the solvent-free systems → higher, more practical 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 solv.
  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 $\rightarrow$ high ionic mobility

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

• **Bellcore (USA) Co.**
  - commercially available gel electrolyte (for Li battery)
  - PVdF-co-HFP (hexafluoropropylene) electrolyte
    (Li salt solution in mixed carbonate esters)
  - HFP $\rightarrow$ decrease crystallinity of PVdF component & enhancing its ability to absorb liquid
  - Hybrid polymer electrolyte: porous polymer with $<$ submicron + organic solvent
Break ？？？
Mechanisms of ion conduction

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

→ ions are transported by the semi-random motion of short polymer segments
How ions transported?

**Solvent & ion transport**

- Cations in liquids or low $M_w$ polymer; ions can move together with their coordinated solvent, not in high $M_w$ polymer.

- When $M_w > 3200$ g/mol, $M_w$ of polymer has no significant effect on cation mobility.

*Variation of log D for $^7$Li in PEO-LiCF$_3$SO$_3$ with an O:Li ratio of 20:1 at (●) 70 and (○) 90°C as a function of polymer molecular weight, M*
For high $M_w$ polymer hosts,
- chain diffusion is small and makes little contribution to mechanism for ion transport
- the motion of ions in polymer electrolytes 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
  - Amorphous PEs depart from the classical Arrhenius relation
    \[ \sigma = \sigma_0 \exp \left[ - \frac{E_a}{k_B T} \right] \]
  - **Vogel-Tamman-Fulcher (VTF)** equation: ions are transported by semi-random motion of short polymer segments
    \[ \sigma = \sigma_0 \exp \left[ - \frac{B}{T - T_0} \right] \]

- **Free volume-based models**: motion occurs as a result of the redistribution of free volume within the system

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

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

● Phase diagrams

Phase diagram of the PEO–LiClO₄ 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 → solvent evap. → heating under vacuum

2) **Hot pressing method**
   - grinding polymer & salt at liquid N₂ Temp. → hot pressed
   ; totally solvent free

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

● Minimum requirements
  - ionic conductivity: $10^{-2}$ – $10^{-3}$ Scm$^{-1}$ ideal at RT
    (min. $10^{-5}$ Scm$^{-1}$ 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**

- lithium metal/PEO → thin layer of third phase formed between two bulk phases

- passive layer composition: LiF (for LiCF$_3$SO$_3$ electrolyte) or Li$_2$O (for LiClO$_4$ electrolytes), inhomogeneous

→ low ionic conductivity
● **Intercalation cathode**
- provide a mechanism for reversible and kinetically fast solid-state electrochemical reactions
- Li secondary battery, electrochromics, sensors, solar cells

\[ MX_n + a\text{Li}^+ + ae^- \rightarrow \text{Li}_aMX_n \]

- e.g., \( V_2O_5/\text{PEO} \) electrolytes with \( \text{LiClO}_4 \)
- 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 electrolytes & nanocomposites

- 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>Li₃N</td>
<td>PEO–LiCF₃SO₃</td>
</tr>
<tr>
<td>γ-LiAlO₂</td>
<td>PEO–LiClO₄</td>
</tr>
<tr>
<td>α-LiAlO₂</td>
<td>PEO–LiClO₄</td>
</tr>
<tr>
<td>NASICON</td>
<td>PEO–NaI</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>PEO–LiClO₄</td>
</tr>
<tr>
<td>β''-Al₂O₃</td>
<td>PEO–NaI</td>
</tr>
<tr>
<td>θ-Al₂O₃</td>
<td>PEO–NaI</td>
</tr>
<tr>
<td>SiO₂</td>
<td>PEO–NaI</td>
</tr>
<tr>
<td>Zeolite, [(Al₂O₃)₁₂(SiO₂)₁₂]</td>
<td>PEO–LiBF₄</td>
</tr>
<tr>
<td>1.2Li₂S·1.6LiI·B₂S₃</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/PEO3LiBF4/Li; (□) Li/PEO3LiBF4 + 10 wt.% nanosize Al2O3/Li;
(○) Li/PEO3LiBF4 + 20 wt.% nanosize Al2O3/Li; (■) Li/PEO3LiBF4 +
20 wt.% microsize Al2O3/Li
• Why ceramic or glass powder render the interface more stable?
  1) **Reactivity**  
  : formation of highly conducting product (Li₃N) 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 conductors

→ anhydrous conductors: PEO-H₃PO₄, PEI-H₂SO₄ or H₃PO₄, PVP-H₃PO₄; high conductivity (∵ high intrinsic conductivity of acid)

→ proton-vacancy conducting polymers: PEOₙNH₂SO₂NH₂
→ hydrated proton conducting membranes: polyelectrolyte + water
→ polymer electrolyte fuel cell employ hydrated perfluorosulfonic acid such as Nafion (DuPont), Dow XUS-13204.10, Chlorine Engineers Membrane C
Polymer electrodes: conjugated polymer

**Polyacetylene**

- $(\text{CH})_x$; room T conductivity;
  - $10^{-5}$ S cm$^{-1}$ for trans, $10^{-9}$ S cm$^{-1}$ 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 \( X \)

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

with total reaction

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

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

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

\( y: \text{ratio btn. dopant ion and polymer repeating unit} \)

\( \rightarrow \text{doping level} \)
• n-doping process
  - exposure to reducing agent (M)
  - formation of negatively charged polymer complex & oxidation of M

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

with total reaction

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

where \(M^+ = \text{Na}^+, \text{Li}^+\ldots\) \(\rightarrow\) dopant counter cation
Heterocyclic polymers
• polypyrrole & polythiophene

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

- prepared electrochemically, by oxidation of aniline in acid media

![Polyaniline structure](image)

- doping $\rightarrow$ not induce changes in the number of electrons associated with the polymer chain, but related to a highly symmetrical $\pi$- delocalized structure
- conductivity vs. $T$; polymer $\sim$ SC
Mechanism of doping processes

• “doping”: same terminology with inorganic semiconductor, but the doping processes of conducting polymers are quite different from those of inorganic semiconductors

- **Semiconductor**: rigid lattice, doping is well described by band models → doping processes; introduction of impurities into the crystal lattice with the intergap energy levels near CB or VB; conduction proceeds via a coherent propagation of electrons and/or holes across the lattice

- **Polymer**: flexible chains, favor localized chain deformation → impurities or doping agents do not become part of the structure, rather are inserted within the polymer chain & can be easily removed by applying an opposite electrical driving force; doping process are reversible; the spinless bipolaronsor solitons transport the current
Mechanism of doping processes

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

● Methods for monitoring the doping processes
  - Optical absorption: intergap transition changes absorption
  - in situ spectroelectrochemical cell measurement

---

Fig. 9.8 Spectral evolution of polydithienothiophene upon electrochemical evolution
- **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

\[ \text{Li} / \text{LiClO}_4-\text{PC} / (\text{C}_4\text{H}_5\text{N})_v \]

Characterized by the following electrochemical process:

\[ (\text{C}_4\text{H}_5\text{N})_v + (xy)\text{LiClO}_4 \xrightarrow{\text{charge}} (\text{C}_4\text{H}_5\text{N}^{3+})(\text{ClO}_4^-)_{xy} + (xy)\text{Li} \]

\[ \xleftarrow{\text{discharge}} \]

● Optical display (electrochromic device)

\[ \text{Li} / \text{LiClO}_4-\text{PC} / [\text{C}_5\text{H}_7\text{S}]_v, \text{ITO}, \text{glass} \]

Display is a battery with a color change.

Electro-chemical process:

\[ [\text{C}_5\text{H}_7\text{S}]_v + (xy)\text{LiClO}_4 \xrightarrow{\text{doping}} [(\text{C}_5\text{H}_7\text{S}^{7+})(\text{ClO}_4^-)_{xy}]_v + (xy)\text{Li} \]

\[ \xleftarrow{\text{undoping}} \]

(red) (blue)