



# Polymer Electrolytes

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# 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/LiClO<sub>4</sub>)
  - polyelectrolytes: covalently attached charged group

# Solid Ionics

## ● Crystalline solid electrolytes

- $H^+$ ,  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Ag^+$ ,  $F^-$ ,  $O_2^-$ , & 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**

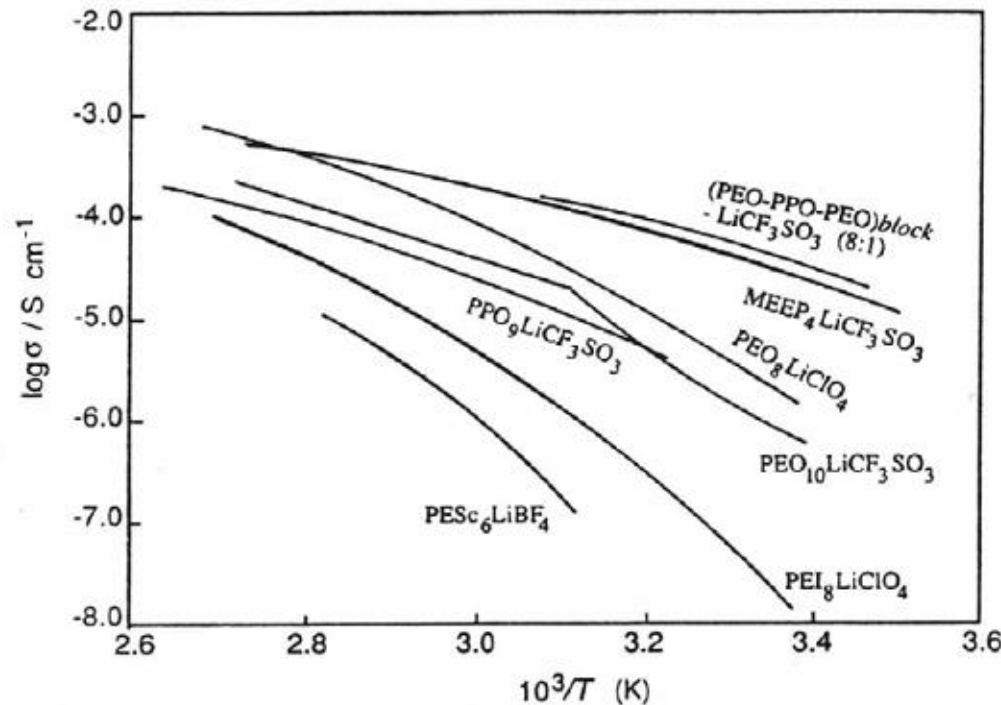
## ● Glass electrolytes : amorphous solid conductors

## ● Molten electrolytes

- molten salts or mixtures high conductivities ( $> 1 \text{ Scm}^{-1}$ )
- e.g., LiCl-KCl eutectic (m.p.  $355 \text{ }^\circ\text{C} < \text{LiCl at } 613 \text{ }^\circ\text{C}$ )
- **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. 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 (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 Mw polymer
- 5. Memb ionomer, H<sup>+</sup> 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, polyesters, 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**  
 **$-(\text{OCH}_2\text{CH}_2)_m-\text{OCH}_2-$** : **amorphous, dimethyl siloxy units**
  
- **Comb-branched copolymers**
  - **enhance flexibility of the system & conductivity**
  
- **Networks**
  - **higher ionic conductivity & dimensional stability by optimized crosslinking**



# Host Polymers

## Amorphous & Rubbery

### ● PEO

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

### ● Atactic poly(propylene oxide), PPO

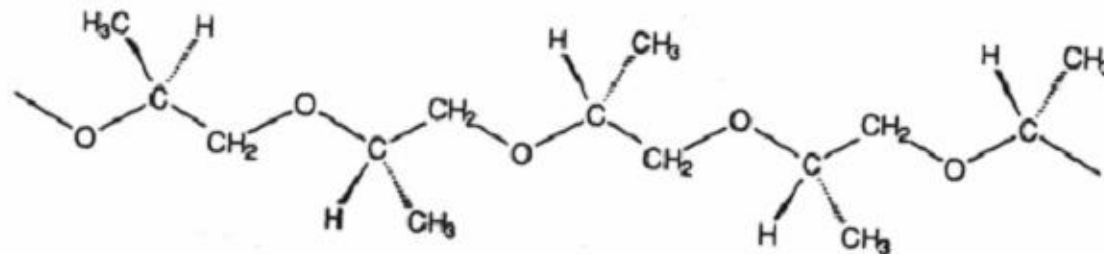
- random arrangement of  $\text{CH}_3$  along the chain

$\rightarrow$  prevent the order necessary for crystallization of polymer

$\rightarrow$  **not best electrolyte** ( $\because$  steric hindrance of  $\text{CH}_3$  side group)

1) limits the segmental motion

2) reduces polymer-cation interaction

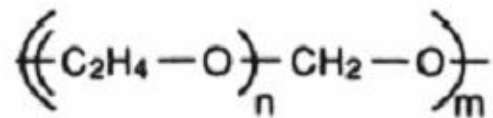


● **Poly (methylene oxide), (CH<sub>2</sub>O)<sub>n</sub>**

- 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**

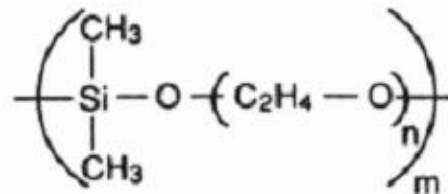
- consists of medium but randomly-variable length segments of PEO joined by methylene oxide units
- methylene oxide units break up the regular helical pattern of PEO and suppress crystallization



Methoxy linked poly(ethylene oxide).

● **PEO with DMS units**

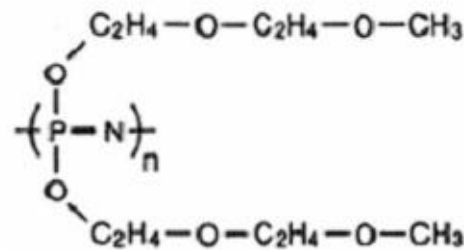
- introduced btn. PEO units to produce an amorphous polymer



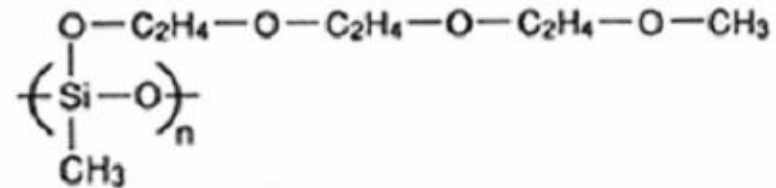
Dimethyl siloxy linked poly(ethylene oxide)

## ● 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



MEEP (poly(bis-(methoxyethoxyethoxy)phosphazene))



Siloxane.

## ● 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) + LiClO<sub>4</sub> + PC**

→ **high conductivities (1.7 x 10<sup>-3</sup> 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*

Name	Monomer unit
Poly(propylene oxide) <sup>a</sup>	$[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_n$
Poly(ethylenimine) <sup>b</sup>	$(\text{CH}_2\text{CH}_2\text{NH})_n$
Poly(alkylene sulfides) <sup>c</sup>	$[(\text{CH}_2)_p\text{S}]_n$
Poly(ethylene succinate) <sup>d</sup>	$[\text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})]_n$
Poly( <i>N</i> -methylaziridine) <sup>e</sup>	$[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)]_n$
Poly(epichlorohydrin) <sup>f</sup>	$[\text{OCH}_2\text{CH}(\text{CH}_2\text{Cl})]_n$
Poly(vinyl acetate) <sup>g</sup>	$\{\text{CH}_2\text{CH}[\text{OC}(\text{O})\text{CH}_3]\}_n$
Poly[bis(methoxyethoxyethoxy)phosphazene] <sup>h</sup>	$\{\text{NP}[\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3]_2\}_n$
Oxymethylene-linked poly(oxyethylene) <sup>i</sup>	$[(\text{CH}_2\text{CH}_2\text{O})_m\text{CH}_2\text{O}]_n$



# Salts

- **Polyatomic anions with monovalent charge** are the best candidates ( $\therefore$  weak anion solvation).
  - e.g., water soluble LiF (strong solvation of F by water)
    - LiF insoluble in PEO
    - LiClO<sub>4</sub> highly soluble in PEO
- **Large, polarizable, monovalent anions low lattice E**
  - better dissolution
  - ClO<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>, (CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>C<sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>
  - I<sup>-</sup> & Br<sup>-</sup> (but Cl<sup>-</sup>, F<sup>-</sup> 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:  $-\text{NR}-$ ,  $-\text{NH}-$  and  $-\text{S}-$
  
- **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  $\text{Li}^+$

### 1) **hard/soft acids**

- (a) **hard: small cations** with no valence electrons,  
e.g., alkali, alkaline earth ions,  $\text{Mg}^{2+}$
- (b) **soft: larger cations** with several valence electrons,  $\text{Hg}_2^+$

### 2) **hard/soft bases**

- (a) **hard: non-polarizable ligands** of high **electronegativity** ( $-\text{O}-$ )
- (b) **soft: more polarizable groups**, e.g., thio group  
 $-\text{O}- > -\text{NH}- > -\text{S}-$

## **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**

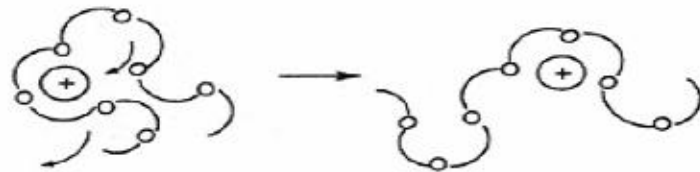


- **Low molecular solvents**
  - propylene carbonate (PC), ethylene carbonate (EC), N,N-dimethyl formamide (DMF),  $\gamma$ -butyrolactone (GBL)
  - high dielectric constant, high B.P.
  - increase salt dissociation
  - low viscosity  $\rightarrow$  high ionic mobility
  
- **Polymeric materials** : 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

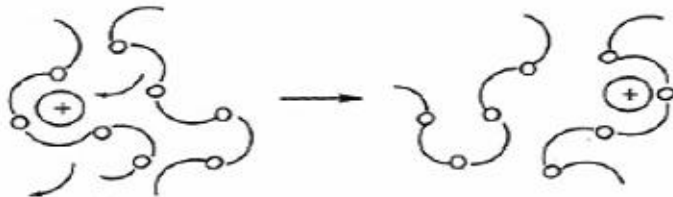


**Break ???**

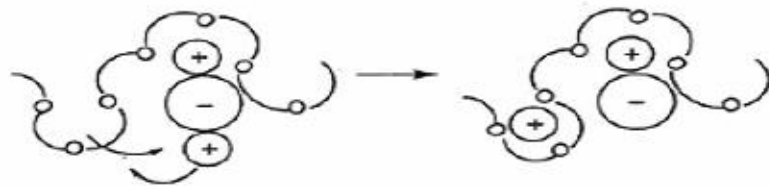
# Mechanisms of ion conduction



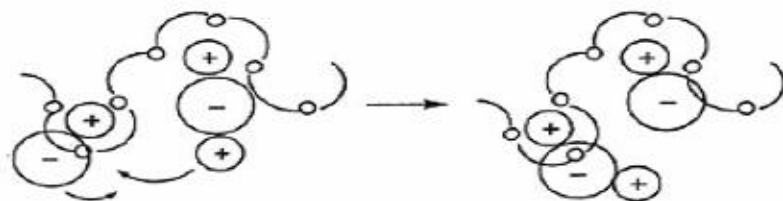
Intrachain hopping



Interchain hopping  
(a)



Intrachain hopping via ion cluster



Intercluster hopping  
(b)

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

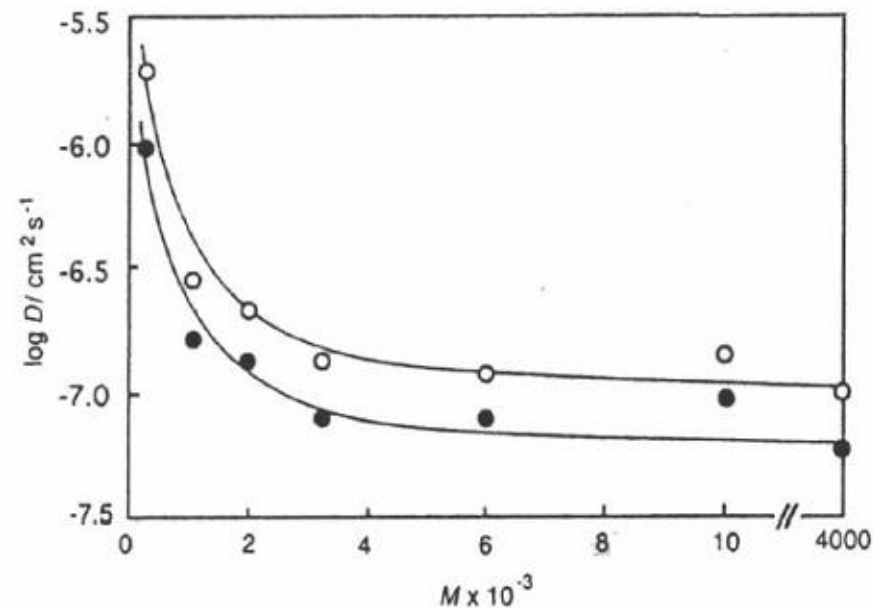
- **'dry' polymer electrolyte: polymer itself is immobile (macroscopically)**

→ **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  ${}^7\text{Li}$  in  $\text{PEO-LiCF}_3\text{SO}_3$  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 → 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 → **making and breaking of coordinate bonds** with motion between coordinating sites
- anion → hopping between **occupied site and void**

# Macroscopic approach

- **Empirical relationship: conductivity vs. temperature**

- **amorphous** PEs depart from the classical Arrhenius relation

$$\sigma = \sigma_0 \exp [ - E_a / k_B T ]$$

- **Vogel-Tamman-Fulcher (VTF)** equation: ions are transported by semi-random motion of short polymer segments

$$\sigma = \sigma_0 \exp [ - B / (T-T_0) ]$$

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

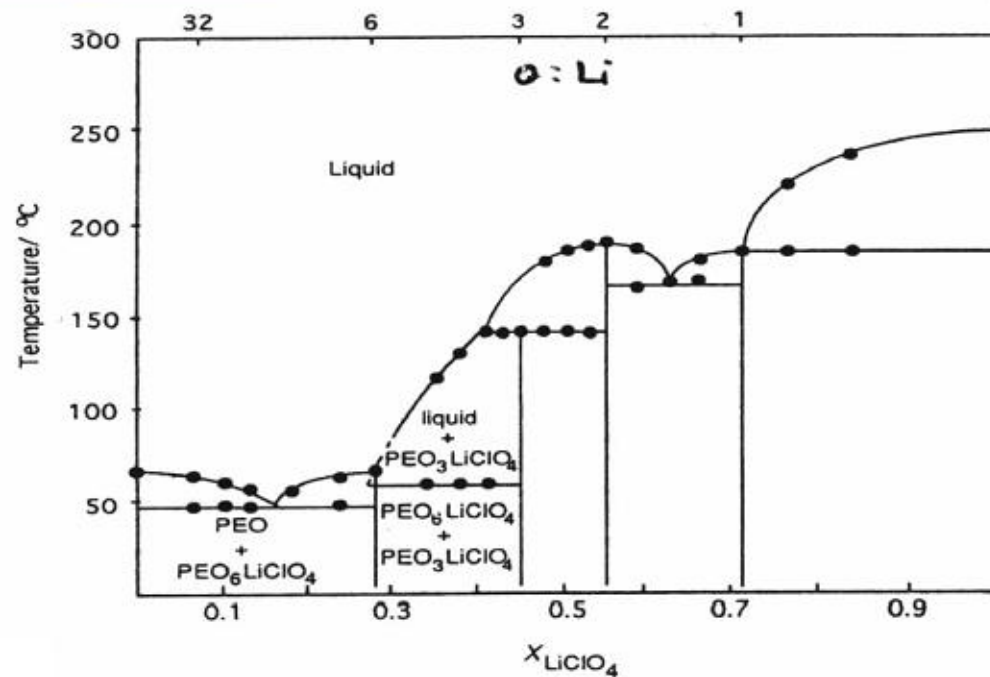
- **Configurational entropy model:** based upon entropy, not volume, with transport modeled on group **cooperative rearrangements** of polymer chains rather than a void-to-void jumping mechanism

# Morphology

- General techniques to characterize polymer electrolyte structure and morphology

- optical microscopy, DSC, NMR, XRD

- Phase diagrams



Phase diagram of the PEO-LiClO<sub>4</sub> 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 N<sub>2</sub> Temp. → hot pressed  
; totally solvent free

## ● Gel electrolyte film: importance of polymer matrix



# Suitable polymer electrolytes?

## ● Minimum requirements

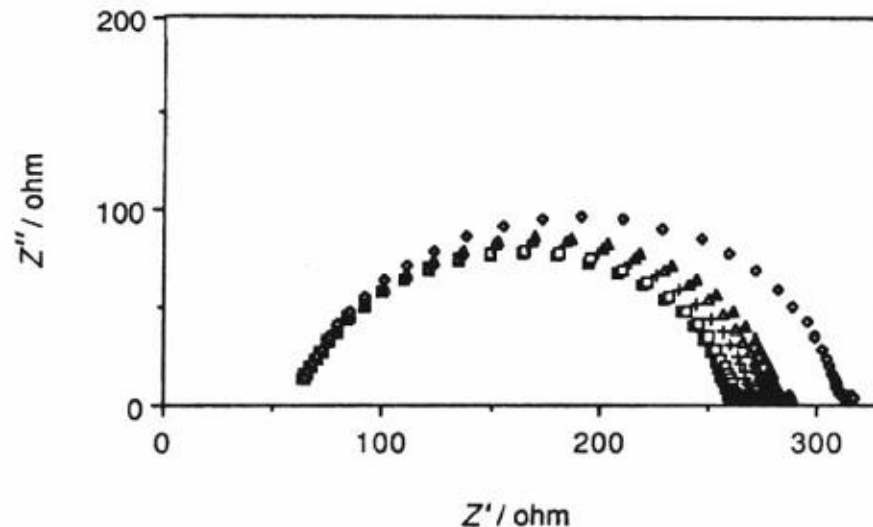
- ionic conductivity:  $10^{-2}$  –  $10^{-3}$   $\text{Scm}^{-1}$  ideal at RT  
(min.  $10^{-5}$   $\text{Scm}^{-1}$  for practical use)
- electrochemical stability in a voltage window-compatibility:  
chemically & electrochemically compatible with electrodes
- Thermal stability
- Mechanical stability
- 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

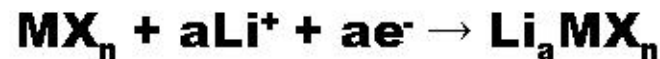


Growth of a passivating layer at a  $\text{PEO}_8\text{LiClO}_4\text{-Li}$  boundary at  $95^\circ\text{C}$ . Ac impedance data taken at  $t = 0$  (■),  $0.5$  h (□),  $2.5$  h (+),  $4$  h (△),  $5$  h (▲) and  $22$  h (◇)

- passive layer composition: **LiF** (for  $\text{LiCF}_3\text{SO}_3$  electrolyte) or **Li<sub>2</sub>O** (for  $\text{LiClO}_4$  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



- e.g.,  $\text{V}_2\text{O}_5$ /PEO electrolytes with  $\text{LiClO}_4$
- two semicircle in a.c. impedance
  - **high frequency** semicircle; ionically conducting surface layer that grows on the  $\text{V}_2\text{O}_5$
  - **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

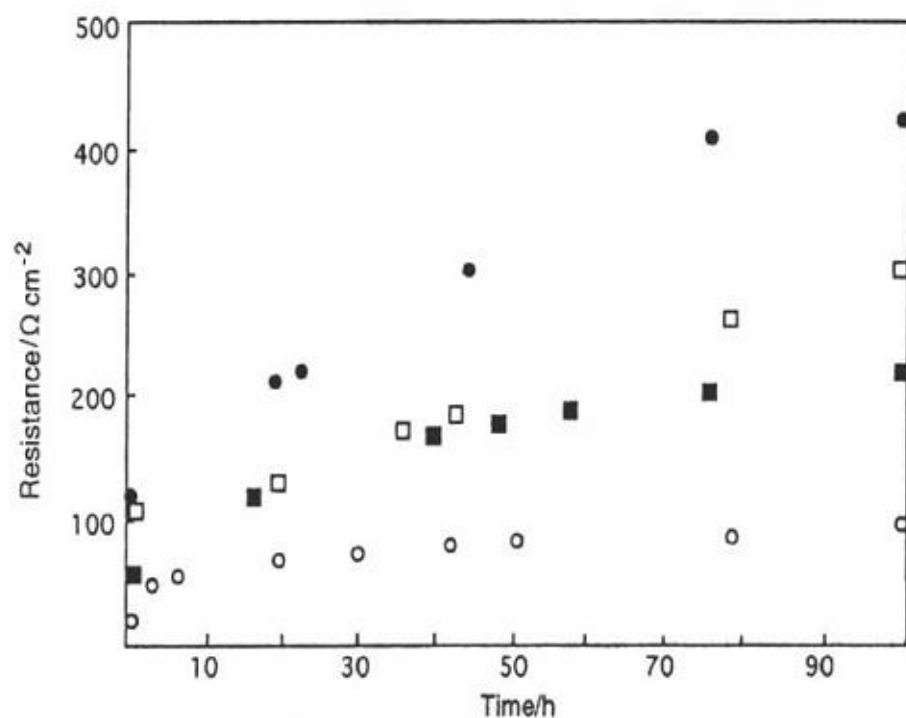
- ceramic or glassy electrolytes vs. polymer electrolytes
  - higher conductivity, better thermodynamic stability
- polymer vs. ceramic/glassy electrolytes
  - flexible, superior interfacial contacts
  - processed as thin large area films
- mixed phase PEs-ceramics of nanometer grain size
  - ⇒ nanocomposites

*Components of some mixed phase electrolytes*

<i>Ceramic</i>	<i>Polymer electrolyte</i>
Li <sub>3</sub> N	PEO-LiCF <sub>3</sub> SO <sub>3</sub>
γ-LiAlO <sub>2</sub>	PEO-LiClO <sub>4</sub>
α-LiAlO <sub>2</sub>	PEO-LiClO <sub>4</sub>
NASICON	PEO-NaI
α-Al <sub>2</sub> O <sub>3</sub>	PEO-LiClO <sub>4</sub>
β''-Al <sub>2</sub> O <sub>3</sub>	PEO-NaI
θ-Al <sub>2</sub> O <sub>3</sub>	PEO-NaI
SiO <sub>2</sub>	PEO-NaI
Zeolite, [(Al <sub>2</sub> O <sub>3</sub> ) <sub>12</sub> (SiO <sub>2</sub> ) <sub>12</sub> ]	PEO-LiBF <sub>4</sub>
1.2Li <sub>2</sub> S·1.6LiI·B <sub>2</sub> S <sub>3</sub>	Polyethylene



- **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|PEO<sub>8</sub>LiBF<sub>4</sub>|Li; (□) Li|PEO<sub>8</sub>LiBF<sub>4</sub> + 10 wt.% nanosize Al<sub>2</sub>O<sub>3</sub>|Li;  
 (○) Li|PEO<sub>8</sub>LiBF<sub>4</sub> + 20 wt.% nanosize Al<sub>2</sub>O<sub>3</sub>|Li; (■) Li|PEO<sub>8</sub>LiBF<sub>4</sub> +  
 20 wt.% microsize Al<sub>2</sub>O<sub>3</sub>|Li

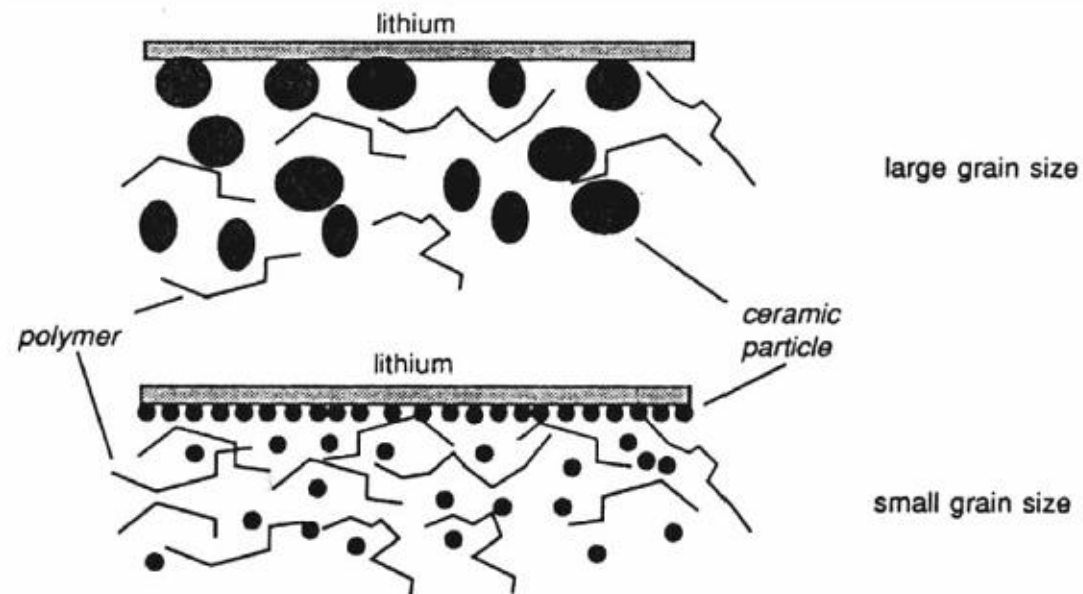
• Why ceramic or glass powder **render the interface more stable** ?

1) **Reactivity**

: formation of highly conducting product ( $\text{Li}_3\text{N}$ ) to facilitate ion transport

2) **Shielding effect**

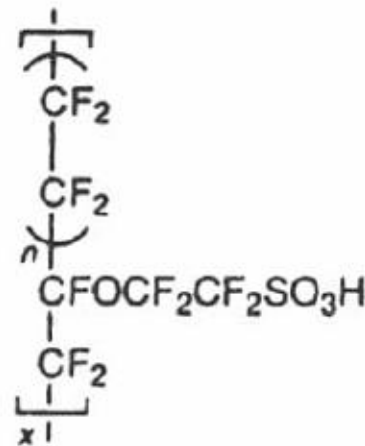
: ceramic/glass reduce the contact between Li and polymer



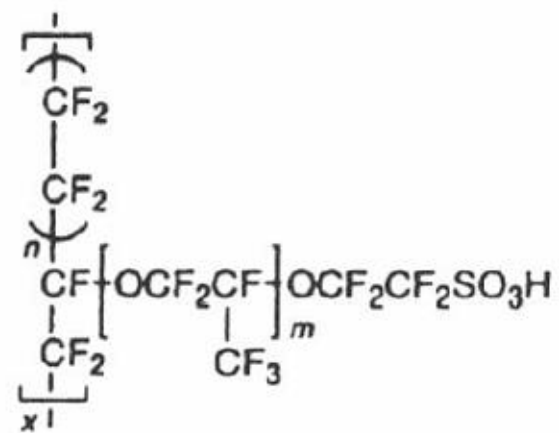
*Schematic diagrams of the lithium-composite-electrolyte interface. The smaller particles are able to cover a greater surface area, minimizing the area of lithium electrode exposed to species that give rise to passivation*

## ● Proton conductors

- **anhydrous conductors: PEO-H<sub>3</sub>PO<sub>4</sub>, PEI-H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>, PVP-H<sub>3</sub>PO<sub>4</sub>; high conductivity (∵ high intrinsic conductivity of acid)**
- **proton-vacancy conducting polymers: PEO<sub>n</sub>NH<sub>2</sub>SO<sub>2</sub>NH<sub>2</sub>**
- **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**



Dow experimental  
membrane  $n = 3.6\text{--}10$



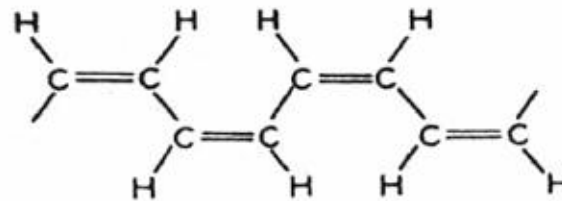
Du Pont's NAFION®  
 $n = 6.6, m = 1$

# Conducting Polymer

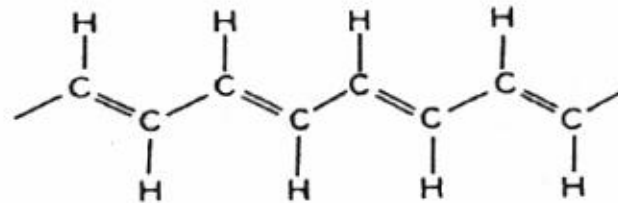
**Polymer electrodes:** conjugated polymer

## Polyacetylene

- $(\text{CH})_x$  ; room T conductivity;  
 $10^{-5} \text{ Scm}^{-1}$  for *trans*,  $10^{-9} \text{ Scm}^{-1}$  for *cis*



CIS



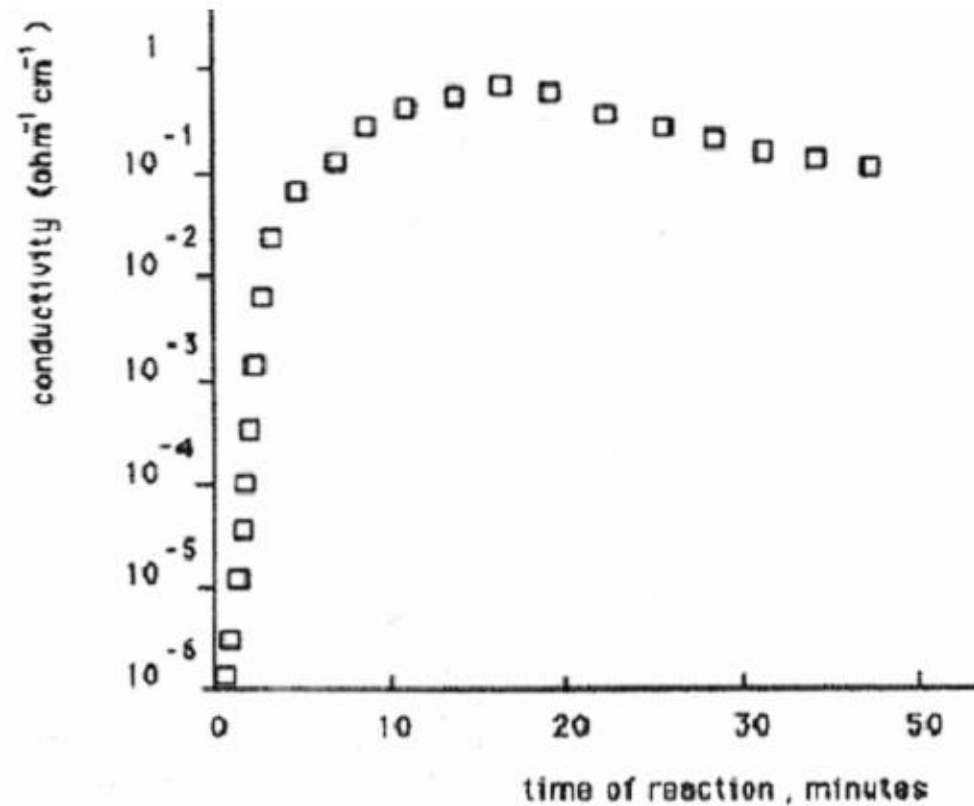
TRANS



● **Exposure to oxidizing or reducing agents**

→ **increase several orders of conductivity**

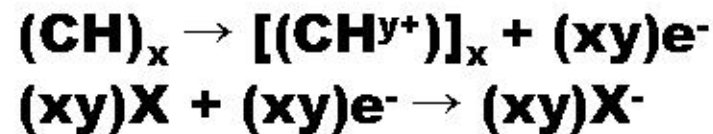
**e.g., exposure to halogens: poor conductor approaching that of metals**



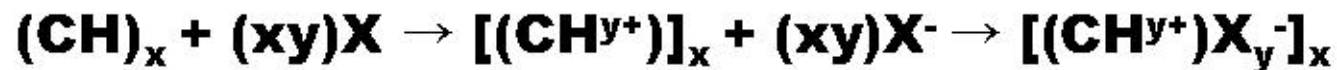
# Doping process

## ● p-doping process

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



with total reaction



where  $\text{X}^- = \text{I}^-, \text{Br}^- \dots$

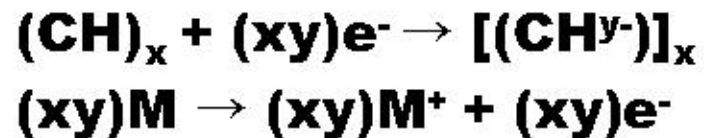
$\text{X}^- \rightarrow$  **dopant counter anion**

**y: ratio btn. dopant ion and polymer repeating unit**

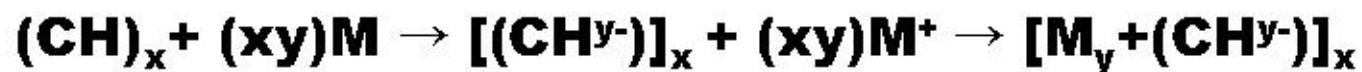
$\rightarrow$  **doping level**

## ● n-doping process

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



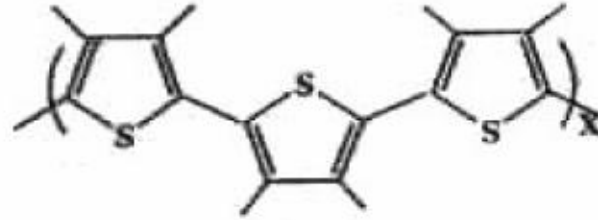
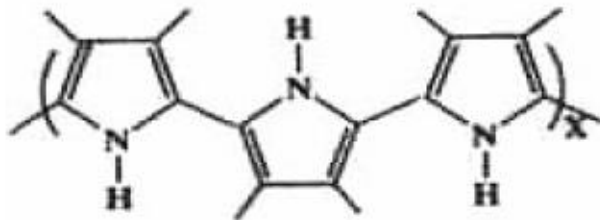
with total reaction



where  $\text{M}^+ = \text{Na}^+, \text{Li}^+ \dots \rightarrow$  **dopant counter cation**

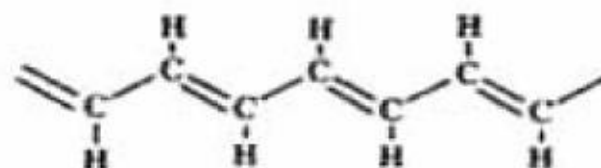
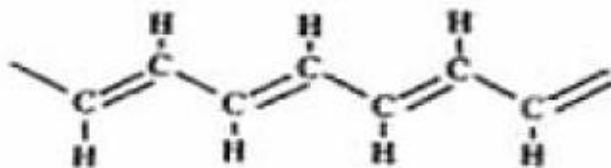
## ● Heterocyclic polymers

- polypyrrole & polythiophene



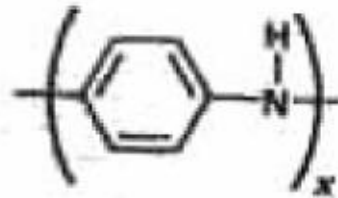
## ● Polyacetylene

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

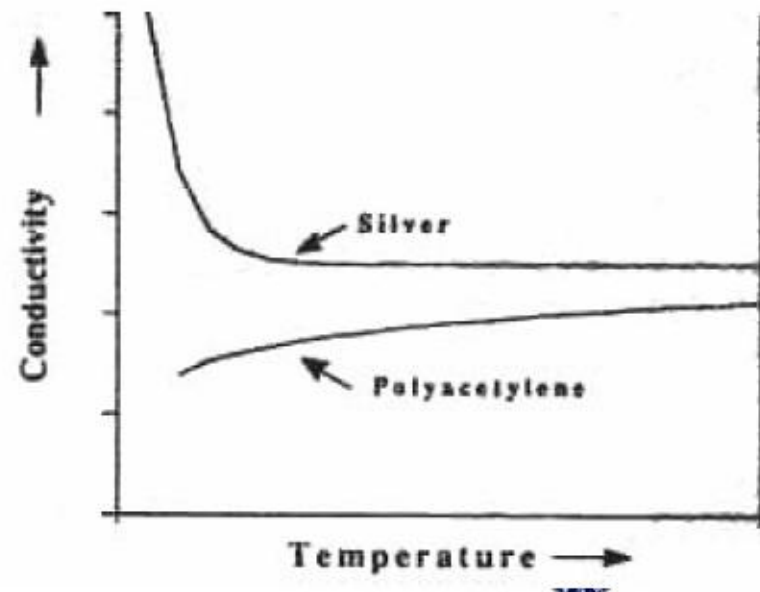


## ● Polyaniline

- prepared electrochemically, by oxidation of aniline in acid media



- doping → 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 ~ 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 bipolarons or solitons transport the current

# 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

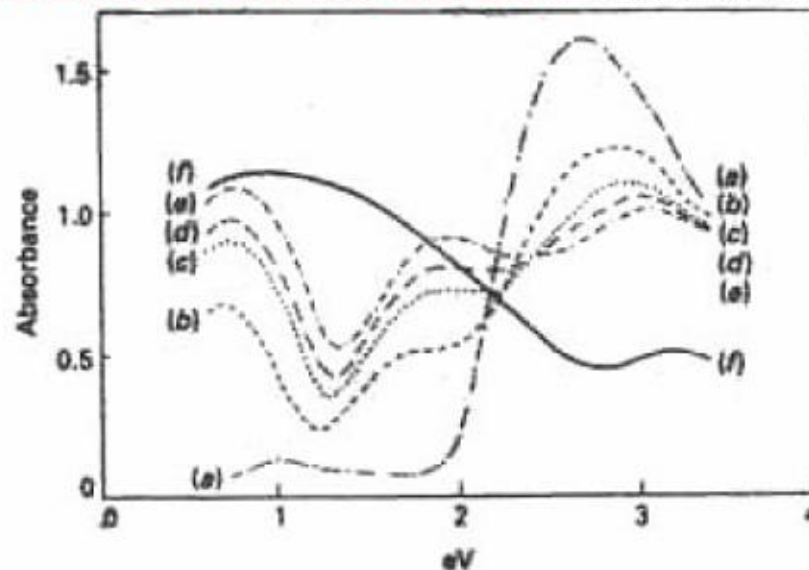


Fig. 9.8 Spectral evolution of polydithienothiophene upon electrochemical evolution

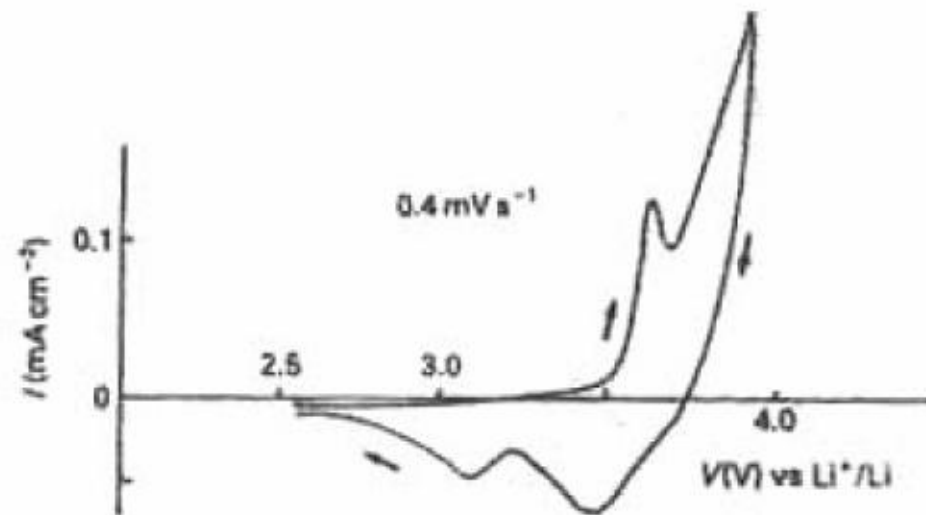
- **Microbalance** (QCM, quartz crystal )

- **Cyclic voltammetry & a.c. impedance**

e.g., CV of  $(\text{CH})_x$  in  $\text{LiClO}_4\text{-PC}$ :

anodic (doping) & cathodic (undoping) peaks

→ reversible process, two structural sites, long tail: diffusion controlled kinetics





# Application of polymer electrode

## ● Batteries ; lithium/polypyrrole batteries



Characterized by the following electrochemical process:



## ● Optical display (electrochromic device)



Display is a battery with a color change.

Electro-chemical process:

