The Role of Nanoparticles in Polymer Electrolyte Systems for Use in Electrochemical Devices

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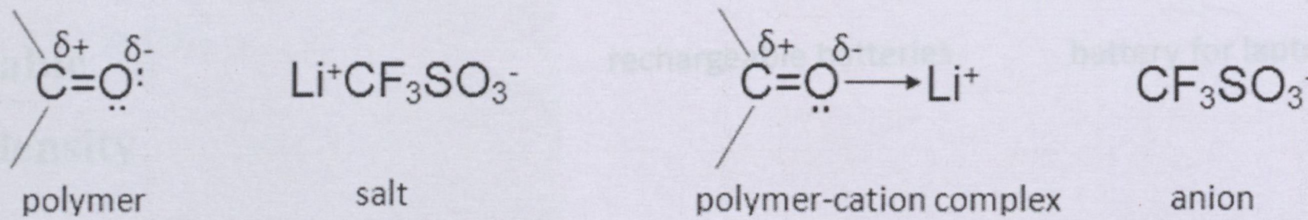
What are Polymer Electrolytes?

Formed when salt is dissolved in polymer host

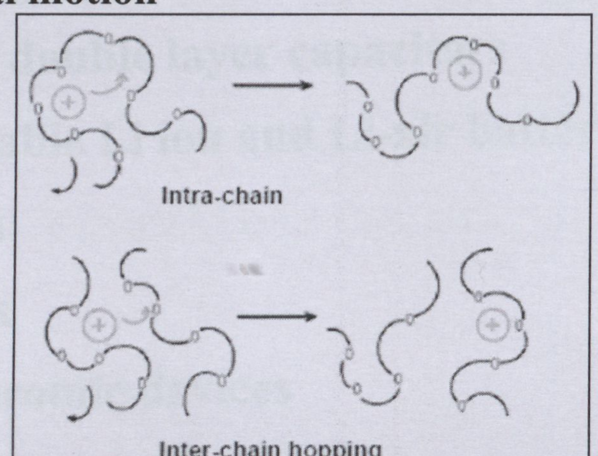
Ion conduction occurs upon application of voltage.

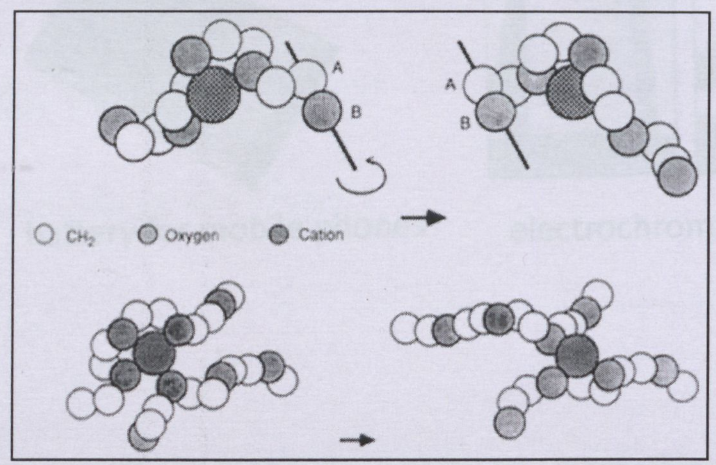
Fundamentals of ionic conduction:

1) labile **coordination** of cation (i.e. Li^+, Na^+, H^+) with lone pair electrons on electronegative atom (i.e. oxygen in C=O, C-O).



2) migration of cation through **hopping** from one coordination site to another or through **polymer segmental motion**





Potential of Polymer Electrolytes

Advantages of polymer electrolytes over commercial liquid electrolytes:

✓ Leakage-free

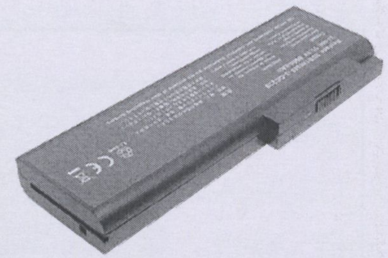
✓ Flexible

✓ Light-weight

✓ Mechanically stable

✓ Higher energy density

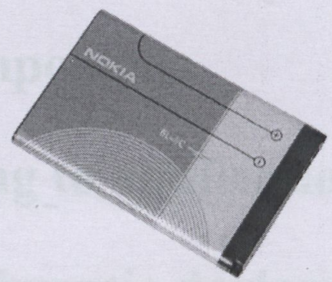
rechargeable batteries



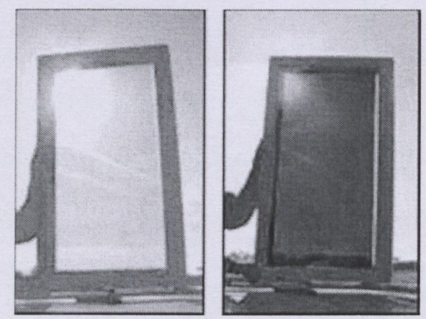
battery for laptops

Applications:

- Electrical double layer capacitors
- Rechargeable Li ion and Li-air batteries
- Fuel Cells
- Solar cells
- Electrochromic devices



battery for mobile phones



electrochromic window

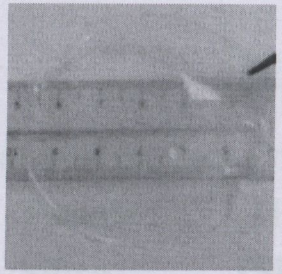
Criteria of Good Polymer Electrolytes

1. Good ionic conductivity (~10^{-4}-10^{-3} S cm^{-1})
2. High cation transport number
3. High thermal stability
4. Good mechanical stability
5. Wide electrochemical window
6. Compatibility with other device components
7. Suitable specific properties according to application

   (i.e. optical transparency in electrochromic devices)

Progress of Polymer Electrolytes (PEs)

Solid Polymer Electrolytes (SPEs)

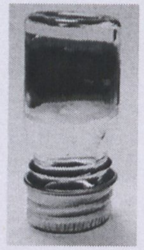


PEMA +
PVdF-HFP +
$LiCF_3SO_3$

Sim et al. (2012)

- Low conductivity
- Mechanically stable
- Can form free-standing films

Gel Polymer Electrolytes (GPEs)

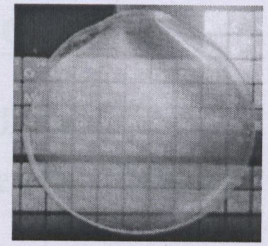


Phthaloyl chitosan +
EC+DMF +
TPAI

Yusuf et al. (2016)

- Higher conductivities than SPEs
- Less mechanically stable than SPEs
- Poor compatibility with lithium electrodes
- Narrow electrochemical window (EW)

Composite Polymer Electrolytes (CPEs)



MG49 +
$LiCF_3SO_3$ +
ZrO_2-TiO_2

L. Tiankhoon (2015)

- Higher conductivities than GPEs
- Higher mechanical strength
- Improved compatibility with electrodes
- Wider EW

PEMA – poly(ethyl methacrylate); PVdF-HFP – poly(vinylidenefluoride-co-hexafluoropropylene); $LiCF_3SO_3$ – lithium trifluoromethanesulfonate; EC – ethylene carbonate; DMF – dimethylformamide; TPAI – tetrapropylammonium iodide; MG49 – 49% poly(methyl methacrylate) grafted on natural rubber; ZrO_2-TiO_2 – zirconia-titania mixed oxide

Passive fillers

- Do NOT take part in ion conduction process
- Enhance polymer electrolytes' properties through physical action

Inert ceramic oxides

Hydroxyl surface groups

- Titania (TiO_2)
- Silica (SiO_2)
- Alumina (Al_2O_3)

Clays

Layered inorganic fillers

- Montmorillonite clay (MMT)

Carbonaceous fillers

High surface area, low cost

- Carbon nanotubes (CNT)

Ferroelectric ceramics

Ceramics with high dielectric constants

Helps to dissociate salt

- Barium titanate ($BaTiO_3$)
- Strontium titanate ($SrTiO_3$)
- Calcium titanate ($CaTiO_3$)
- Lead zirconate titanate ($Pb[Zr_xTi_{1-x}]O_3$
- $SrBi_4Ti_4O_{15}$

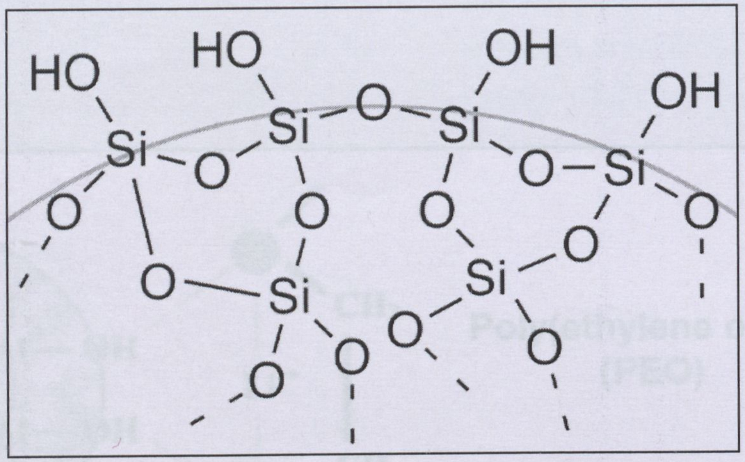
Molecular sieves & zeolites

Hydrated aluminosilicates; mesoporous silica; large pore size

- SBA-15
- MCM-41

Inert Ceramic Oxide: Silicon dioxide or silica (SiO_2)

- A giant covalent molecule
- Insoluble in water & organic solvents
- Does not conduct electricity
- Has high melting point ≈ 1700 °C

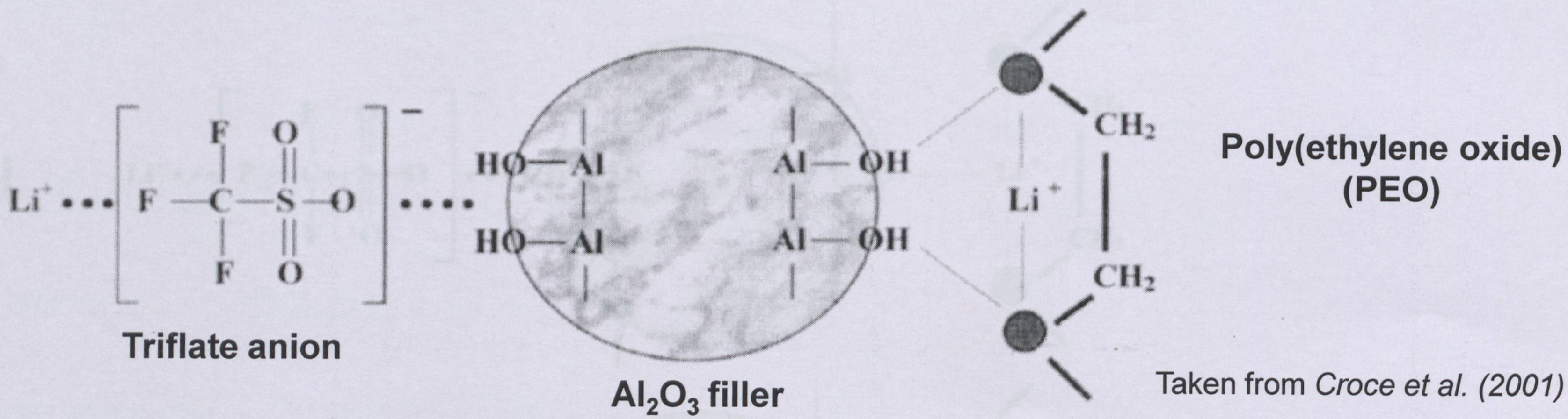


- Hydrophilic due to **silanol (Si-OH)** groups on the surface

- OH groups = Lewis acid centres
    - Can form **Lewis acid-base interactions** with polymer and salt

Ion transport mechanism in passive nanofillers

- **Filler-polymer interactions**
  - Lewis acid surface groups (OH) of NPs form complexes with polymer (i.e. PEO)
  - **compete** with Li^+ cations
  - Increases amorphous phase fraction



Taken from *Croce et al. (2001)*

- **Filler-anion interactions**
  - OH groups interact with anions of salt
    - Lowers ionic coupling – promotes salt dissociation – increases free ions
  - NPs act as crosslinking centres between PEO and anion
    - Lowers crystallinity in PEO

Different surface groups of NPs:

Triflate anion

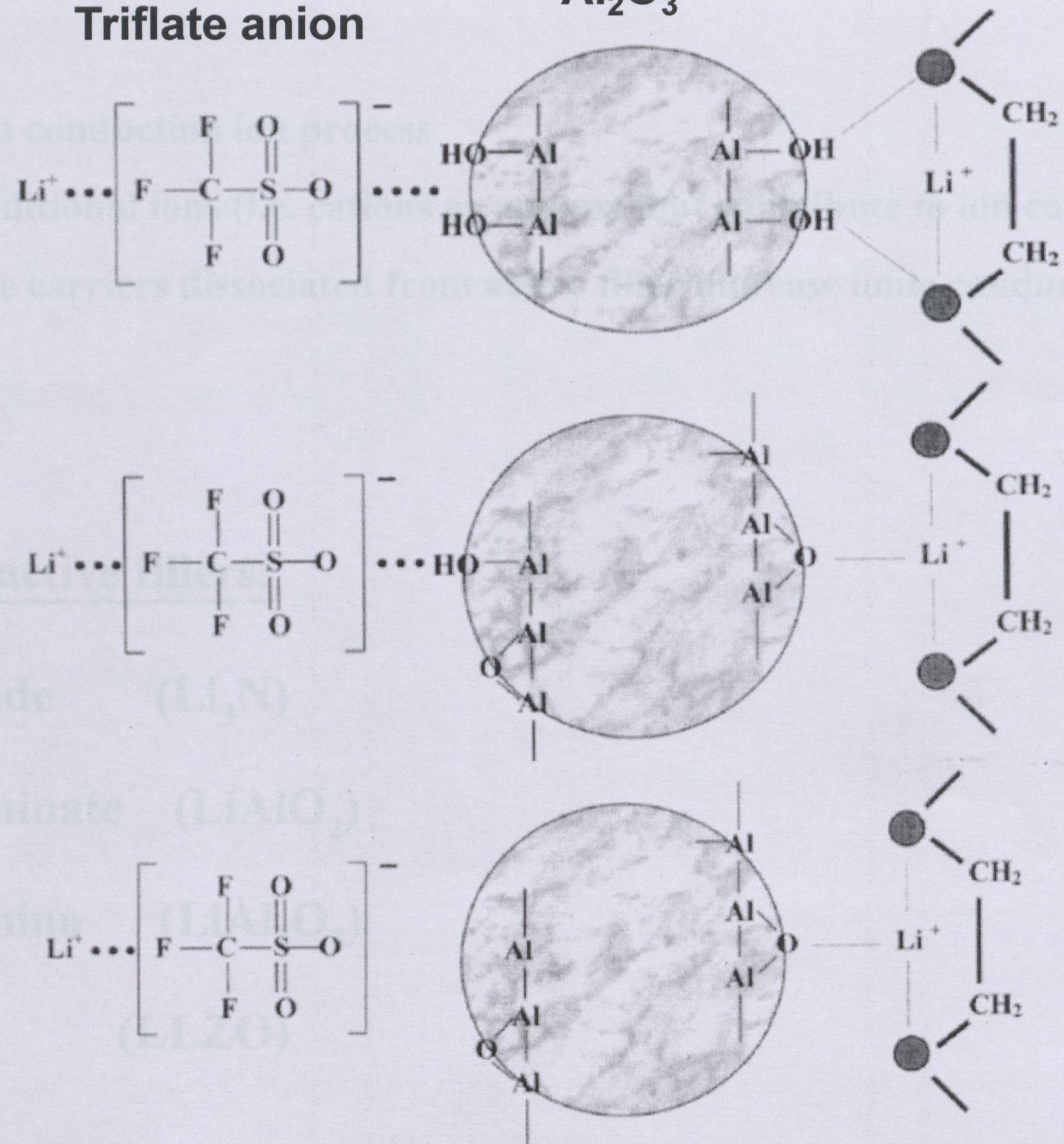
Al_2O_3

PEO

a) Acidic

b) Neutral

c) Basic



Highest conducting

- can interact with anions and produce more mobile Li cations

Taken from *Croce et al. (2001)*

Active fillers

- Take part in conduction ion process
- Provides additional ions (i.e. cations or anions) that contribute to ion conduction
  - Charge carriers dissociated from active filler increase ionic conductivity

Examples of active fillers:

Lithium nitride (Li_3N)

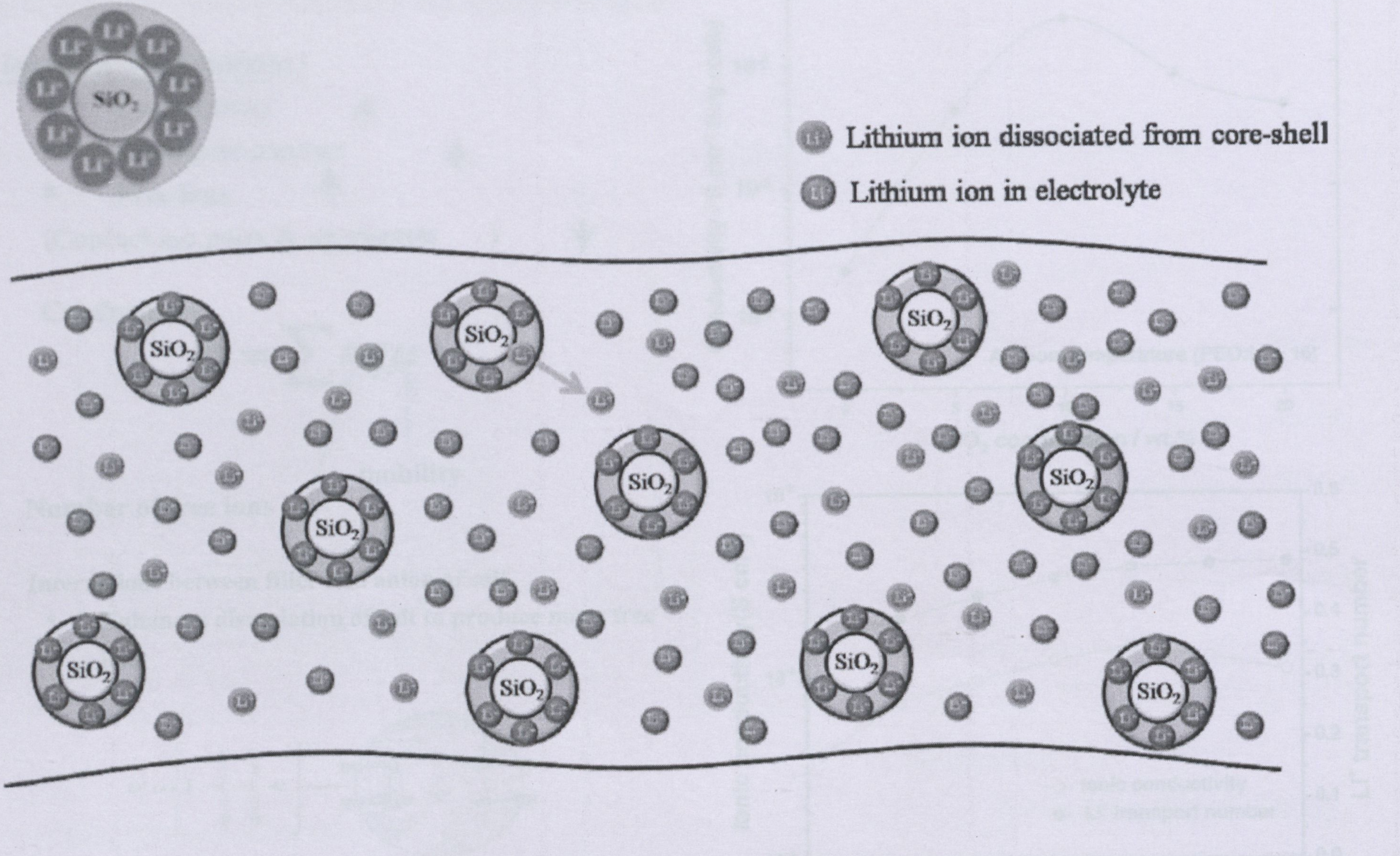
Lithium aluminate ($LiAlO_2$)

Lithium alumina ($LiAl_2O_3$)

$Li_7La_3Zr_2O_{12}$ (LLZO)

$SiO_2(Li^+)$

Ion transport mechanism in active nanofillers



Schematic representation of Li^+ ion conduction in CPE containing core-shell structured $SiO_2(Li^+)$ NPs

Taken from Lee et al. (2013)

Advantages of CPEs

1. Increase ion transport

- Conductivity ↑
- Transport number ↑
- Free ions ↑

(Contact ion pairs & aggregates) ↓

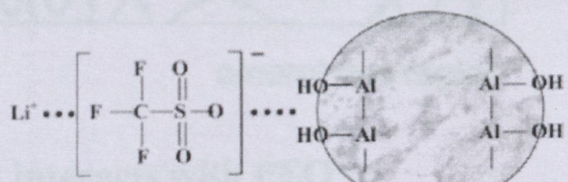
Conductivity

$$\sigma = \sum nq\mu$$

Number of free ions

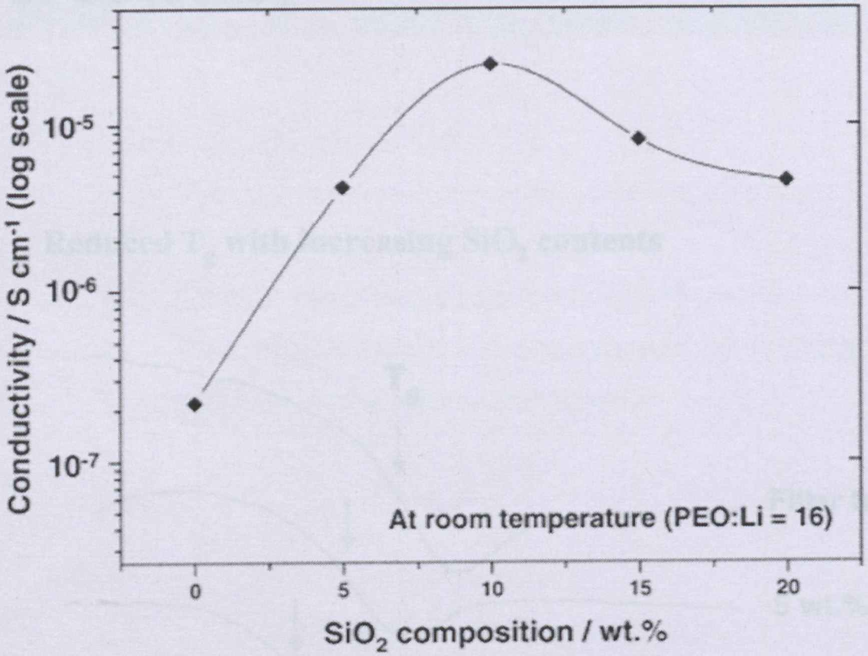
mobility

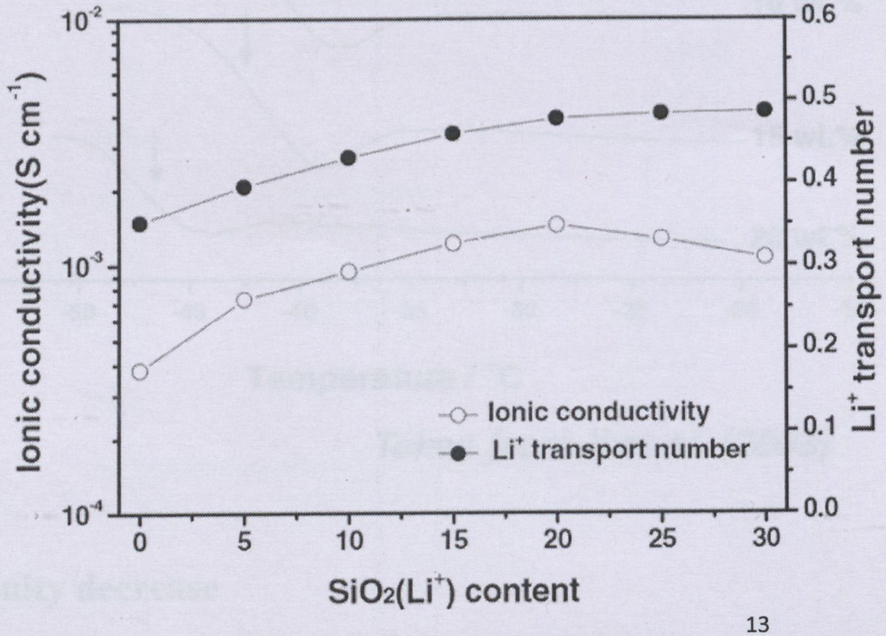
- **Interactions between filler and anion of salt**
  - **Enhances dissociation of salt to produce more free ions**



- **Dissociation of Li^+ from $SiO_2(Li^+)$ increases cation transport number**

Taken from Ji et al. (2003)





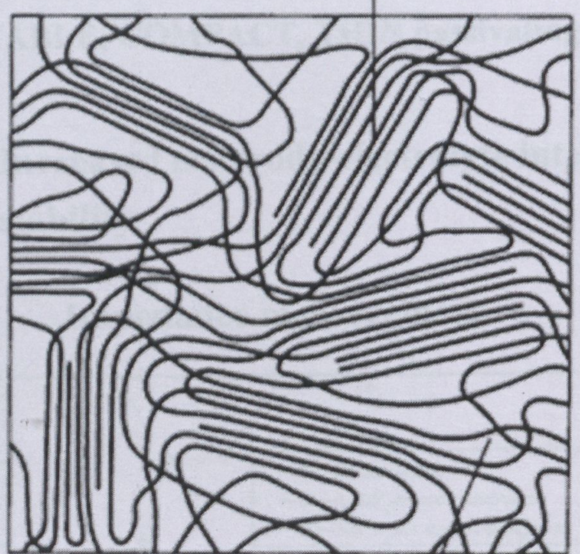
Taken from Lee et al. (2013)

Advantages of CPEs (cont')

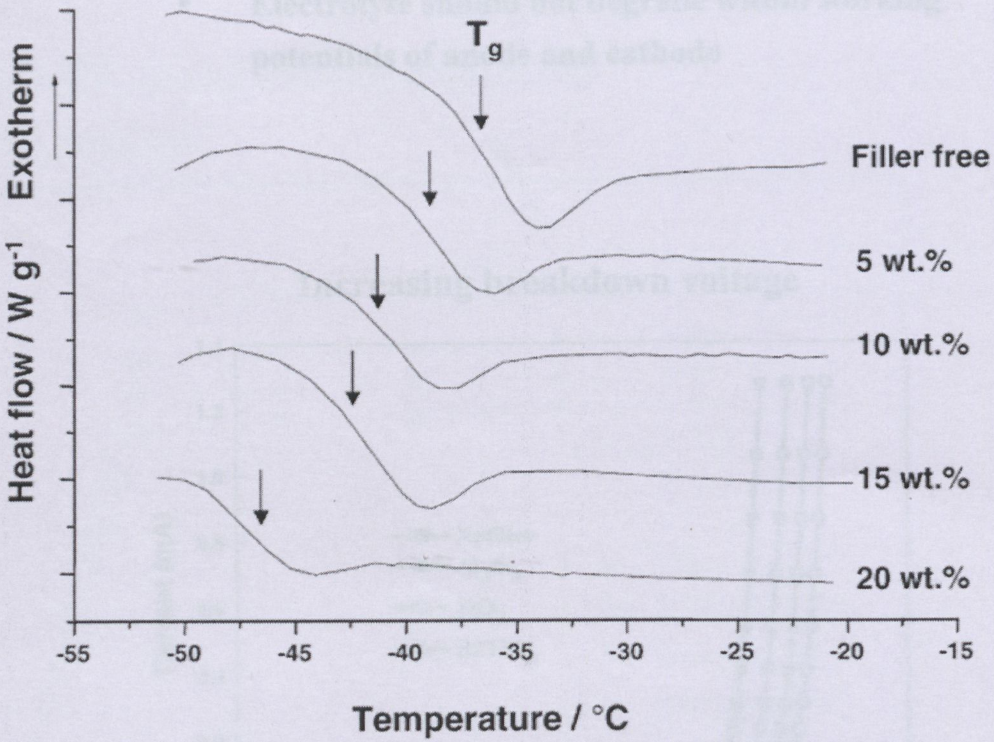
2. Increase polymer segmental motion

Degree of crystallinity ↓

Glass transition temperature (T_g) ↓



Reduced T_g with increasing SiO_2 contents



Taken from Ji et al. (2003)

- **SiO_2 interacts with PEO**
- **SiO_2 penetrate the space between PEO chains**
- **PEO segmental motion increase & degree of crystallinity decrease**

Advantages of CPEs (cont')

3. Increase interfacial stability & electrochemical window

- Li electrode reacts with electrolyte to form a passivating layer or solid electrolyte interface (SEI)
- Cyclability of Li-ion battery is affected by nature & morphology of passivating layer

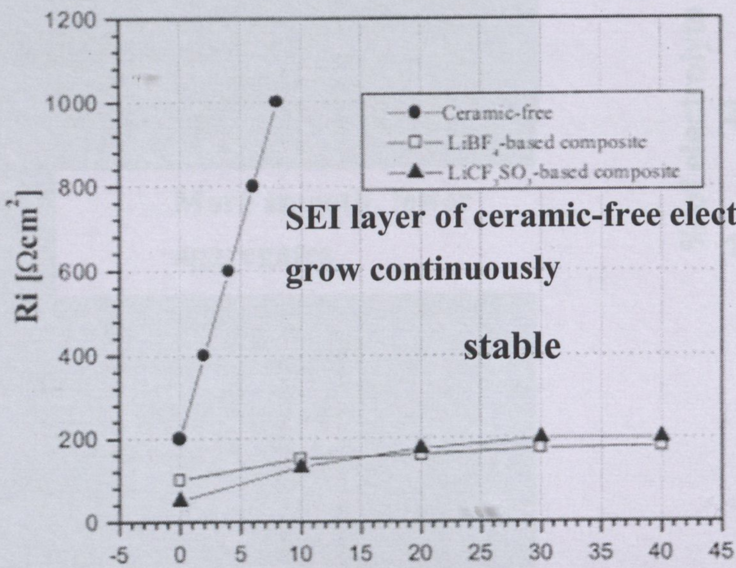
Electrochemical window:

- Voltage range where substance is neither oxidized nor reduced
- No side reactions during cycling of devices
- Electrolyte should not degrade within working potentials of anode and cathode

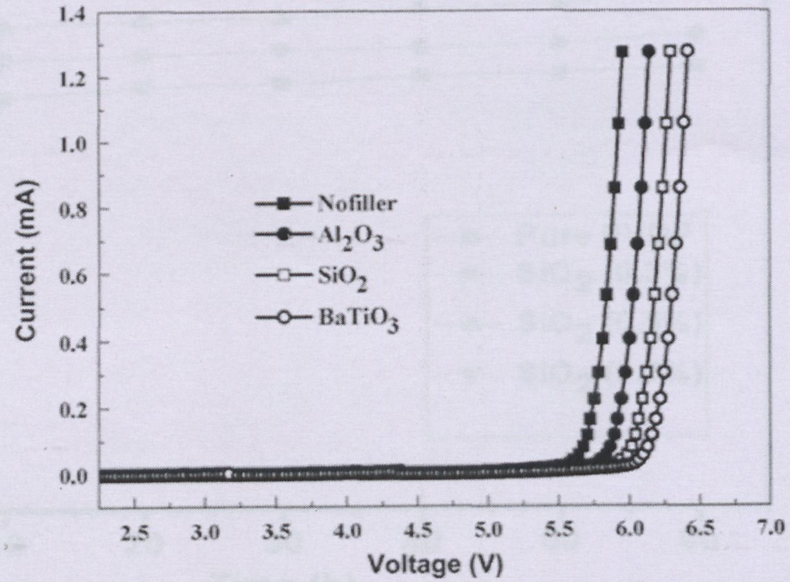
Aim: STABLE, COMPACT, THIN passivating layer

Increased electrode-electrolyte interfacial stability

Impedance measurement

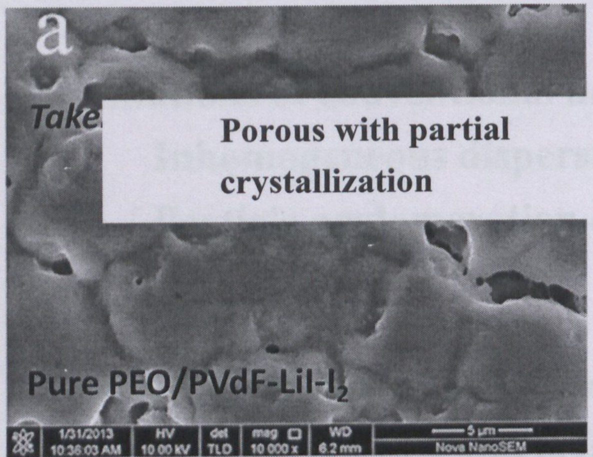


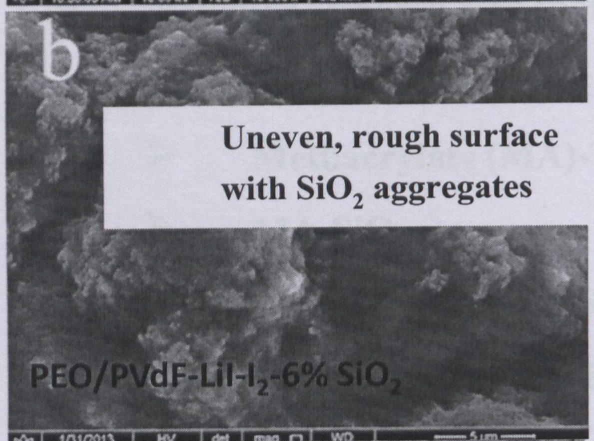
Increasing breakdown voltage

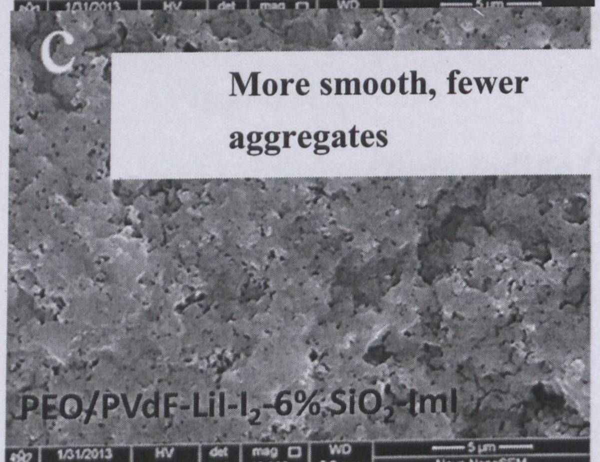


Taken from Raghavan et al. (2010)

Advantages of CPEs (cont')



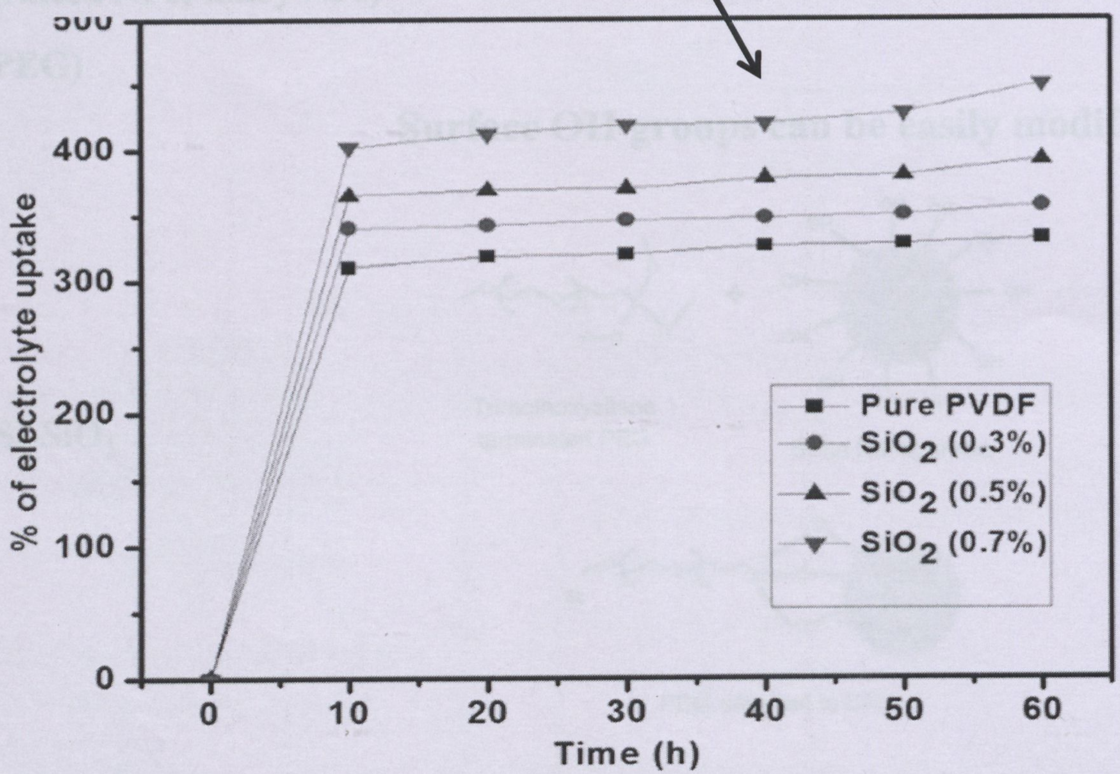




4. Improve morphology

- Porous structure
- Enhanced electrolyte uptake

Increased $LiPF_6$–based electrolyte uptake at higher SiO_2 contents



Taken from Sethupathy et al. (2013)

Functionalized Nanoparticles

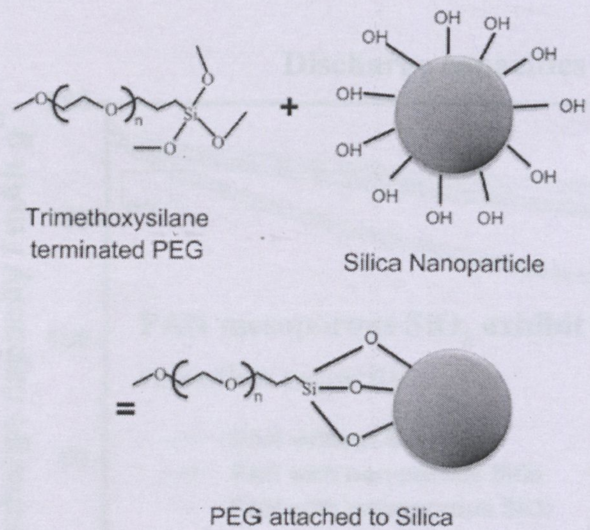
Limitations of conventional nanofillers:

- **Inhomogeneous dispersion of nanoparticles in electrolyte**
- **Particle agglomeration & phase separation**

Types of functionalized nanofillers:

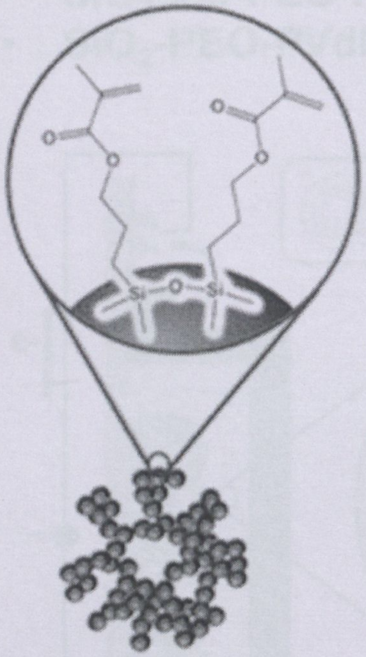
- **Polymer-tethered NPs (polymer-grafted NPs; hairy NPs)**
  - **SiO_2-poly(ethylene glycol) (PEG)**
  - **Methacrylate (MA)-TiO_2**
  - **MA-SiO_2**
- **Hydrochloric acid (HCl)-SiO_2**
- **Dodecanoic acid (DOA)-SiO_2**
- **Dodecyl-tri-methoxysilane (DTMS)-SiO_2**
- **Vinyl-TiO_2**
- **SiO_2-imidazolium iodide (ImI)**

Surface OH groups can be easily modified

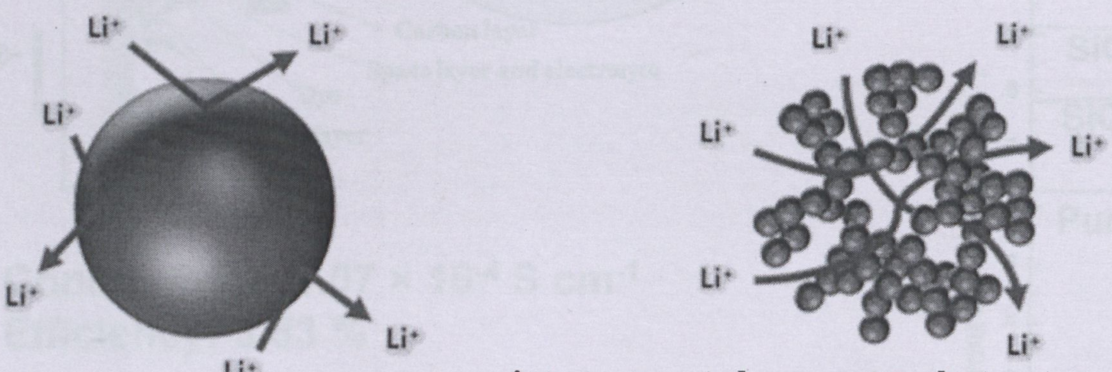


SiO_2-PEG

Functionalized Nanoparticles – MA-SiO_2

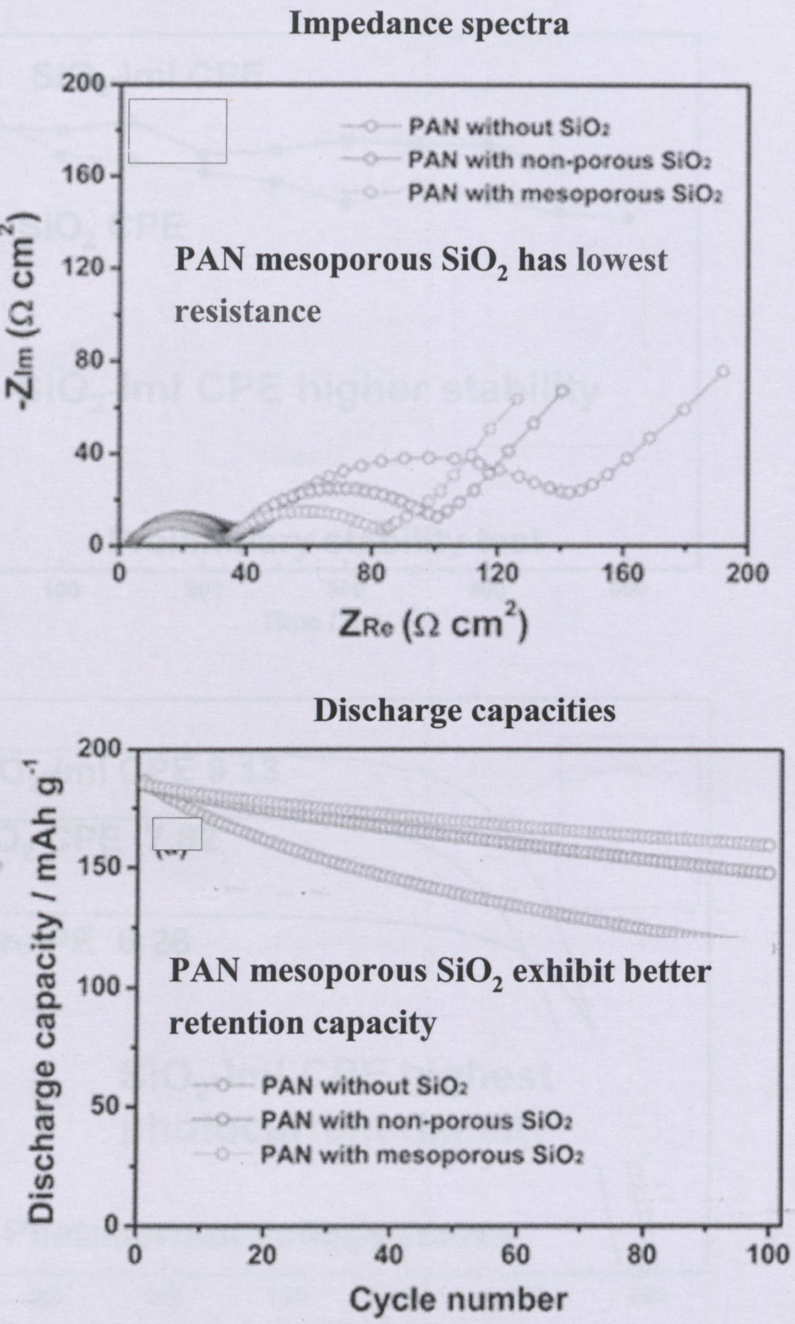


- Reactive methacrylate (MA) groups as cross-linking sites
- Mesoporous
- Li^+ ions can pass through mesoporous SiO_2 particles due to intraconnected pore network structure



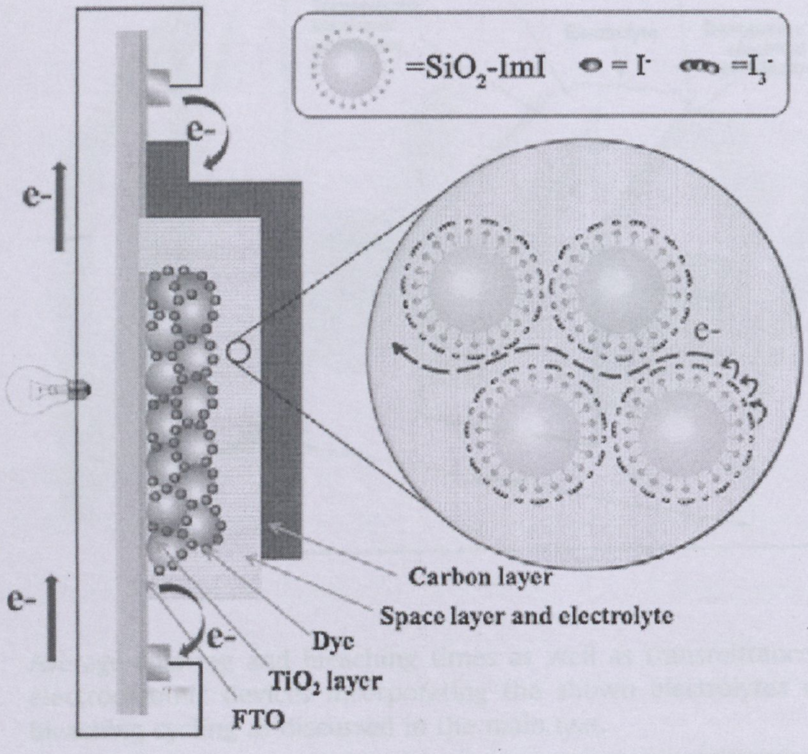
Li ion transport behavior in MA-SiO_2 NPs

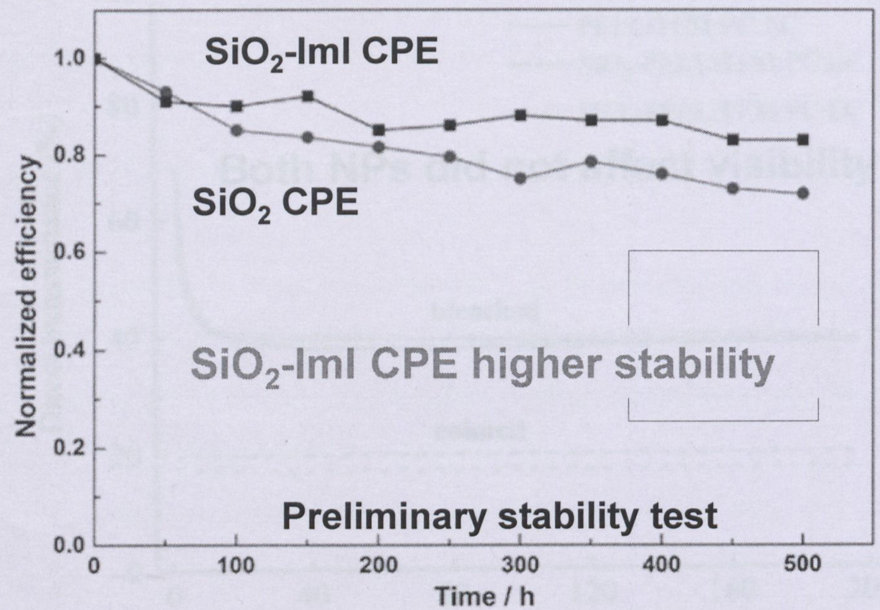
Taken from *Shin et al. (2016)*

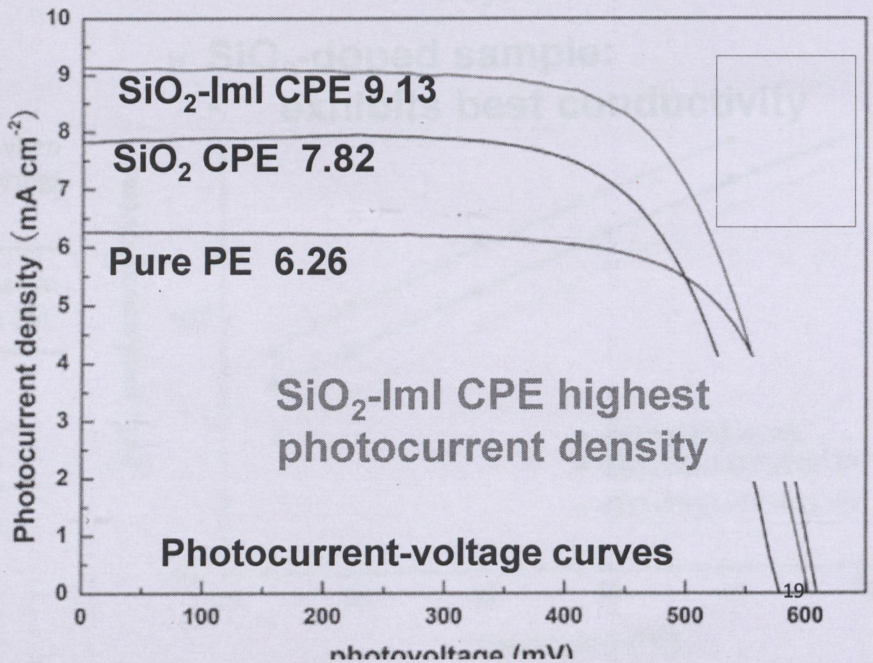


Nanoparticles in Dye-Sensitized Solar Cell (DSSC)

- SiO_2-ImI-PEO-PVdF
- SiO_2-PEO-PVdF







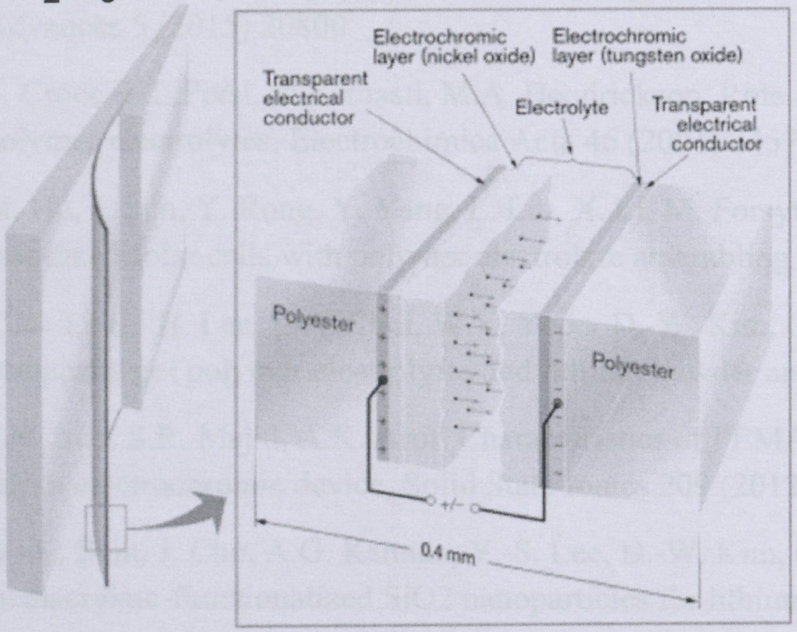
Conductivity: 1.07×10^{-4} S cm^{-1}
Efficiency: 3.83 %

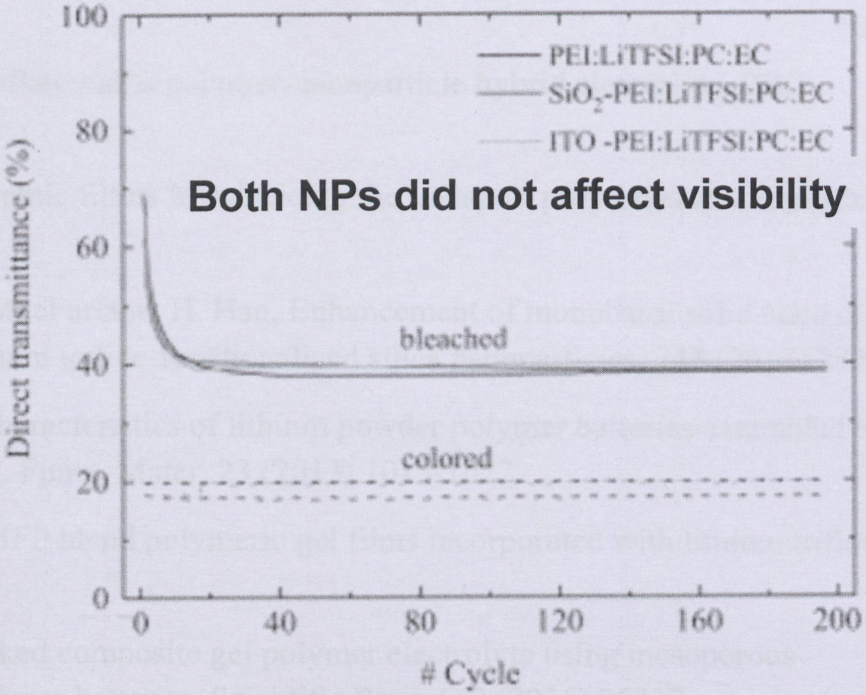
Less aggregation, better dispersion of SiO_2-ImI in PEO/PVdF matrix as compared to SiO_2 NPs

Taken from *Hu et al. (2014)*

Nanoparticles in Electrochromic Device (ECD)

- SiO_2-PEI:LiTFSI:PC:EC
- In_2O_3:Sn (ITO)-PEI:LiTFSI:PC:EC

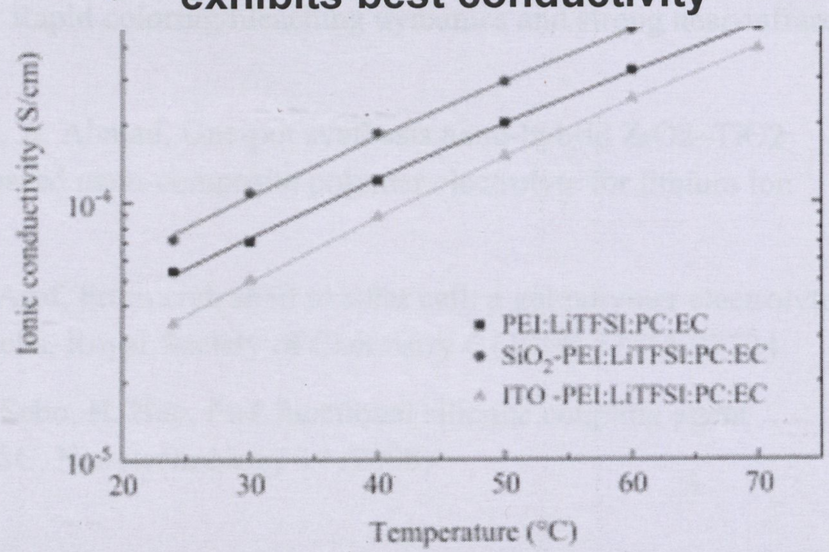




Both NPs did not affect visibility

SiO_2-doped sample:

- **exhibits best conductivity**



Average coloring and bleaching times as well as transmittance difference when electrochromic devices incorporating the shown electrolytes undergo coloring/bleaching cycling as discussed in the main text.

Electrolyte	Coloring time (s)	Bleaching time (s)	Transmittance difference (%)
PEI:LiTFSI:PC:EC	74	147	18
SiO_2-PEI:LiTFSI:PC:EC	31	146	22
ITO-PEI:LiTFSI:PC:EC	31	146	20

Taken from *Pehlivan et al. (2014)*

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