Electrolytes for lithium batteries and fuel cells

Center for Nanomaterials Design and Assembly

http://www.pa.msu.edu/~duxbury/CND/CND.html

January 24th : Jim McCusker (Chemistry - MSU), *"Photochemical control of charge transfer complexes for improved solar cells"*

January 31st : Keith Promislow (Mathematics - MSU), *"The role of nanomorphology in proton conduction through polymer electrolytes"*

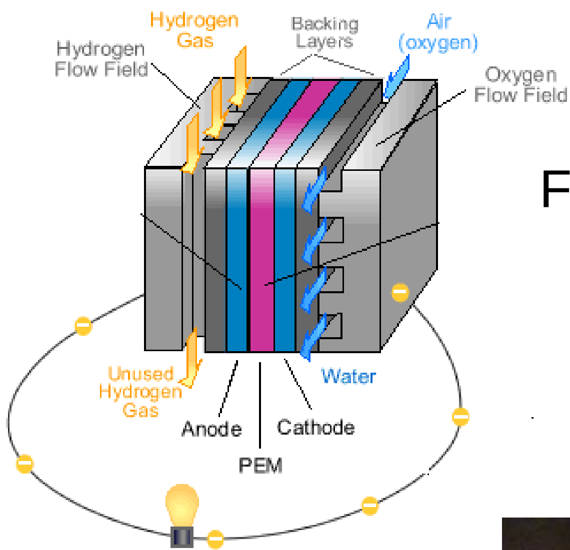
February 7th : Greg Baker (Chemistry - MSU), *"Materials for Fuel Cells"*

February 14th : Don Morelli (Materials Science - MSU), *"Introduction to high ZT thermoelectric materials and their applications"*

February 21st : Special Energy Seminar : Wolfgang Bauer (Physics, MSU) *Is bio-gas generation a cost-effective option for the Michigan energy economy?*

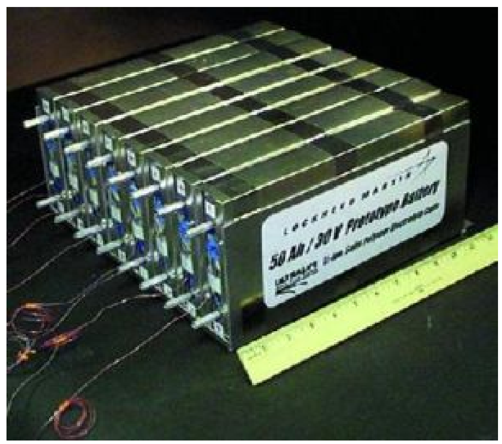
February 28th : Phillip Duxbury (Physics - MSU) *"Theoretical and practical limits on solar conversion efficiency : Why use nanostructured materials?"*

Organic (ion-conducting) membranes in energy applications



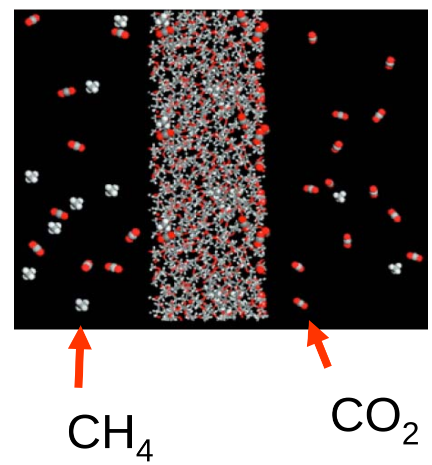
Fuel cells

supercapacitors



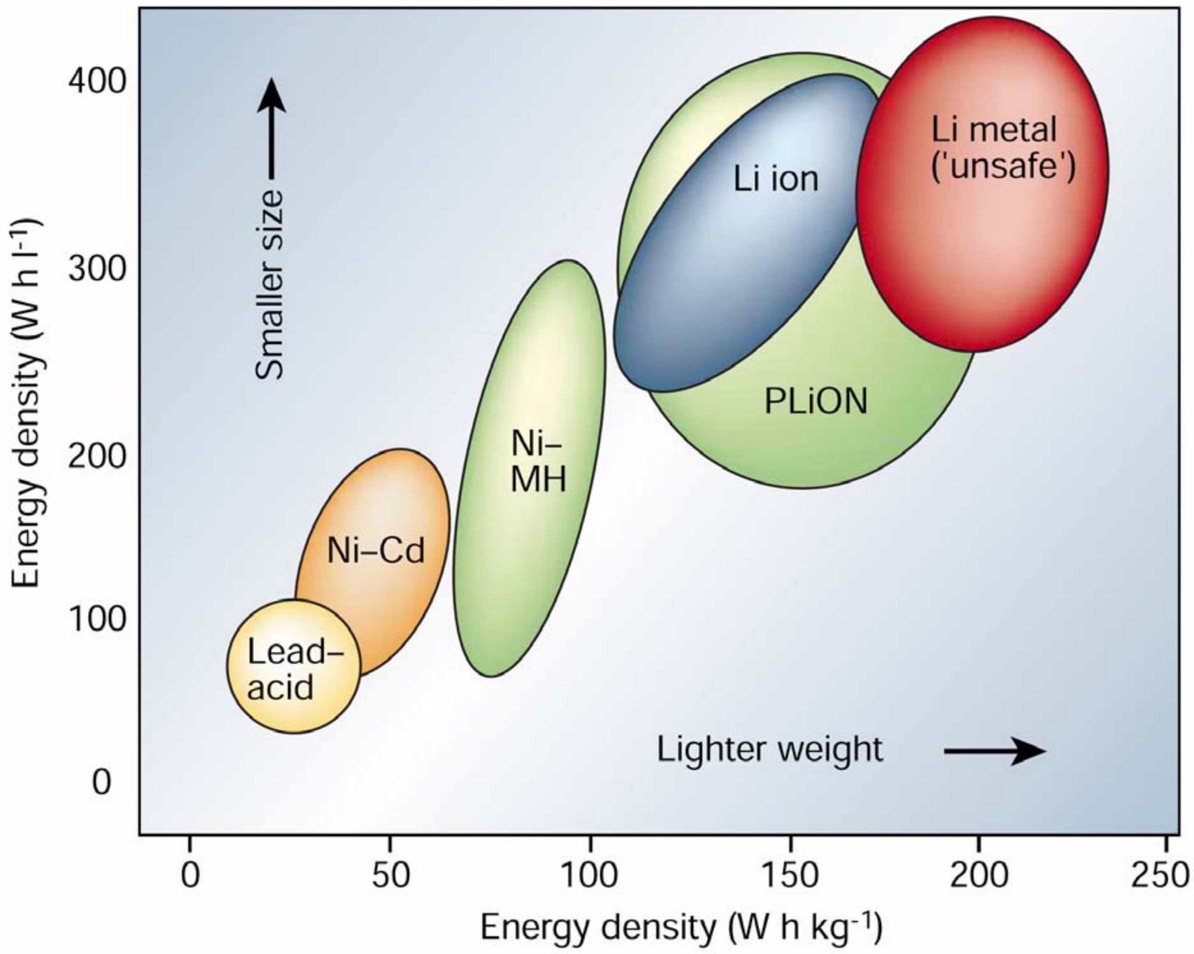
Li ion batteries

CO_2 sequestration



solar cells

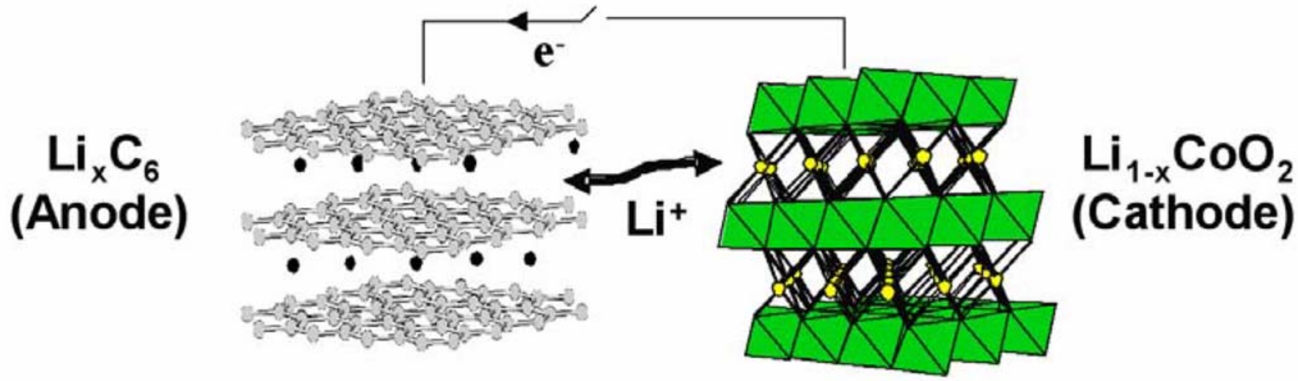
Rechargeable Batteries



High reactivity with solvents used for electrolytes - only polyethers are compatible with Li metal

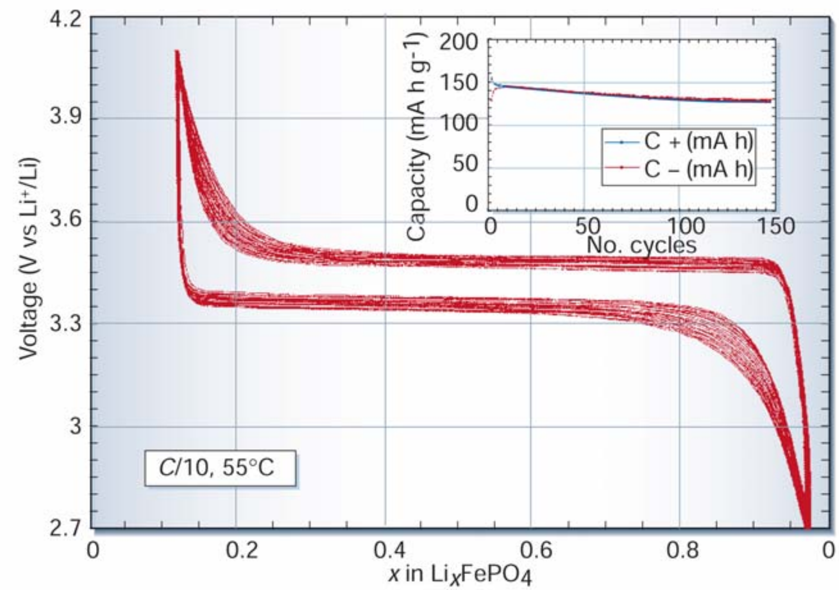
Tarascon, J. M.; Armand, M., **2001,** 414, (6861), 359-367

"Rocking Chair" batteries (Lithium Ion Cells)



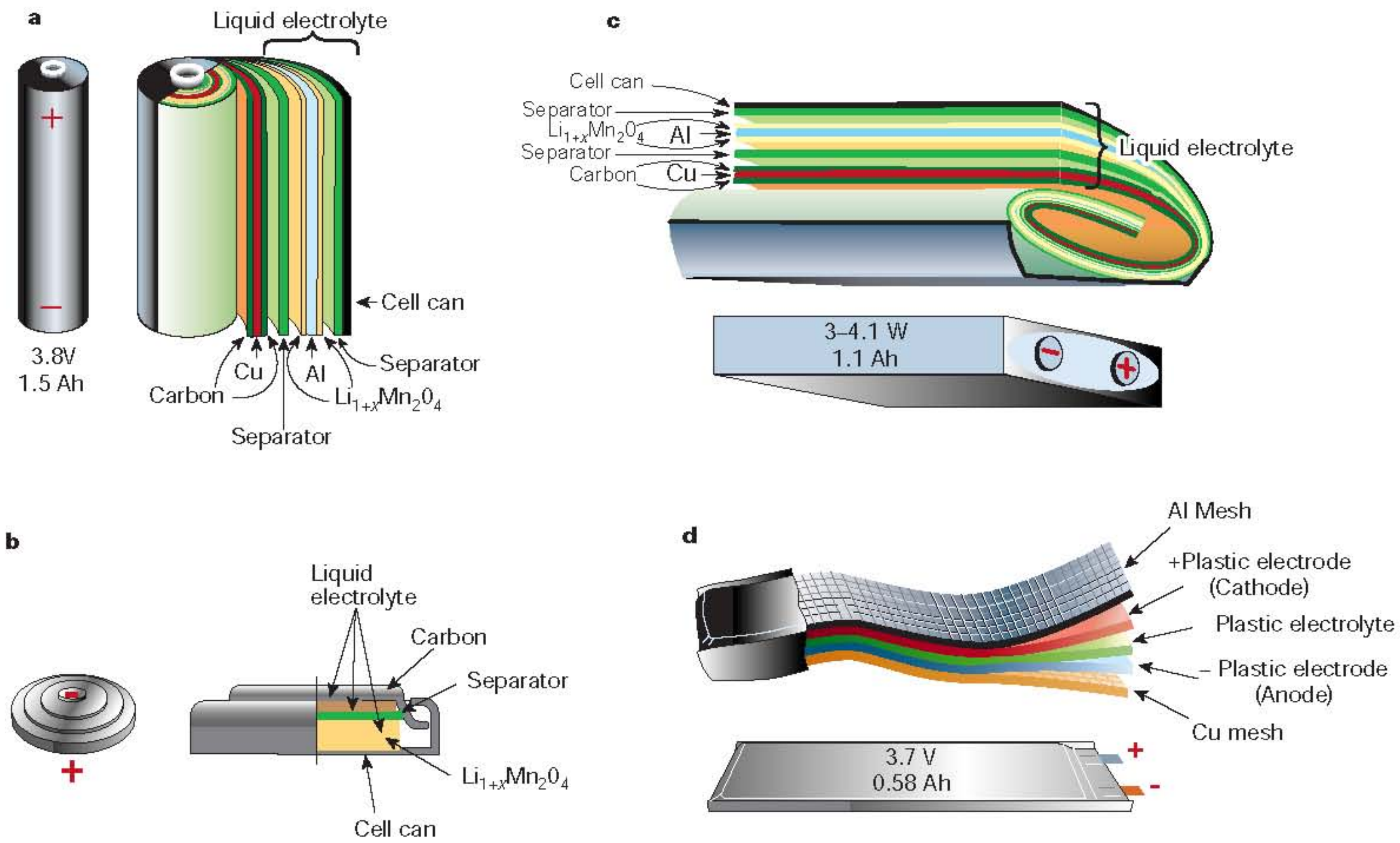
Cathode:	$MO_x + Li^+ + e^- \rightarrow LiMO_x$ (where *M* is Co, Ni, Mn, V, etc.)	
Anode 1:	$LiC_6 \rightarrow Li^+ + e^-$	2.5 to 4.5V, ~600 Wh/kg
Anode 2:	$Li \rightarrow Li^+ + e^-$	3 to 5 V, ~900 Wh/kg

applications: laptops, cell phones, power tools,



Tarascon, J. M.; Armand, M., **2001,** 414, (6861), 359-367

Making batteries is as simple as baking ...



Tarascon, J. M.; Armand, M., **2001,** 414, (6861), 359-367

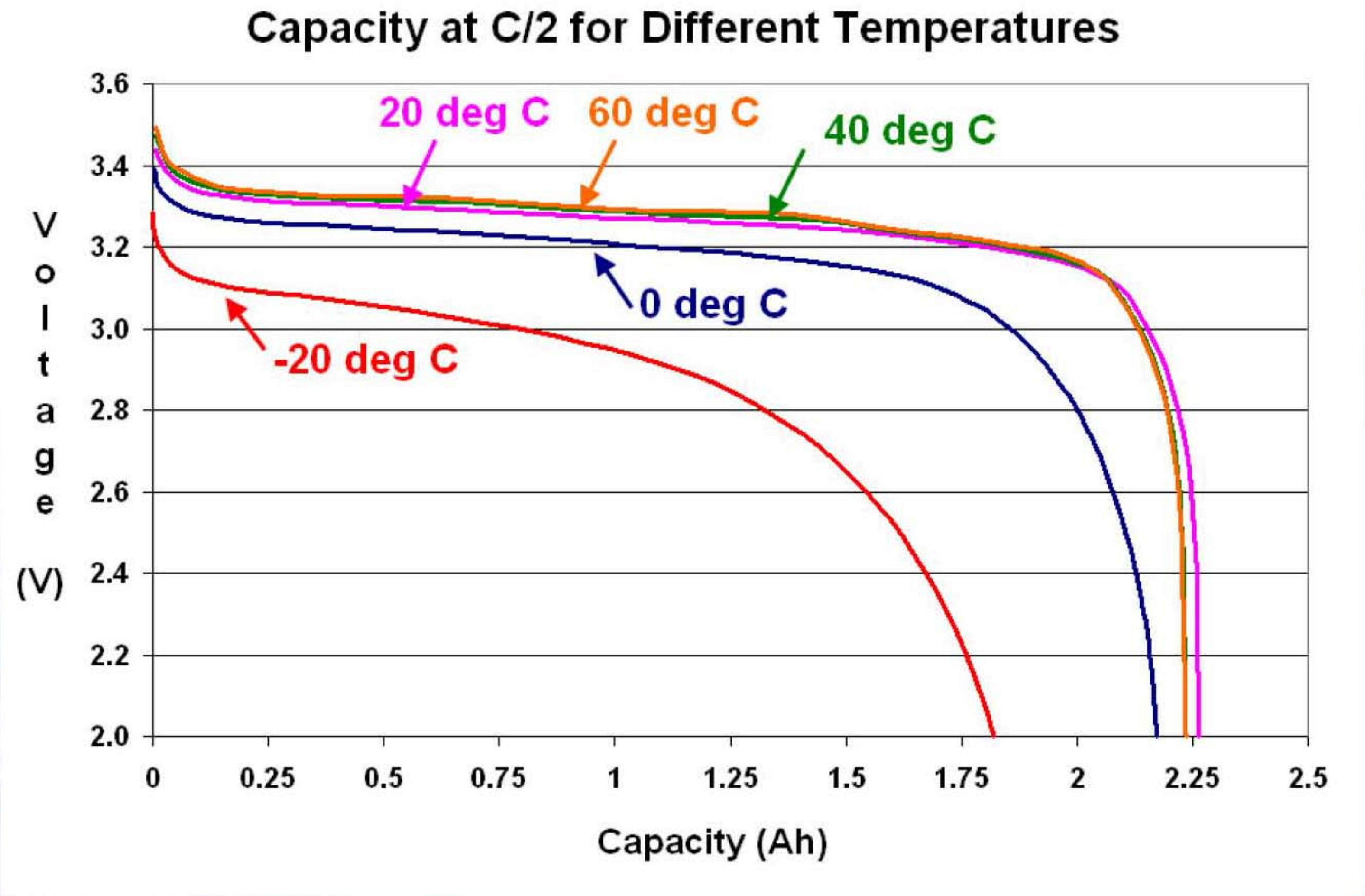
Properties of real lithium batteries

Table 8. Performance specifications reported for various lithium-ion battery products

	Li-ion ($LiCoO_2$) (MoliCel, model ICR-18650J)	**Li-ion ($LiMn_2O_4$) (MoliCel, model IMR26700)**	**Li-ion ($LiFePO_4$) (A123 Systems, ANR26650M1)**
Nominal voltage	3.75 V	4.2–2.5 V	3.3 V
Nominal capacity	2.4 Ah	3.0 Ah	2.3 Ah
Energy density	188 Wh/kg; 520 Wh/l	285 Wh/l	
Power density		1500 W/kg at 20s	
Discharge current	4.0 A max		70–120 A (pulse)
Charge current	2.4 A max		10 A
Internal impedance			(1 kHz ac) 8 mΩ
Dimensions (mm, diam × length)	18.24×65 mm	26.4×70 mm	26×65 mm
Weight	47 g	47 g	70 g
Cycle life at 10°C, 100% DOD			> 1000 cycles
Operating temperature: discharge	–20 to 60°C		
charge	0 to 45°C		

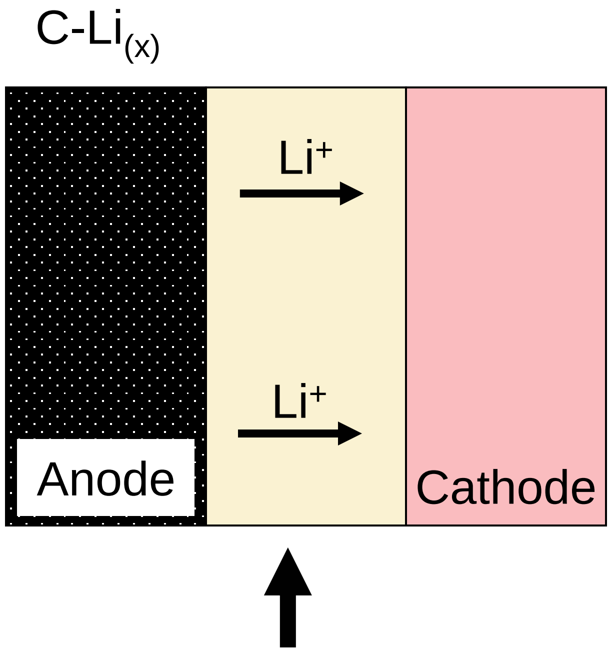
DOE Workshop on *Basic Research Needs For Electrical Energy Storage*, 2007,
http://www.sc.doe.gov/bes/reports/abstracts.html

Performance Testing Results



- Charged at C/2 to 3.6V at discharge temperature, voltage held, taper limit of C/50

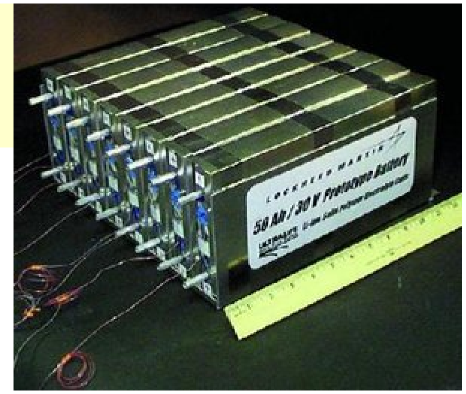
Advanced batteries



$LiCoO_2$
(Sony)

$LiMn_2O_4$
(Bellcore/Telcordia)

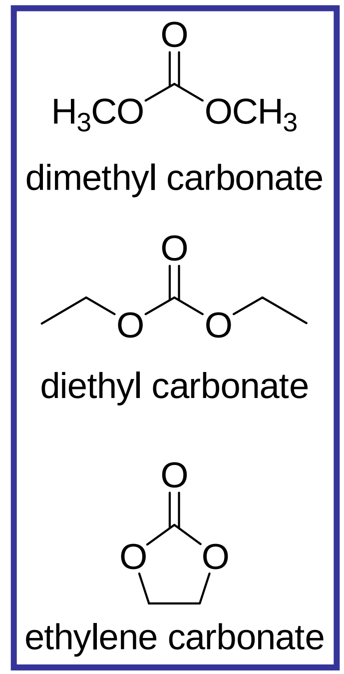
$LiFePO_4$
(A123 systems)



A prototype Lithium-Ion Polymer Battery at NASA Glenn Research Center.

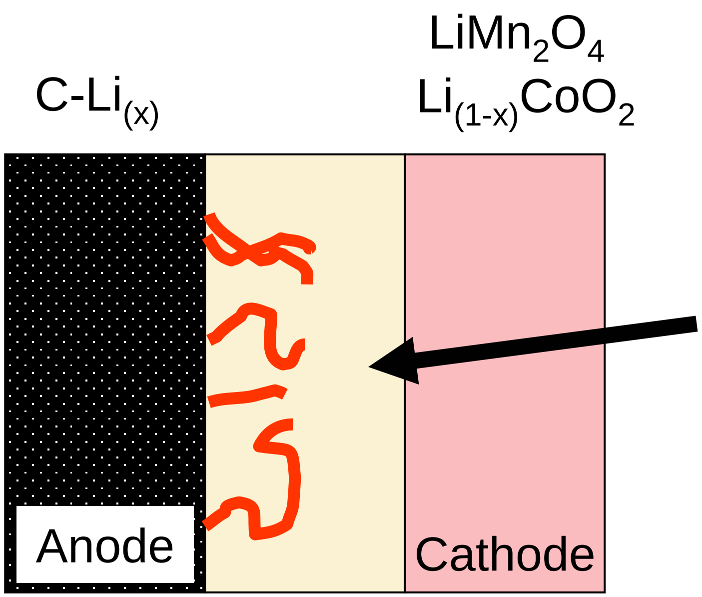
Current technology:

- liquid electrolyte or gel electrolyte (liquid dispersed in a PVDF gel, allows flat packaging, rather than metal cans).
- Li^+PF_6 or similar salt
- mixtures (usually) of ethylene carbonate, dimethyl carbonate, diethyl carbonate

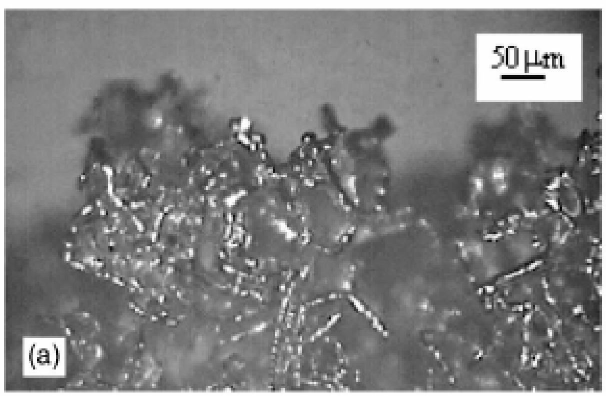


Flambeau de laptop ...

- over charging leads to dendrite formation
- excessive dendrite growth leads to a short
- a short leads to heat, venting, fire, ...



liquid or polymer electrolyte
(*flammable!* organic)



Lithium dendrites

X-W Zhang, Y. Li, S. A. Khan, P. S. Fedkiw, J. Electrochem. Soc., 2004, 151, A1257-A1263.

http://www.theinquirer.net/en/inquirer/news/2006/06/21/dell-laptop-explodes-at-japanese-conference

The moral of the story ....

"....... the theoretical specific energy of a lithium thionyl chloride battery is on the order of 1420 Wh/L, which is comparable to the theoretical specific energy of TNT at 1922 Wh/L."

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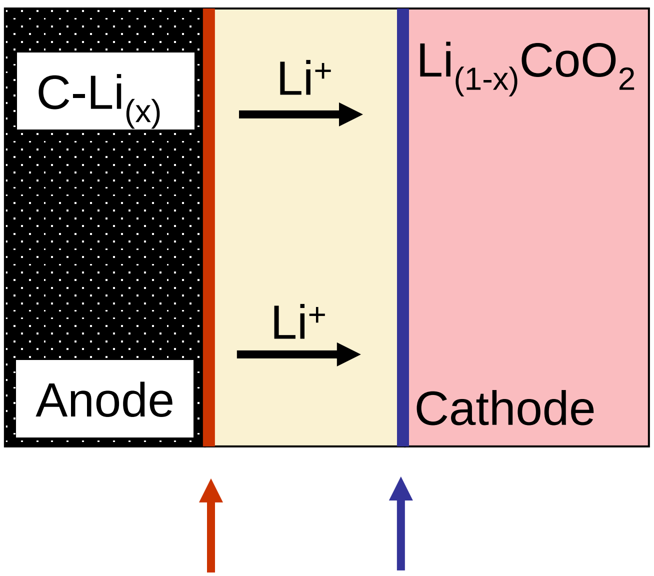

passivating layers (SEI)

most organic solvents are inherently unstable to high oxidation and reduction potentials at cathode and anode, small molecule easily transported to electrodes

Solvent Electrode Interface:

- ionic conductor, electrical insulator
- mechanically robust through repeated cycling
- inhibit dendrite formation

BASIC RESEARCH NEEDS FOR ELECTRICAL ENERGY STORAGE
(DOE Workshop, 2007, http://www.sc.doe.gov/bes/reports/abstracts.html)

3.5.3 Technical and Cost Barriers

Technical Barriers and needs

Anodes
- Alternative anodes (e.g., intermetallics, oxides) to improve safety and performance
- Enhanced specific and volumetric capacity and rate capability
- Reduced first-cycle capacity loss and volumetric expansion of intermetallic electrodes
- Enhanced stability and robustness of SEI layers
- Elimination of lithium dendrites (lithium metal anode)
- Prevention of mossy lithium formation (lithium metal anode)

Cathodes
- Enhanced specific capacity, rate capability, stability over a wide composition range
- Enhanced stability/robustness of high-potential electrode surfaces (>4.2 V vs. Li^0)
- Reduced solubility of transition metal ions
- Low cost materials, for example, manganese- or iron-based systems

Electrolytes and separators
- Nonflammable liquid electrolytes with adequate Li^+-ion conductivity
- Expanded electrochemical stability window, to 5 V
- Low-cost, non-toxic salts
- Improved low-temperature performance
- Effective redox shuttles for overcharge protection
- Electrolyte additives for effective SEI layer formation
- Stable ionic liquids and solid polymer electrolytes with acceptable conductivity
- Lower cost and improved shutdown properties of separators

suggests polymer-based, ionic liquid, or other solutions

BASIC RESEARCH NEEDS FOR ELECTRICAL ENERGY STORAGE

(DOE Workshop, 2007, http://www.sc.doe.gov/bes/reports/abstracts.html)

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- Stable ionic liquids and solid polymer electrolytes with acceptable conductivity
- Lower cost and improved shutdown properties of separators

a partial wish list ...

inherent safety
stable, reproducible passivating layers
infinite cycling
high capacity
low temperature performance

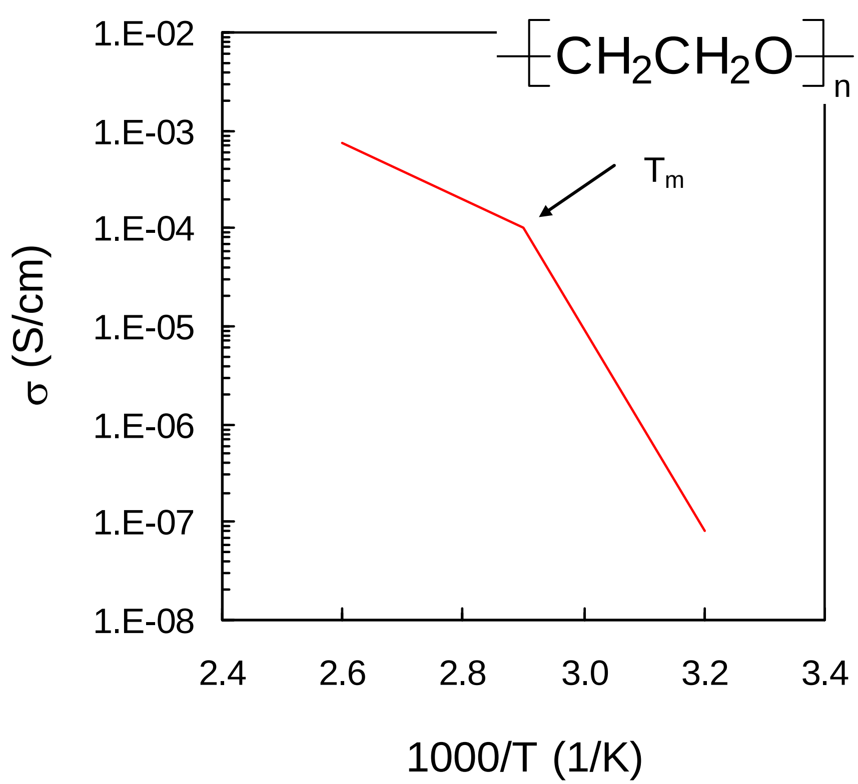
could be solved via immobile (polymer) electrolytes
inherent kinetic stability

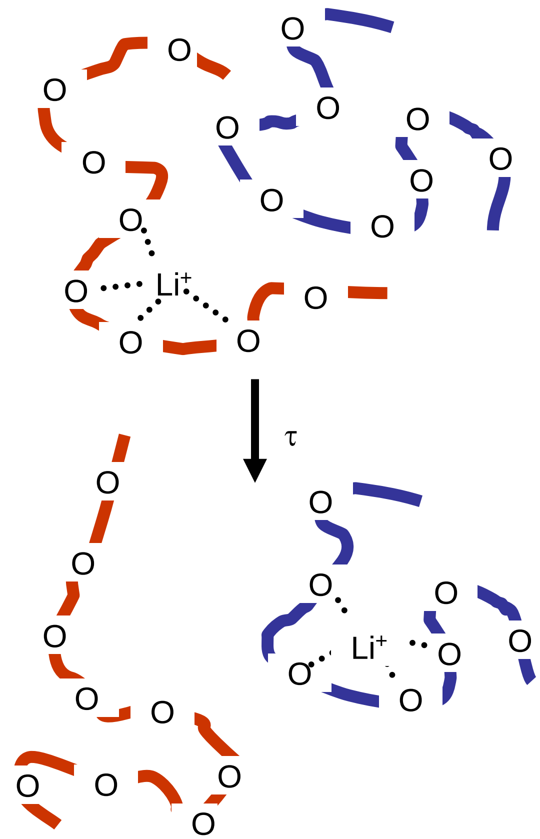
suggests polymer-based, ionic liquid, or other solutions

Ion-conduction in polyethers

of charge carriers → n; mobility → μ; charge/carrier → q

$$\sigma = n \bullet q \bullet \mu$$



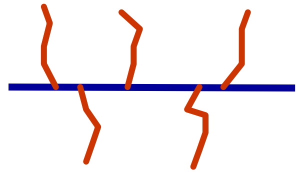


- dissolves Li salts well
- ion mobility correlated with segmental motion of the PEO chain
- crystallinity limits the conductivity below 60 °C

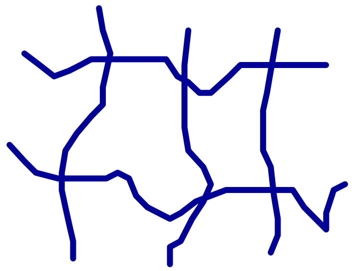
Typical Approaches to Enhance Conductivity

Structures designed to limit crystallinity

- •"blocky" polymers



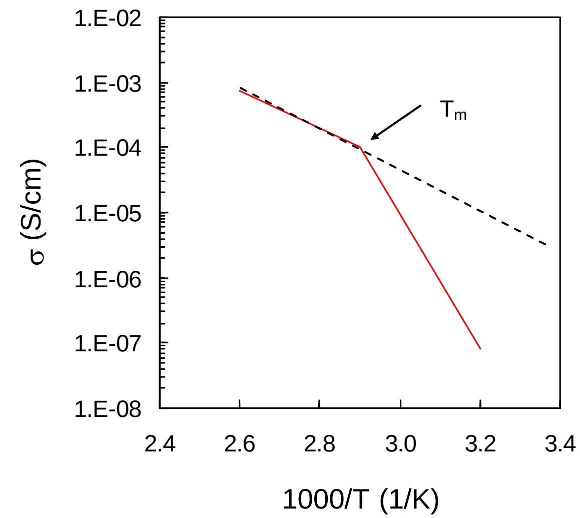
- •branched copolymers



- •network polymers

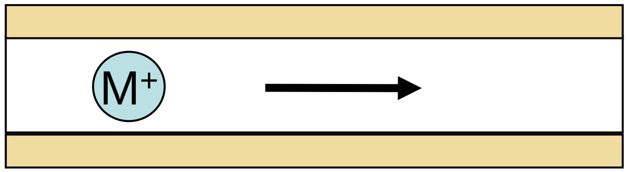
Additives designed to limit crystallinity

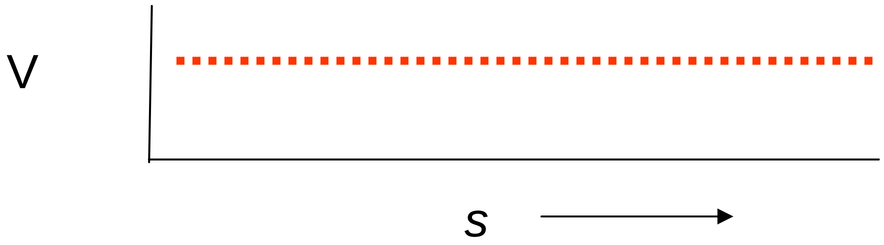
- •polymer blends
- •polymer-filler composites



Limited success (10^{-4}-10^{-5} S/cm @ room temperature, vs. 10^{-1} -10^{-5}S/cm for liquids

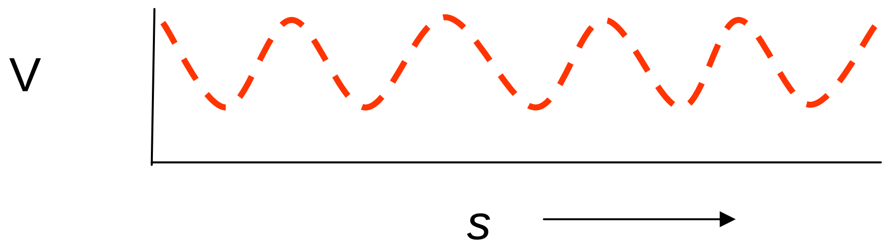
Idealized ion transport





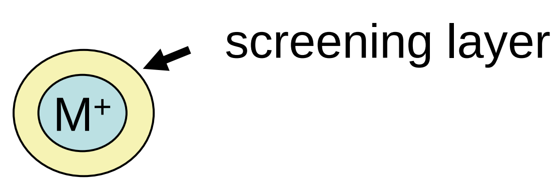
ions diffusing in a uniform potential - weak coupling limit

highest mobility



ion hopping: - strong coupling

chaperone approach
(a compromise)



classifying electrolytes systems by function (mechanical, σ)

"coupled" systems

σ and E derived from a single material

"de-coupled" systems

σ and E derived from separate components

inorganic oxides and glasses

PEO/salt complexes

low molar mass electrolytes + inert separator

composite systems - inert fillers + electrolyte

bicontinuous block copolymers

classifying electrolytes systems by function (mechanical, σ)

"coupled" systems

σ and E derived from a single material

"de-coupled" systems

σ and E derived from separate components

inorganic oxides and glasses

vacancy-based diffusion, thermally activated (high T)

PEO/salt complexes

transport coupled to chain mobility

low molar mass electrolytes + inert separator

composite systems - inert fillers + electrolyte

bicontinuous block copolymers

classifying electrolytes systems by function (mechanical, σ

"coupled" systems

σ and E derived from a single material

↔

"de-coupled" systems

σ and E derived from separate components

inorganic oxides and glasses

PEO/salt complexes

low molar mass electrolytes + inert separator

current technology has safety issues, stuck with "canned" batteries *to be displaced by ionic liquids?*

advantages for manufacture providing the morphology can be controlled.
- but will the electrolyte be a liquid (high σ, but safety issues) or a polymer (low σ)

⇨

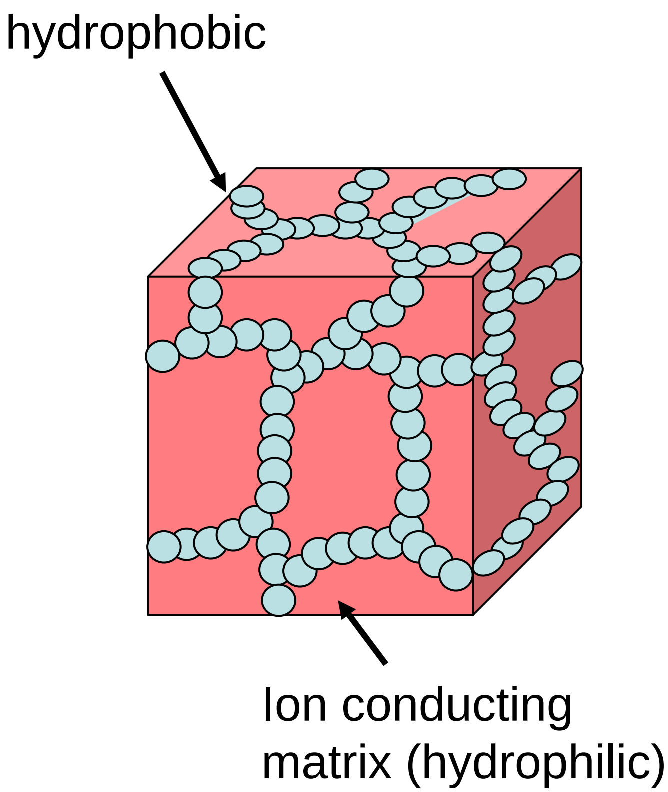
composite systems - inert fillers + electrolyte

bicontinuous block copolymers

*high molecular weight and cross-linked polymers are kinetically stable - no transport to the electrode surface

Bicontinuous phase approach to electrolytes

- conducting phase, high σ
- network structure, mechanical stability



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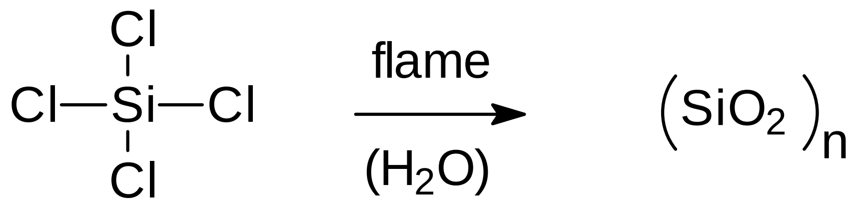
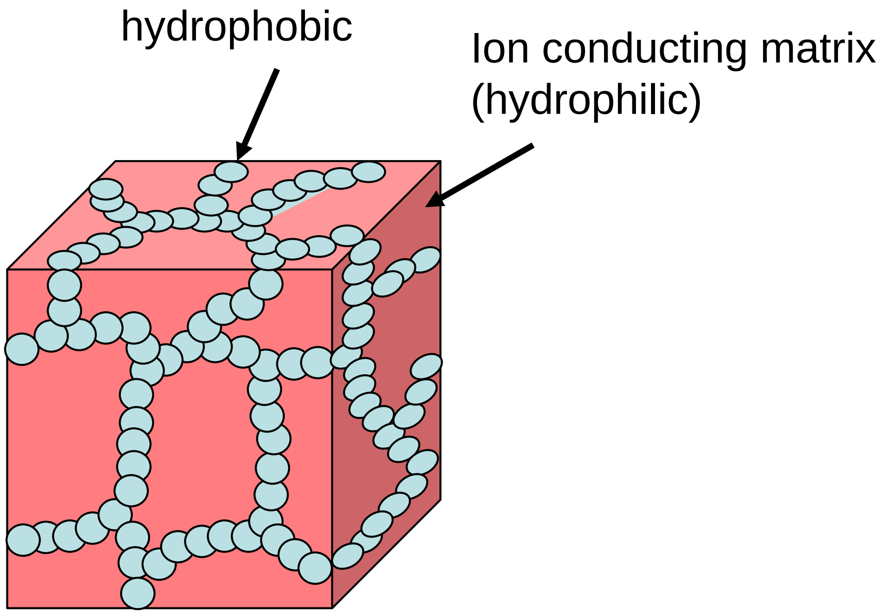
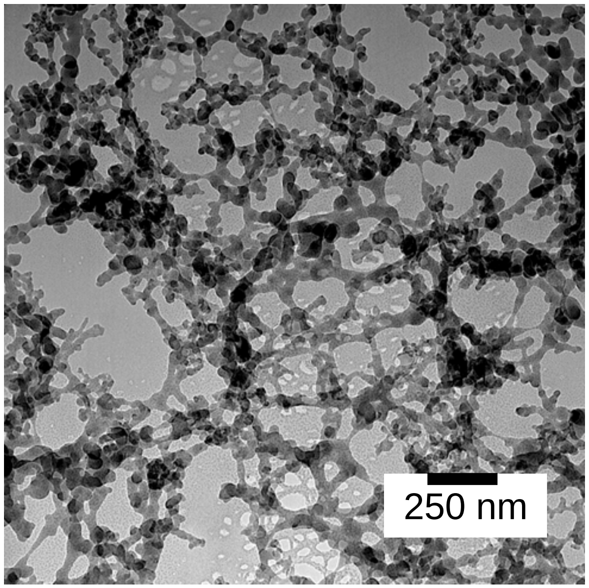




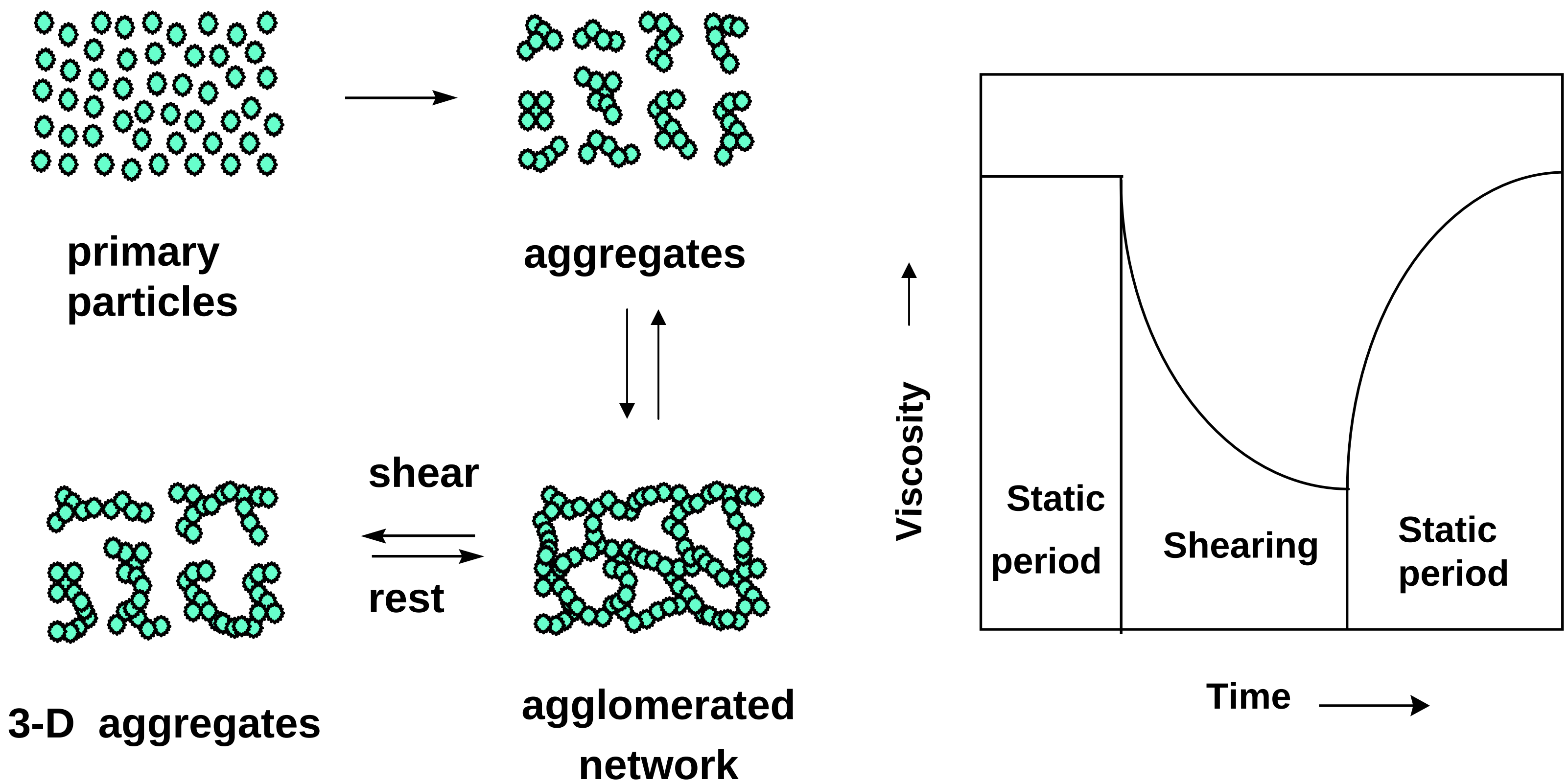


- irregularly shaped particles
- 20-100 nm in diameter
- SiOH surface groups
- aggregate in liquids and form gels

Applications:

- thickening agents for paints, coatings, cosmetics, ...
- moisture control in powders

Thickening & Thixotropy



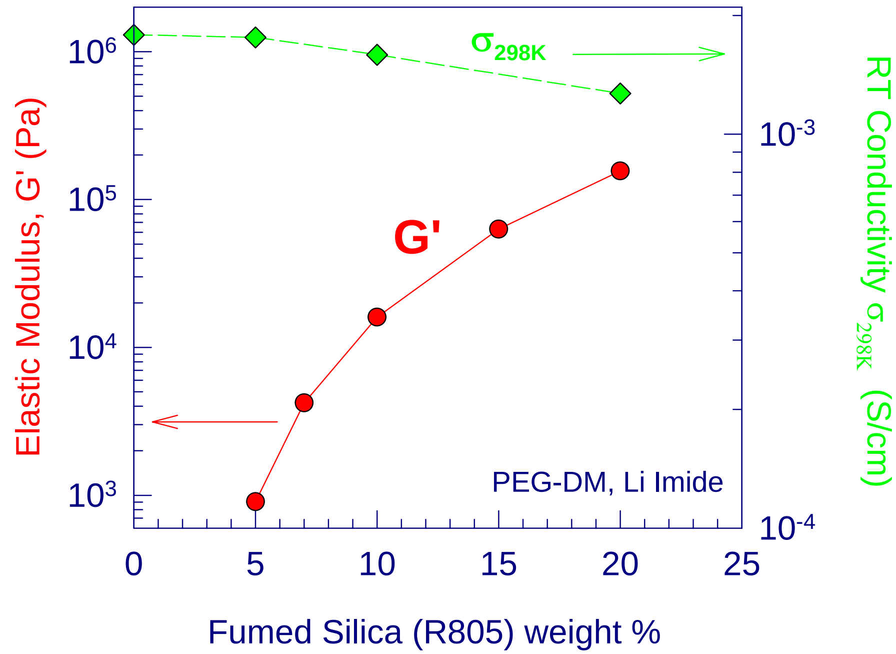
Driving force:

phase separation
H-bonding (SiOH surfaces)
van der Waals (alkyl-terminated)

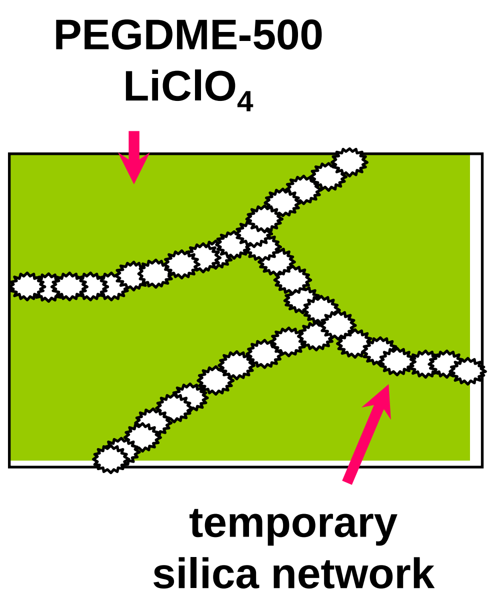
Particle-based Li^+ conductors

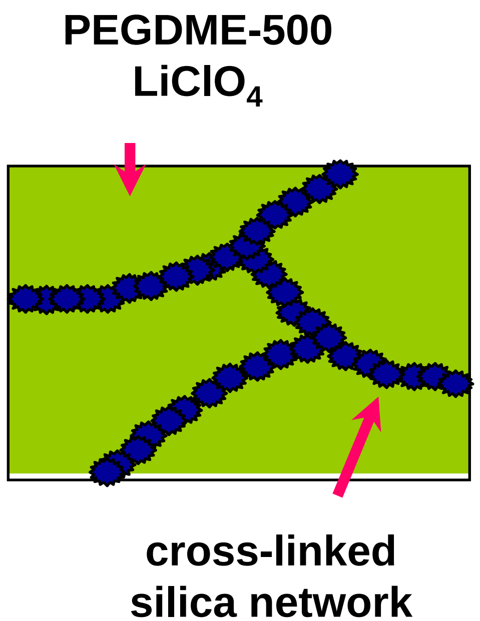
***Strategy*:**

- •fumed silica provides reversible structure formation
- •low molecular weight PEO/Li salt provides good conductivity
- •both properties can be optimized independently to give highly conductive electrolytes that can easily be processed.

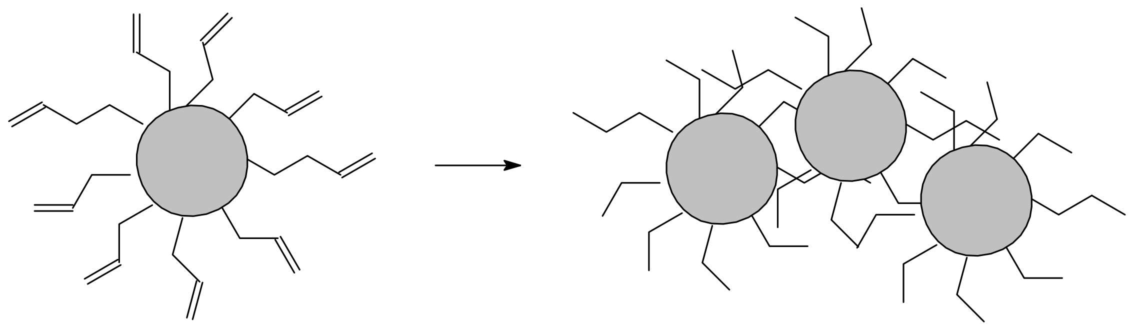


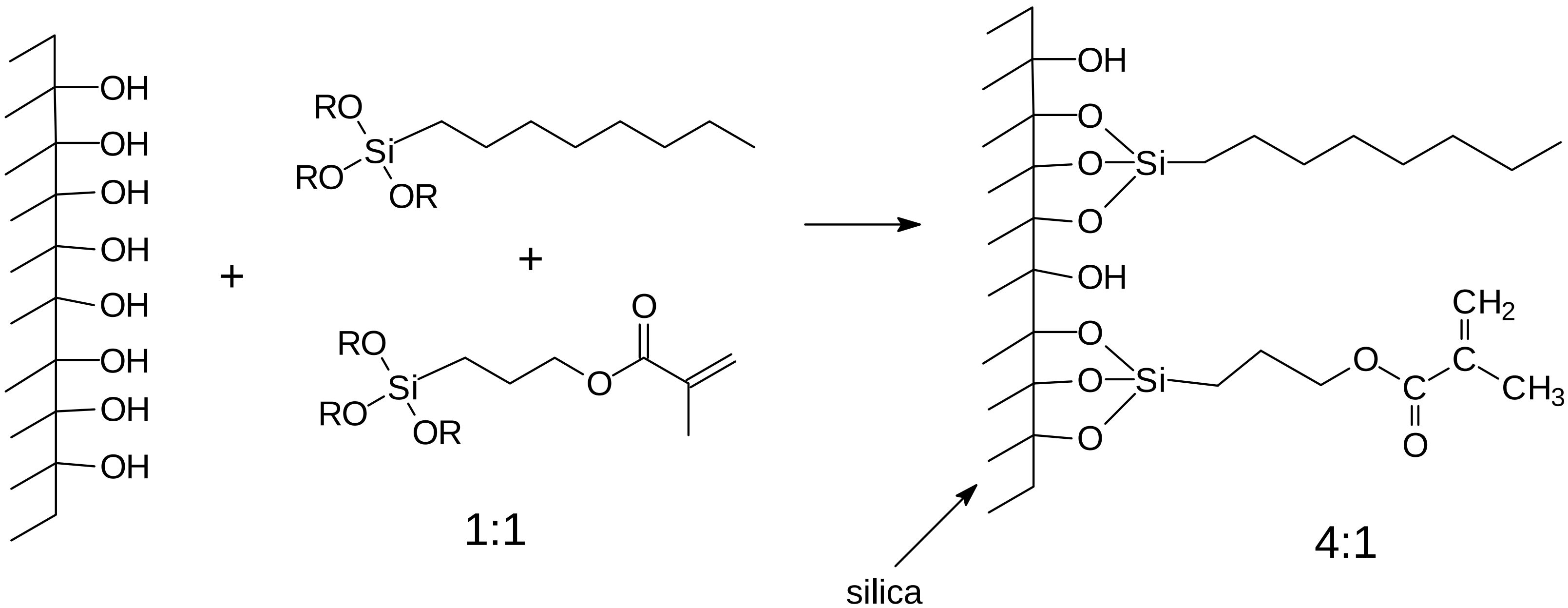
$CH_3O(CH_2CH_2O)_nCH_3$ PEGDME−500
hydrophobic fumed silica (R805)
$LiClO_4$ or Li imide



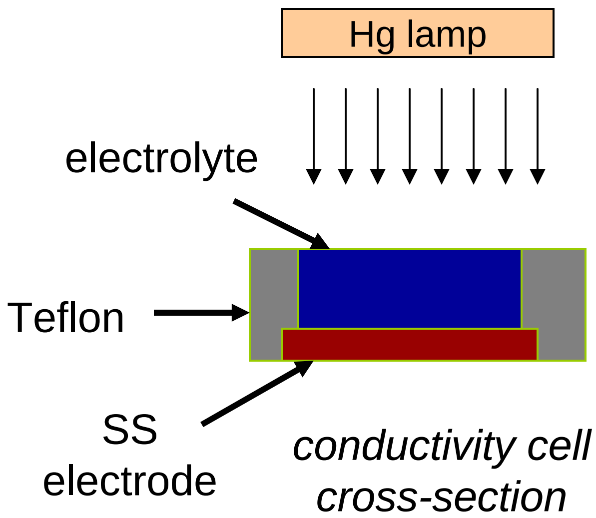


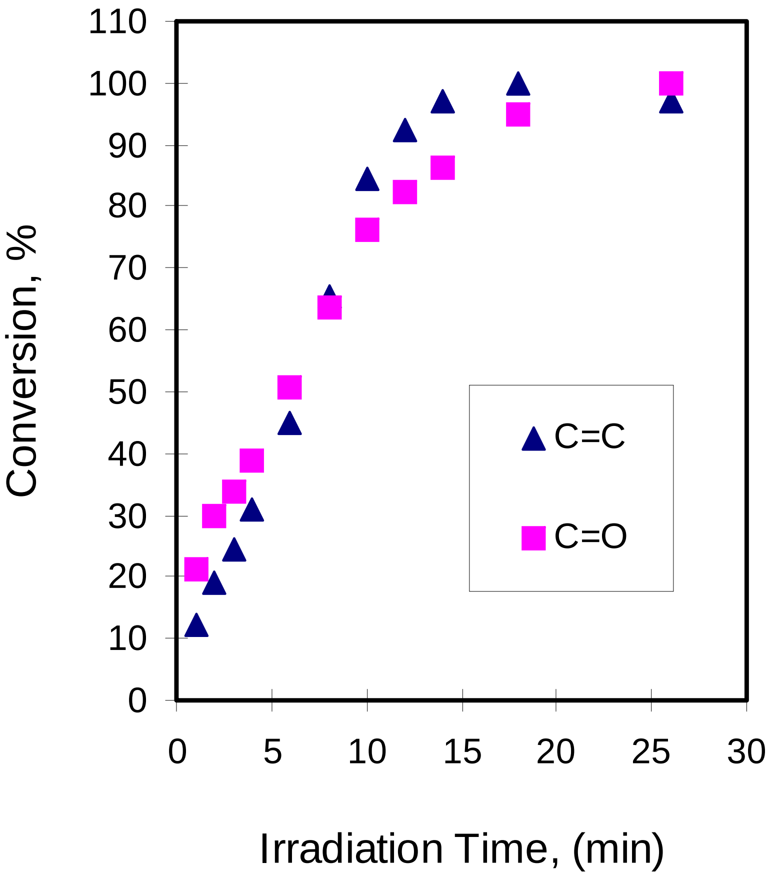
Preparation of Modified Silicas





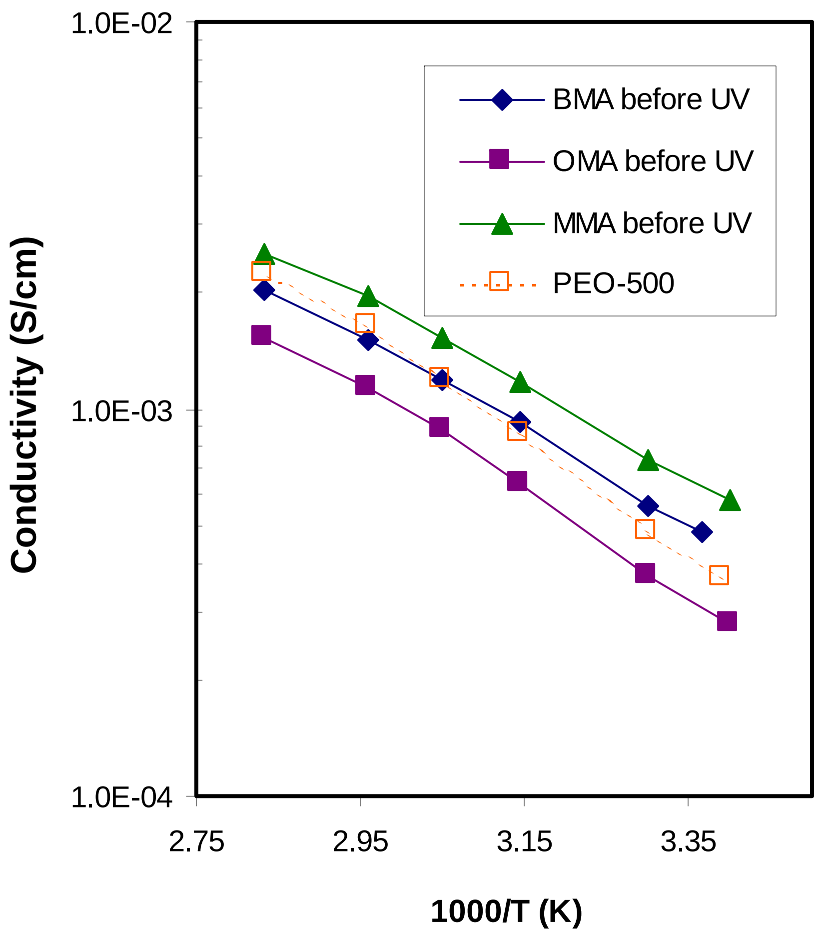
Photocuring of Composites

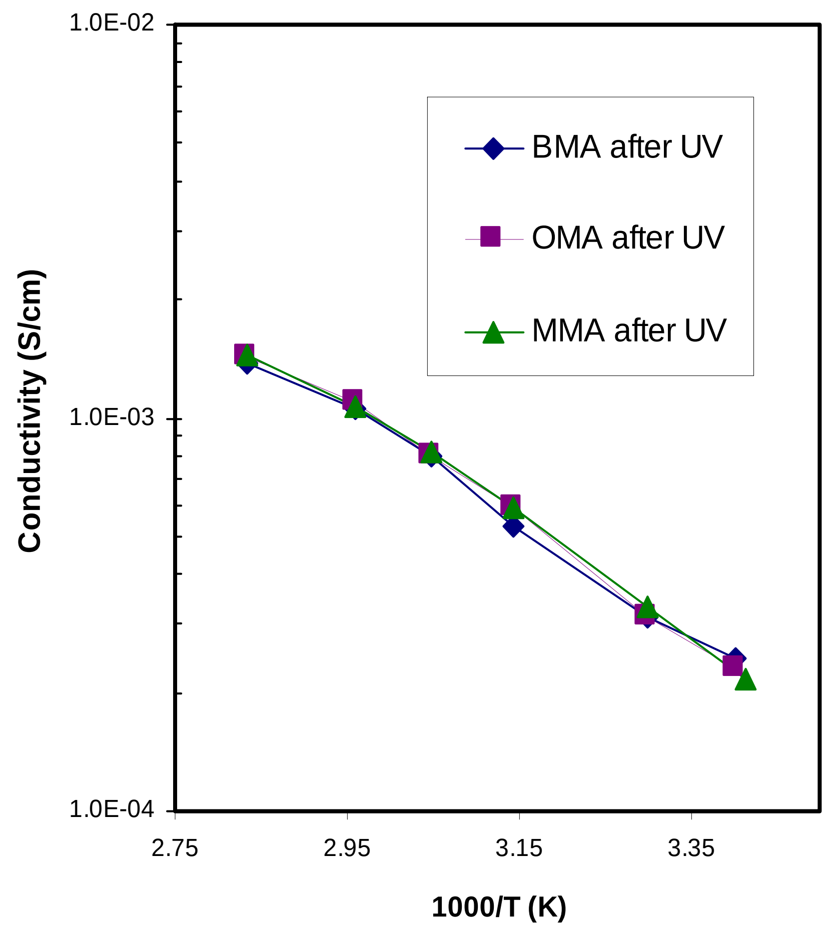




- Irradiate with medium pressure Hg lamp at 30 °C
- Follow loss of C=C and shift of C=O

Conductivities Before and After Curing





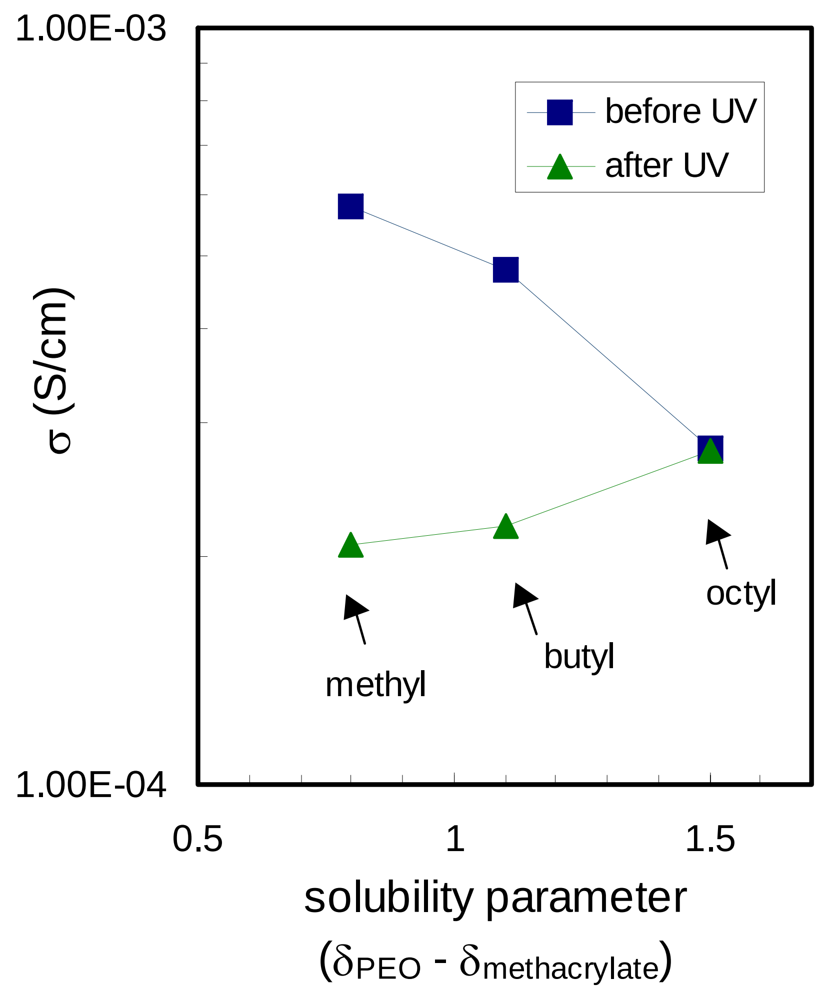
- Difference in initial conductivities reflect solubility of monomer
- Same final σ implies no polymer in electrolyte phase

Effect of Added Monomer: a viscosity effect

PEGDME-500, cross-linkable fumed silica $LiClO_4$

Conductivity of composites related to mis-match in solubility parameters.

Supports phase separation model.



Single-ion Conductors Prepared from Sulfonimides Immobilized on Fumed Silica Nanoparticles

Transference number

t_+ = the fraction of current carried by a charge species

$$t_+ = \frac{i_+}{i_+ + i_-}$$

$$\sum (t_+ + t_-) = 1$$

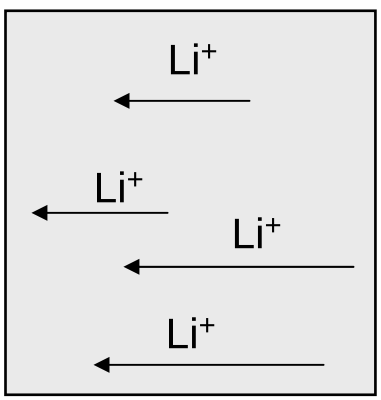
For common binary salts:

$LiClO_4$, $LiN(SO_2CF_3)_2$ (LiTFSI), ..

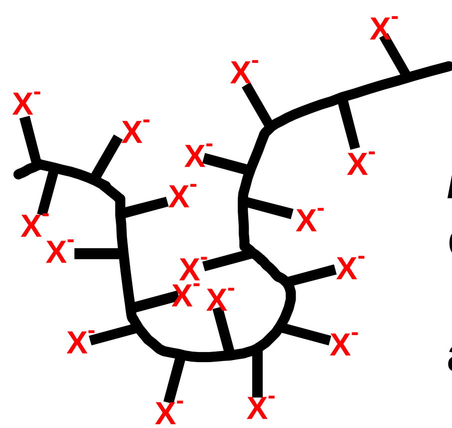
t_+ ~0.2-0.4

Polarization – decreased cell performance

solution: immobilize anions

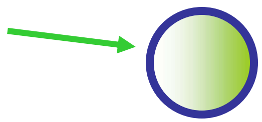


anions part of a rigid solid (low σ)



Design issues: single component, but must optimize transport and tether ions at the same time

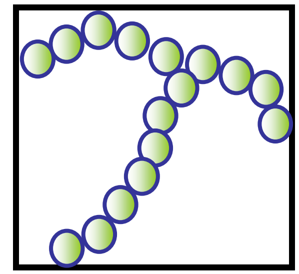
Composite electrolytes: 2-component solutions to electrolyte design



hydrophobic particles

low molecular weight PEO

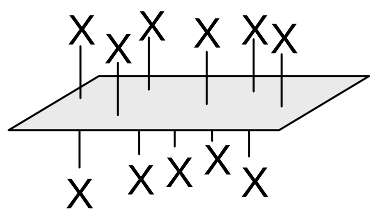
Li^+X^-



Network formation

Improved mechanical properties

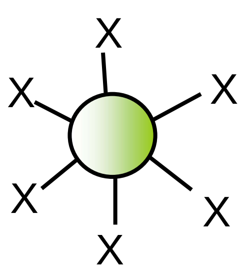
σ unchanged



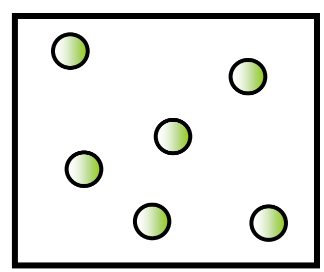
Ion-exchanged clays

3-d network structure, high $t_{Li}{}^+$

For an overview see:
Electrochimica Acta **2003** *48*, 2071-2077



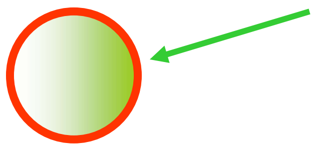
“massive” relative to Li^+,
$\mu \sim 0$



hydrophilic particles dispersed in PEO

Approaches

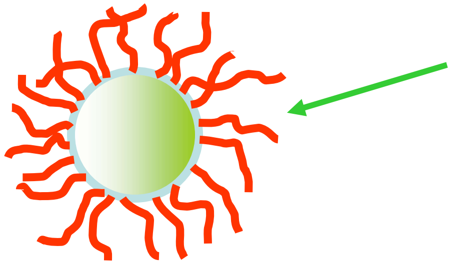
Particles with a monolayer of anions tethered to the surface



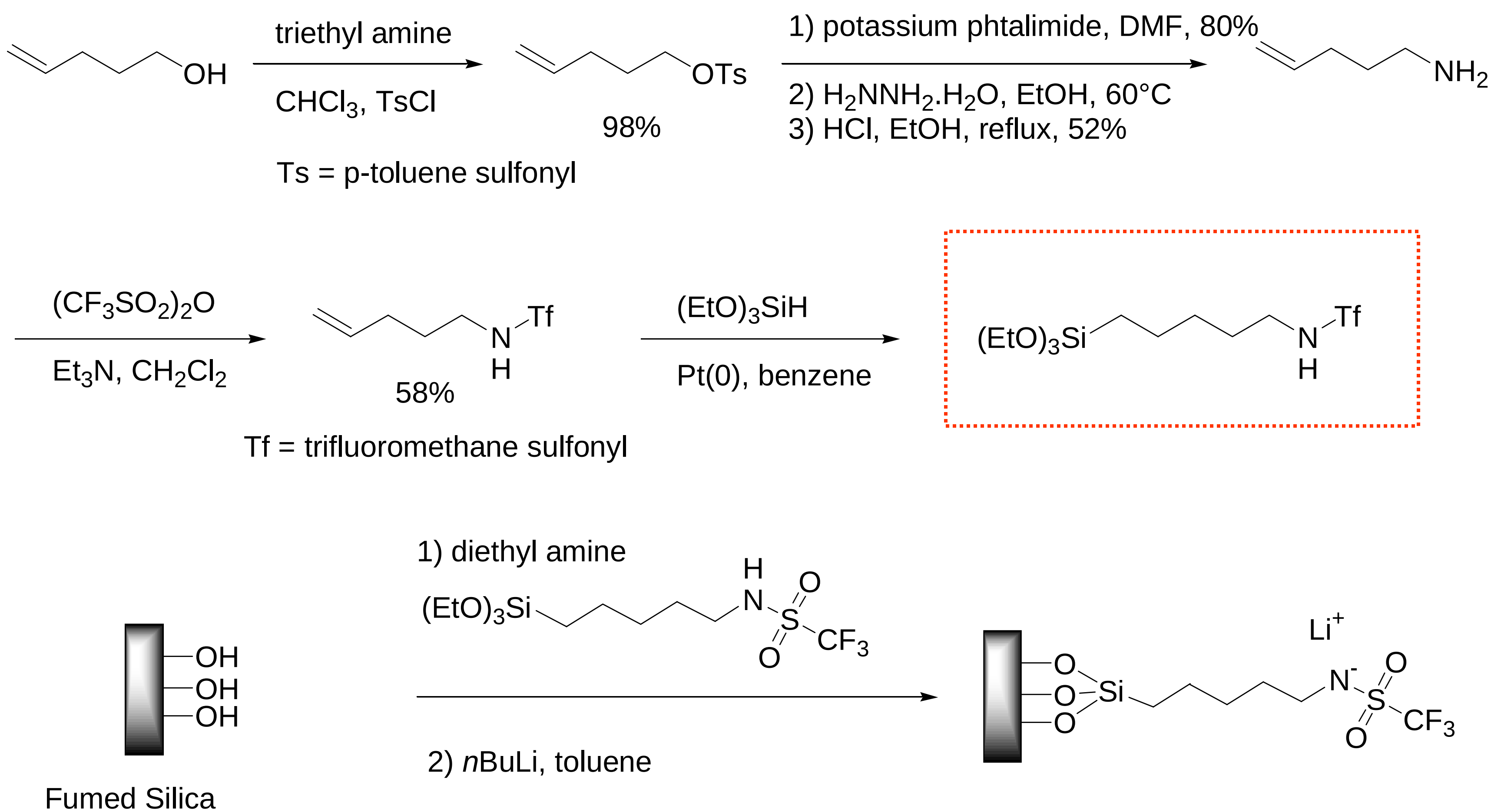
$$\sigma = n \bullet q \bullet \mu$$

Particles with polymer tethers decorated with multiple anions/chain

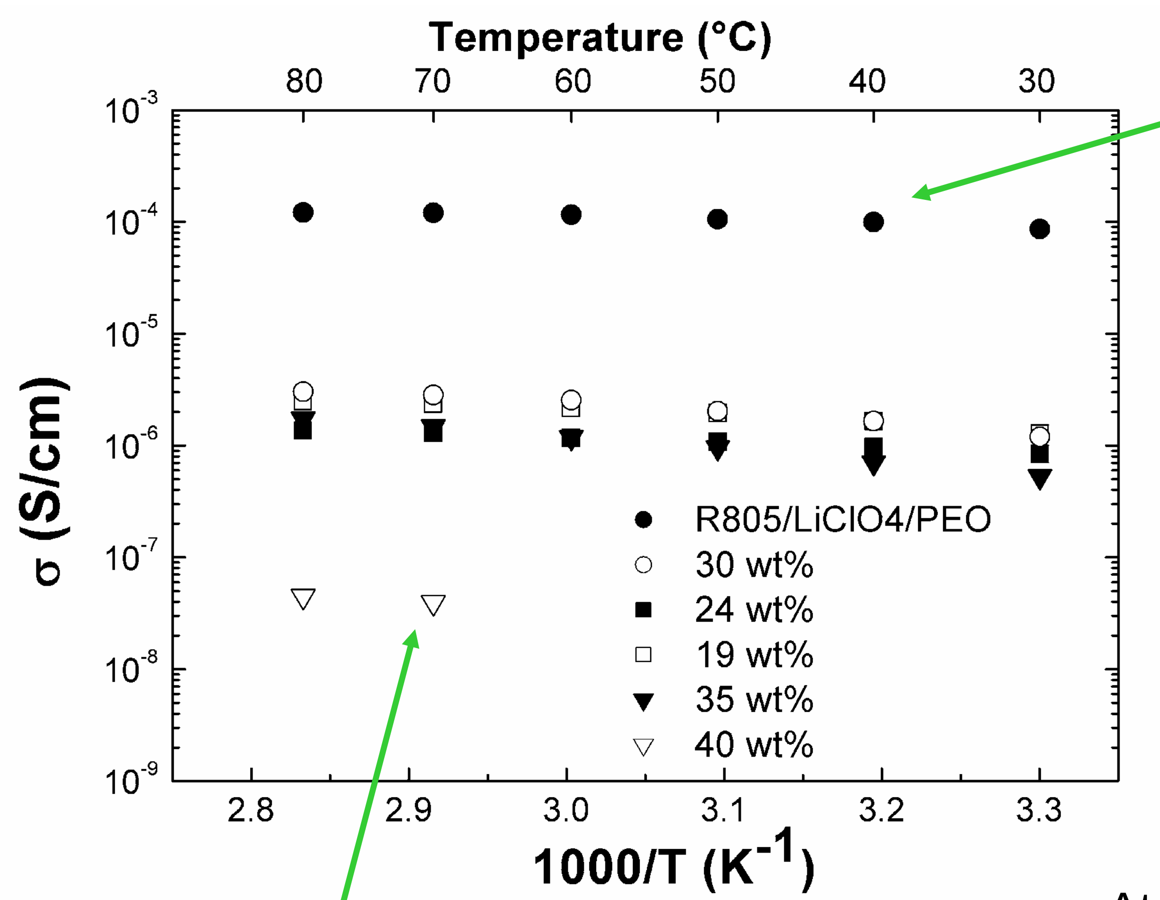
(increased carrier concentration, easily 10X)



Synthetic route to tethered Li imides



Conductivity data



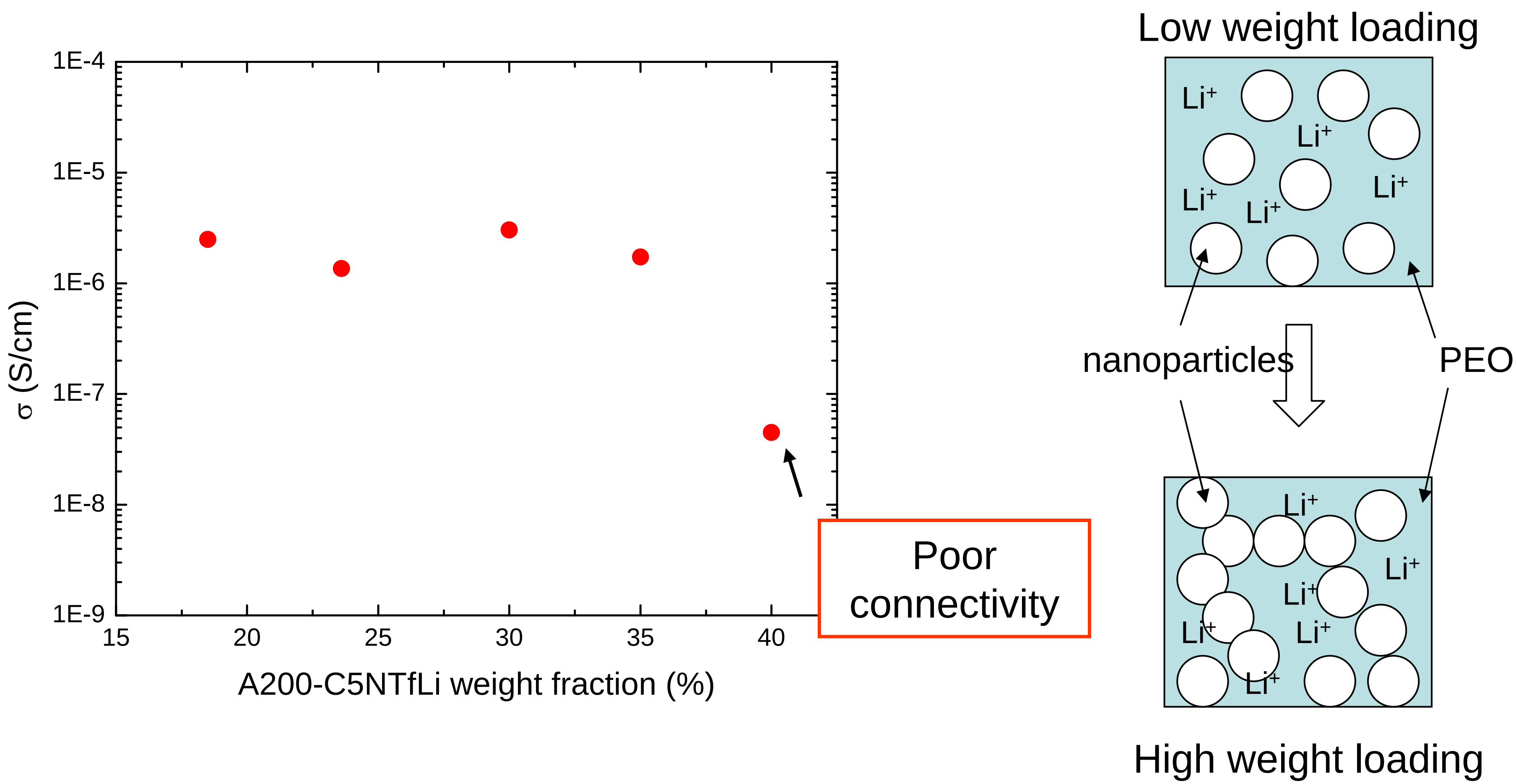
Data for PEO/$LiClO_4$/ hydrophobic fumed silica

- Li^+ concentrations:
  - –40 wt% ≈ O:Li = 250
  - –35 wt% ≈ O:Li = 310
  - –30 wt% ≈ O:Li = 390
  - –19 wt% ≈ O:Li = 710

At 10 & 15 wt % - $\sigma<10^{-8}$ S/cm (few charge carriers)

At 40 and 50 wt% - poor ionic conductivity discontinuous polymer matrix

Connectivity issues

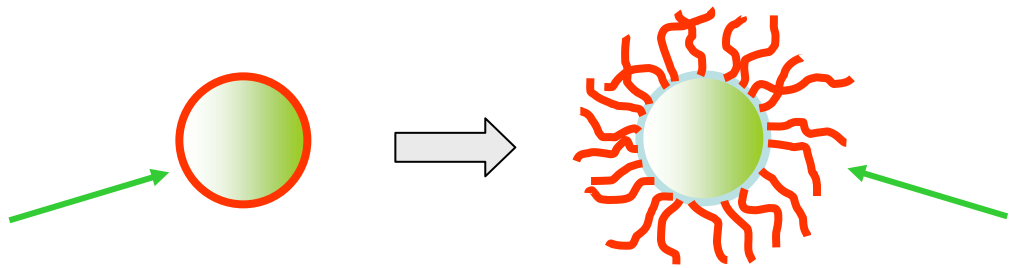


non-continuous conducting phase

Interim conclusions

- $\sigma < 10^{-8}$ S/cm for 10, 15 and 50 wt% particles in PEGDME500/.
  - For 10, and 15 wt%, low lithium concentrations.
    (O/Li > 1000)
  - For 50 wt%, discontinuity of the polymer phase.

- Weak dependence on temperature

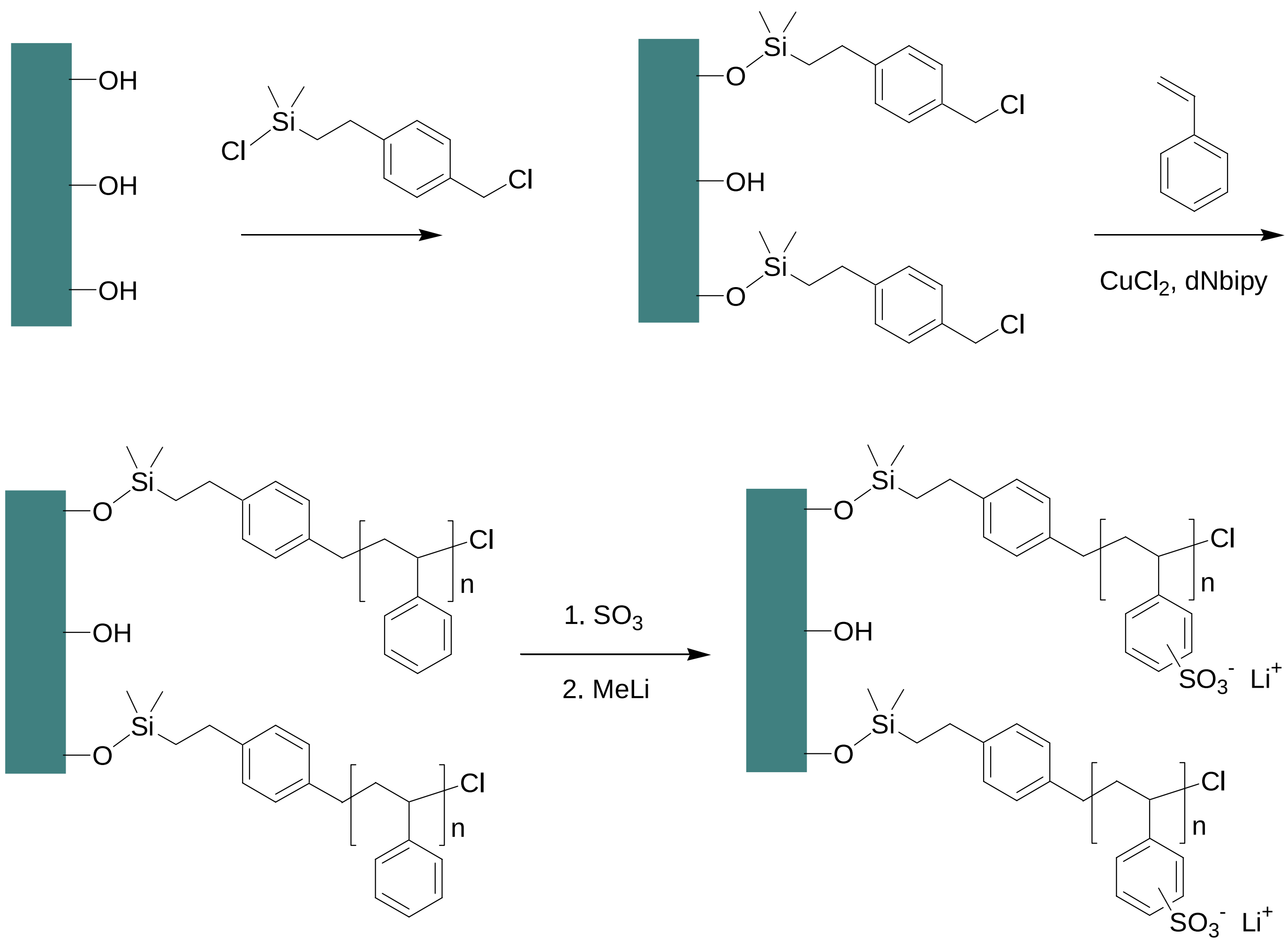


Need more charge carriers!

Particles with polymer tethers decorated with multiple anions/chain have increased carrier concentrations, easily a 10X increase.

Growth of polymer tethers from particle surfaces

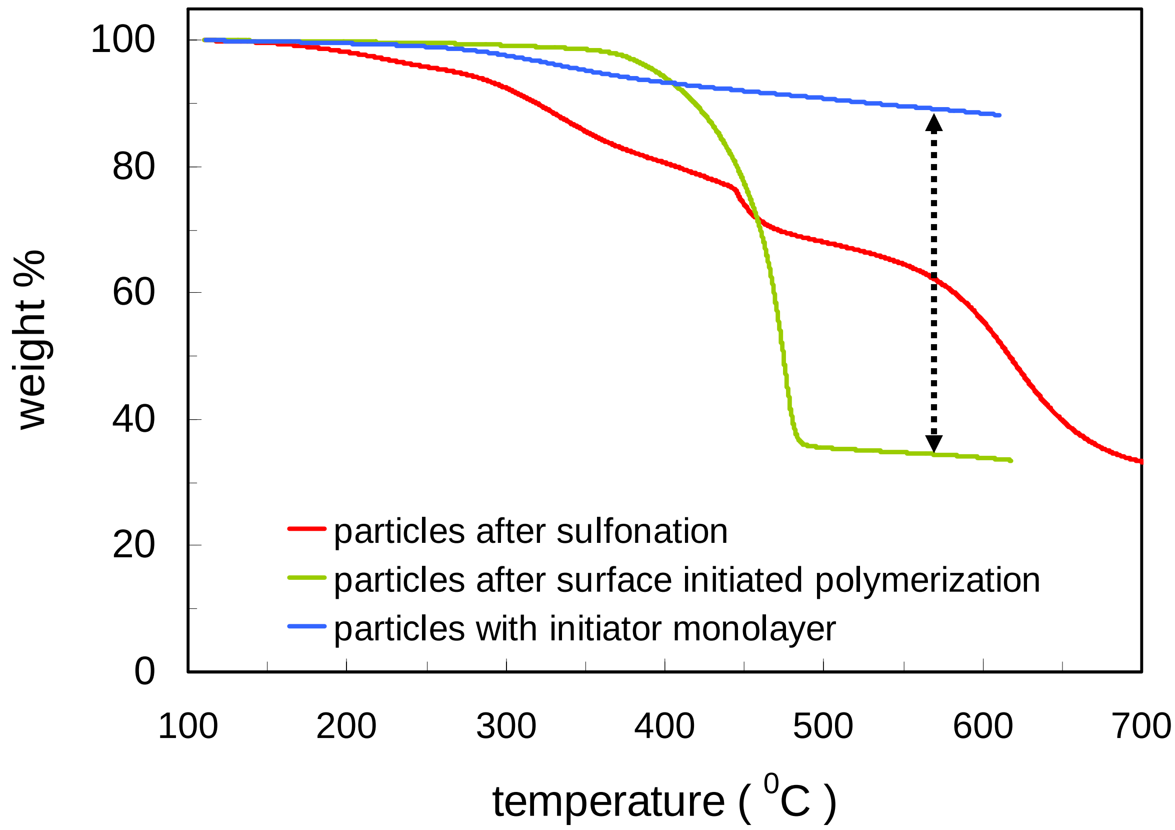
- Increase number of anions on silica nano-particles



Thermal gravimetric analysis of modified nanoparticles

Weight loss data can be analyzed to estimate the number of functional groups on the surface.

Cleaving chains from surface with HF would give molecular weight.



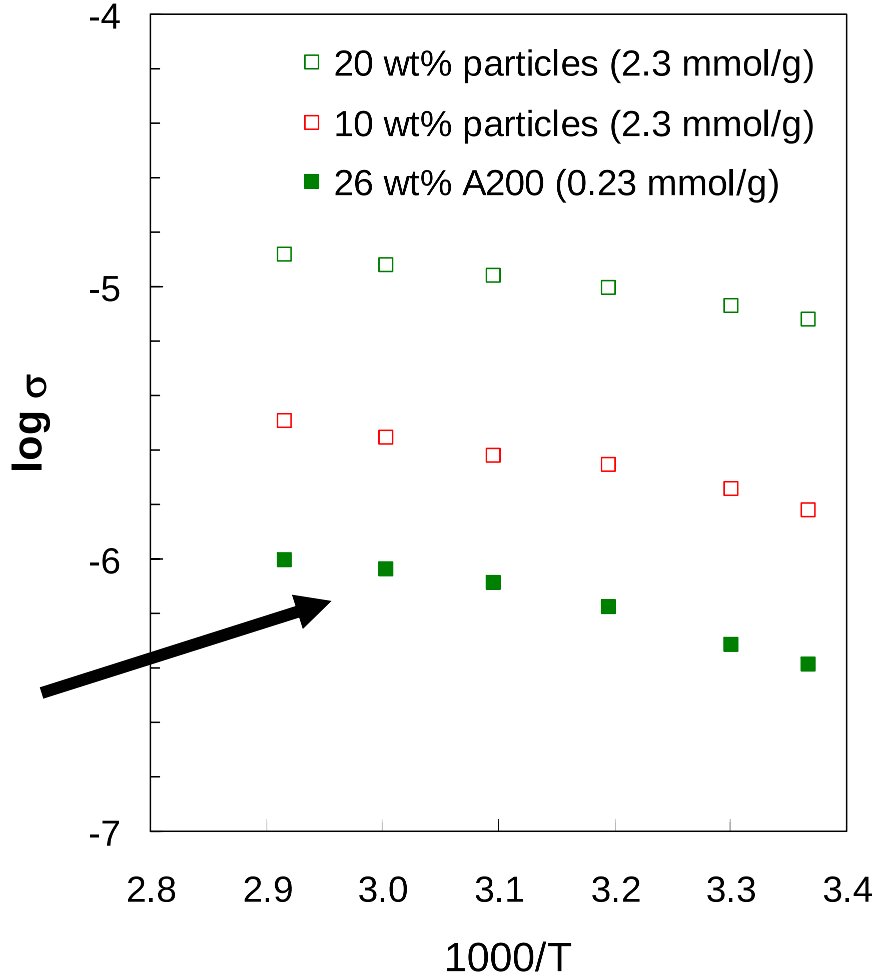
2.3 mmol/g (titration)

Li^+ conductivity of nanoparticles in PEG-DME 350

10 fold increase in conductivity

$>10^{-5}$ even for aryl sulfonates

single layer of
immobilized anions



BASIC RESEARCH NEEDS FOR ELECTRICAL ENERGY STORAGE

(DOE Workshop, 2007, http://www.sc.doe.gov/bes/reports/abstracts.html)

Cross-Cutting Science: technology challenges

Liquid electrolytes

- **Provide the needed high conductivity for electrochemical capacitors but can have safety and containment issues.**
- **Have voltage windows that limit the device performance range.**
- **Contain electrolyte impurities that lead to degradation in performance.**

Electrolytes can be the weak link limiting innovations in electrode materials, and associated power and power density.

Need new electrolytes with high ionic conductivity, low fluidity, easily purified.

Low nucleophilicity and electrophilicity - unreactive in both electron transfer and acid-base chemistry.

BASIC RESEARCH NEEDS FOR ELECTRICAL ENERGY STORAGE

(DOE Workshop, 2007, http://www.sc.doe.gov/bes/reports/abstracts.html)

Cross-Cutting Science: technology challenges

"Solid" electrolytes

- **Difficult to combine the electrolyte and electrode separator functions in a single material.**
- **Modeling provides a recipe for high conductivity - polymers with low glass transition temperatures - but low Tg polymers have poor mechanical properties.**
- **Two-phase materials provide a partial solution - favorable mechanical properties, but with the electrochemical characteristics and problems of low molecular weight liquid electrolytes (electrolyte decomposition, flammability, ...).**

New approaches to electrolyte design are needed that go beyond incremental improvements.

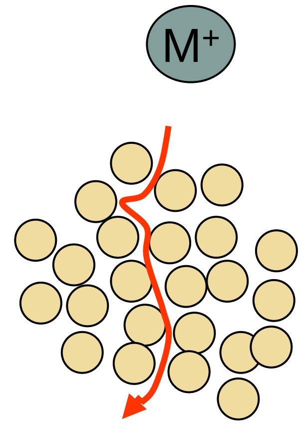
Cross-Cutting Science: Electrolytes for Energy Storage

- **Establish design rules that define the relationship between electrolyte structure and performance, including ion mobility, electrochemical stability new concepts for electrolytes.**
- **Precisely define the double layer and interaction of electrolyte and solvent at electrode surfaces. Create self healing/self regulating electrolytes for the electrode/electrolyte interface.**
- **Expand the range of weakly coordinating anions (BARF, carboranes, dicationic ionic liquids, ions linked by electronically conducting segments) to broaden the spectrum of electrolytes available for batteries and capacitors.**
- **Investigate electrochemical phenomena in molten salts establish electrolytes with high conductivities, stabilities, and wide potential windows.**
- **Establish the thermodynamic properties of electrolytes.**

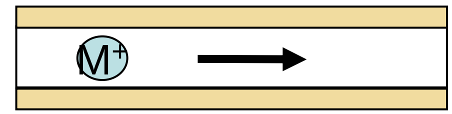
Cross-Cutting Science: basic-science challenges, opportunities

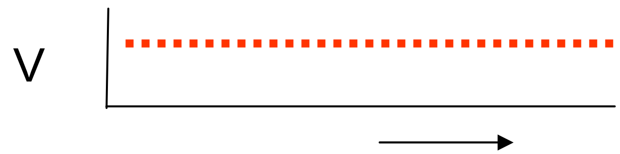
Solid electrolytes

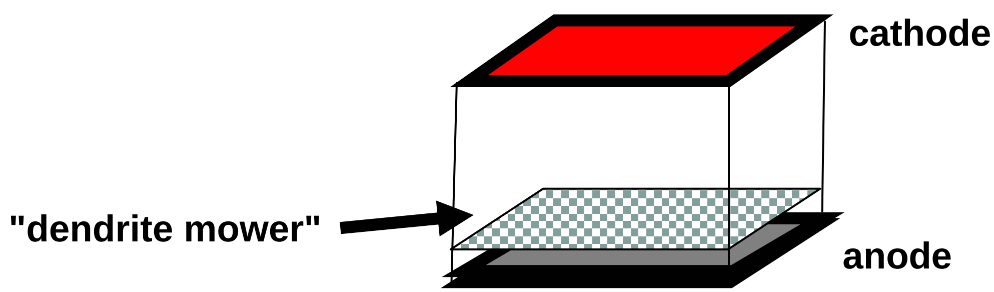
- Nanoparticle composites that exploit the interstitial space in ensembles of high surface area nanoparticles and provide conductive channels for ion transport.



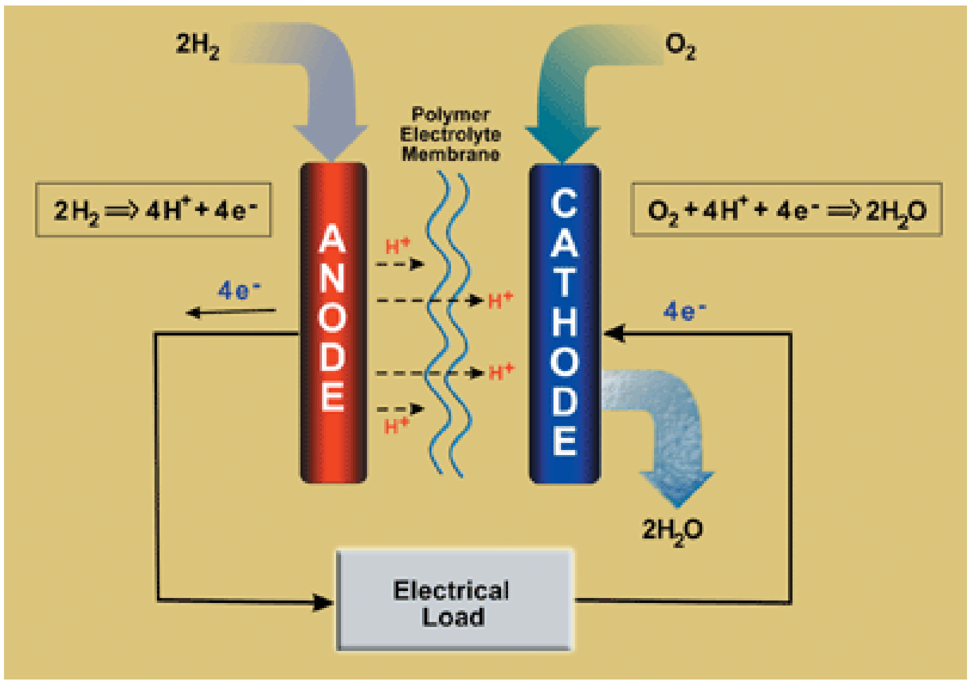
- Design smart materials that respond that moderate temperature excursions within batteries, polymer layers that selectively remove lithium dendrites, or restore conductive pathways in composite electrode structures - potentially dramatic improvement in device reliability, lifetime, and *safety*.



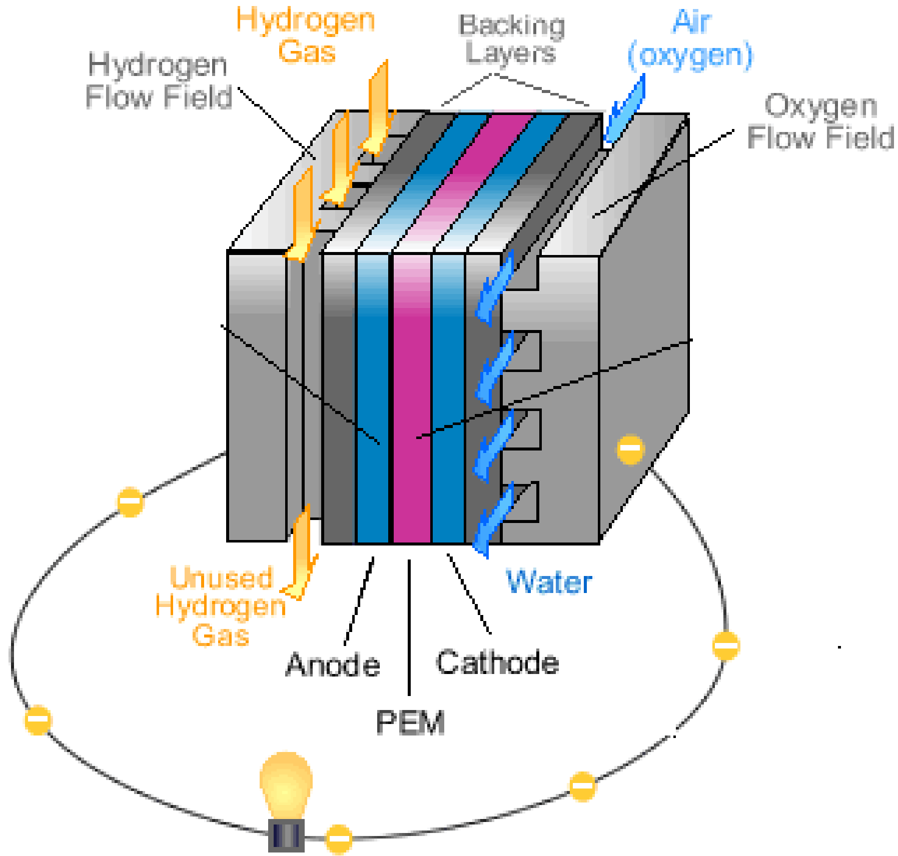




Fuel Cells



http://www.epa.gov



Fuel cell issues

Costs. Platinum (1 mg/cm²) and membrane costs. Nafion® membranes are ~$400/m²!

Water management (in PEMFCs).

too little water: dry membranes, increased resistance, failure by cracking, creating a gas "short circuit" where hydrogen and oxygen combine directly, generating heat that damages the fuel cell.

too much water: electrodes flood, preventing the reactants from reaching the catalyst.

Fuel and oxygen flow control.

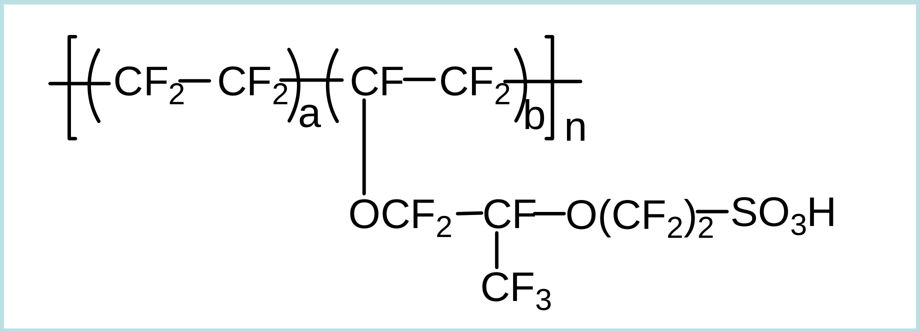
Temperature management.

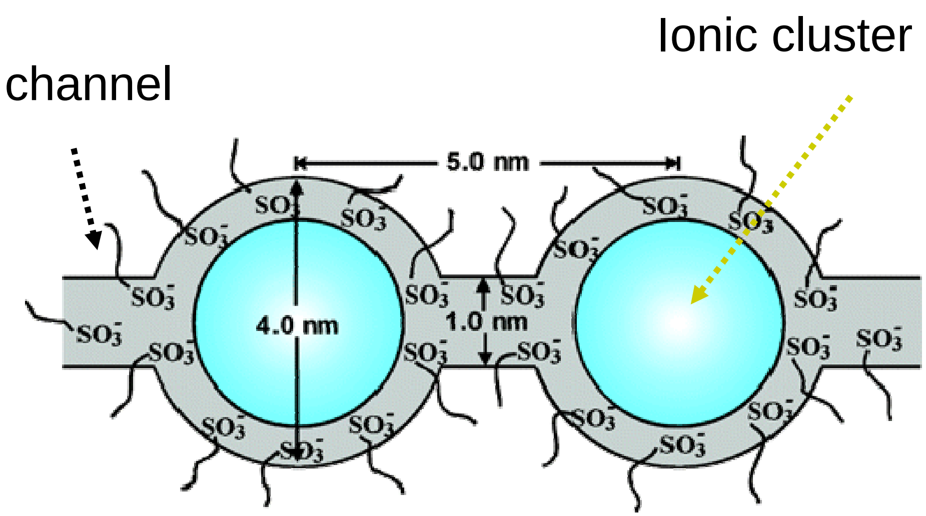
Limited carbon monoxide tolerance of the anode.

Advantages of high temperature operation:

- Reduce CO poisoning effect on electrode catalyst.
- Enhance reaction kinetic at higher temperature.
- Simplify water management.

Nafion, the prototype PEM





Perfluorinated polyethylene backbone affords chemical and mechanical stability; sulfonic groups attached on side chains provides mobile protons when hydrated.

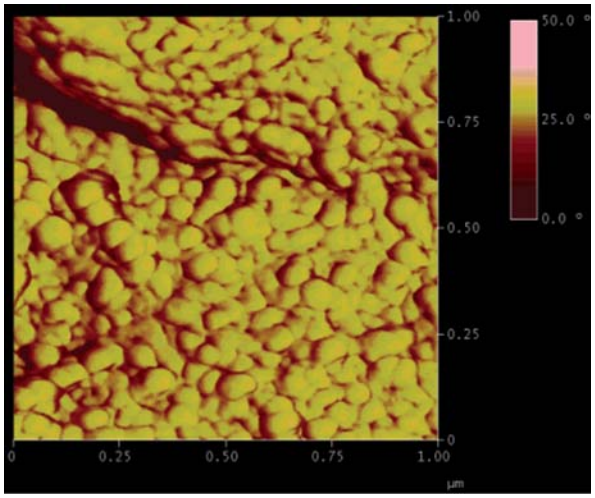
- Chemically stable
- Mechanically stable
- High conductivity

Limitations:

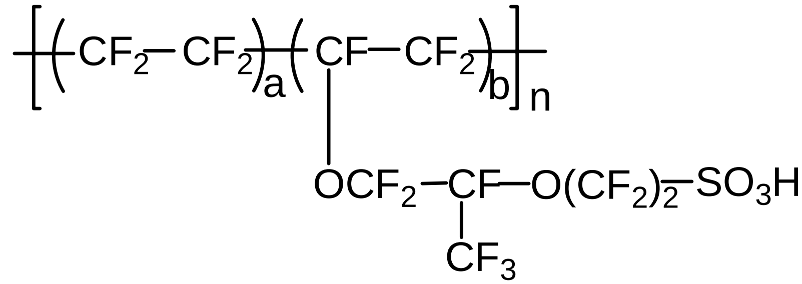
- Cost. ~$400/m^2
- Poor high temperature performance (80-90 °C)
- Low conductivity at low humidity or high temperature
- CH_3OH permeability

Hickner, M. A.; Pivoar, B. S.; *Fuel Cells*, **2005**, *5*, 213-229Hickner, M. A.; Pivoar, B. S.; *Fuel Cells* **2005**, *5*, 213.
Hsu, W. Y.; Gierke, T. D.; *J. Membr. Sci*. **1983**, *13*, 307. Mauritz, K. A.; Moore, R. B.; *Chem. Rev*. **2004**, *104*, 4535.

"Diat tubes"

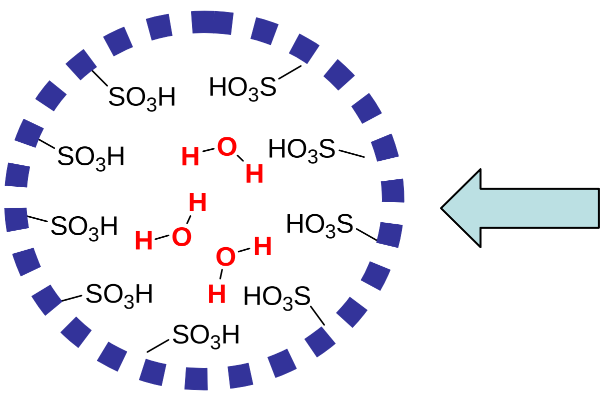


1 µm x 1µm

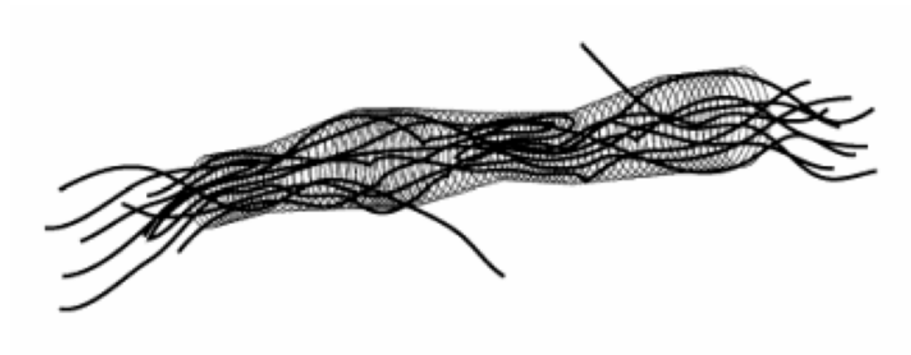


AFM image of Nafion at RT,
30% relative humidity

Nafion "tube" structure inferred from scattering data



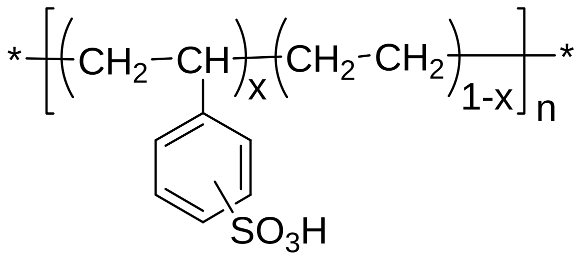
end view



Rubatat, L.; Gebel, G.; Diat, O., *Macromolecules* **2004,** 37, (20), 7772-7783.

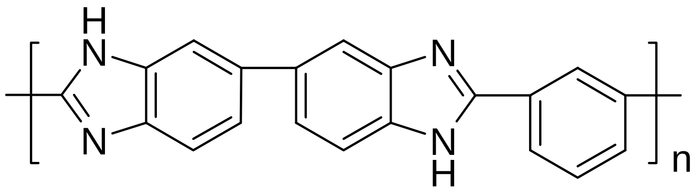
Commercial alternatives to Nafion

Sulfonated ESI (Dais-Analytic)



Commercial Dow Insight product,
30-60% sulfonation
85 °C max temp
(T_m of polyethylene crystallites)

Polybenzimidazole (Celanese Ventures) with Honda, PlugPower

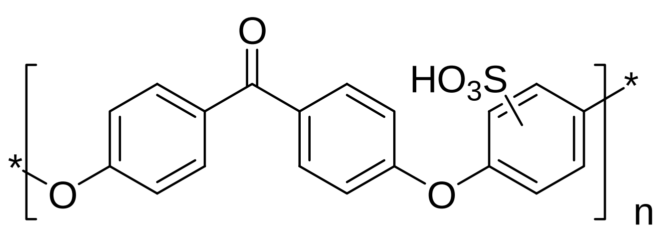


Polybenzimidazole (PBI)

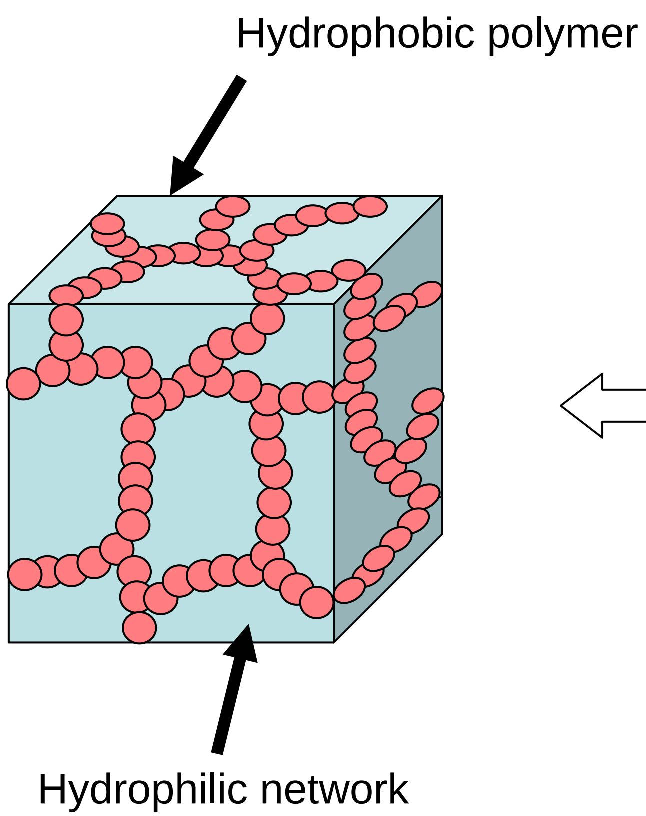
PBI soaked with 11M H_3PO_4 showed conductivity of **0.02 S/cm** at 130 °C, 0.3 atmosphere water vapor pressure.

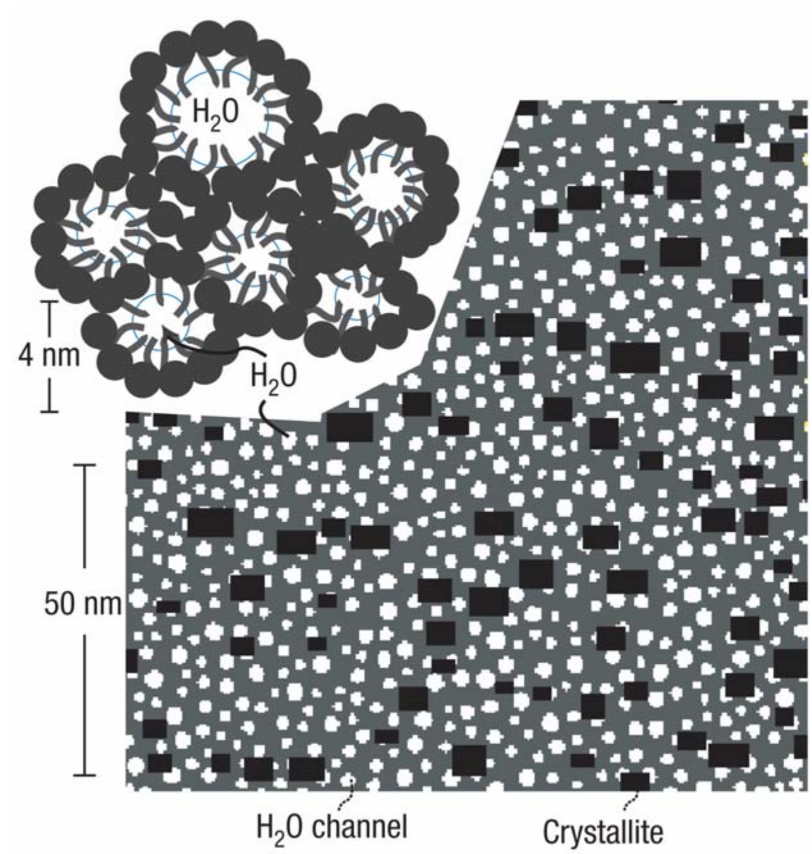
150-190 °C maximum, CO tolerant

Sulfonated PEEK (Vitrex/Ballard)



Nafion model from neutron scattering

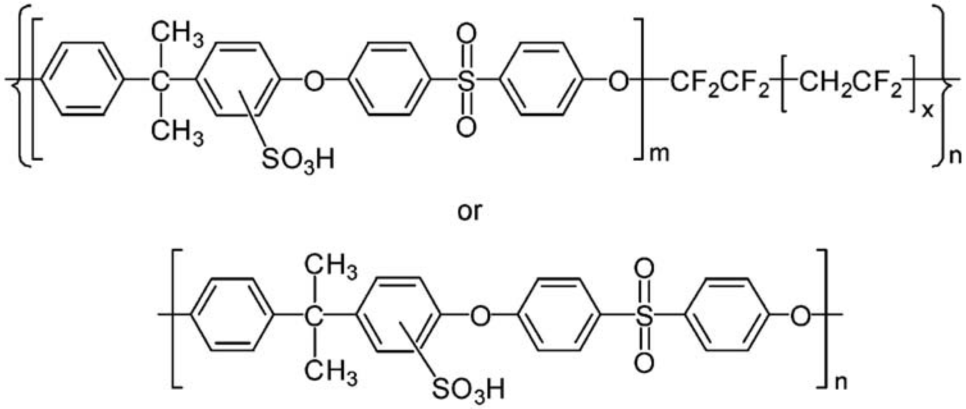




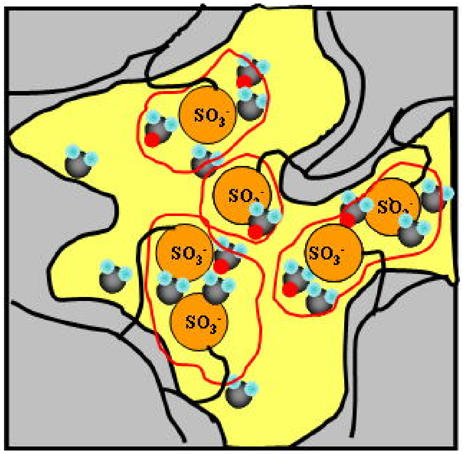
The bicontinuous phase structure is an analog of the cluster-network model (Nafion)

Schmidt-Rohr, K.; Chen, Q., *Nat. Mater.* **2008,** 7, 75-83.

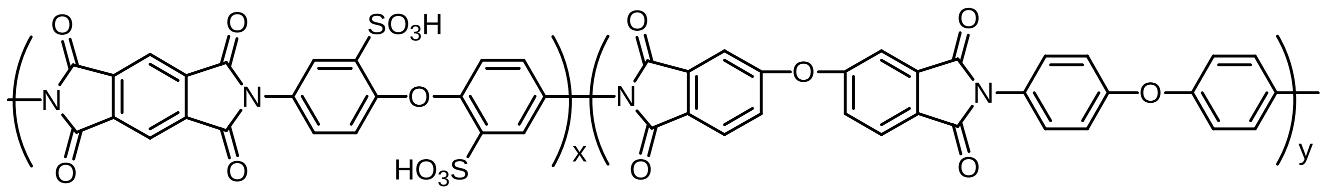
More Nafion alternatives



Yang, Y. S.; Shi, Z. Q.; Holdcroft, S., *Macromolecules* **2004,** 37, (5), 1678-1681.



Nafion's bicontinuous structure

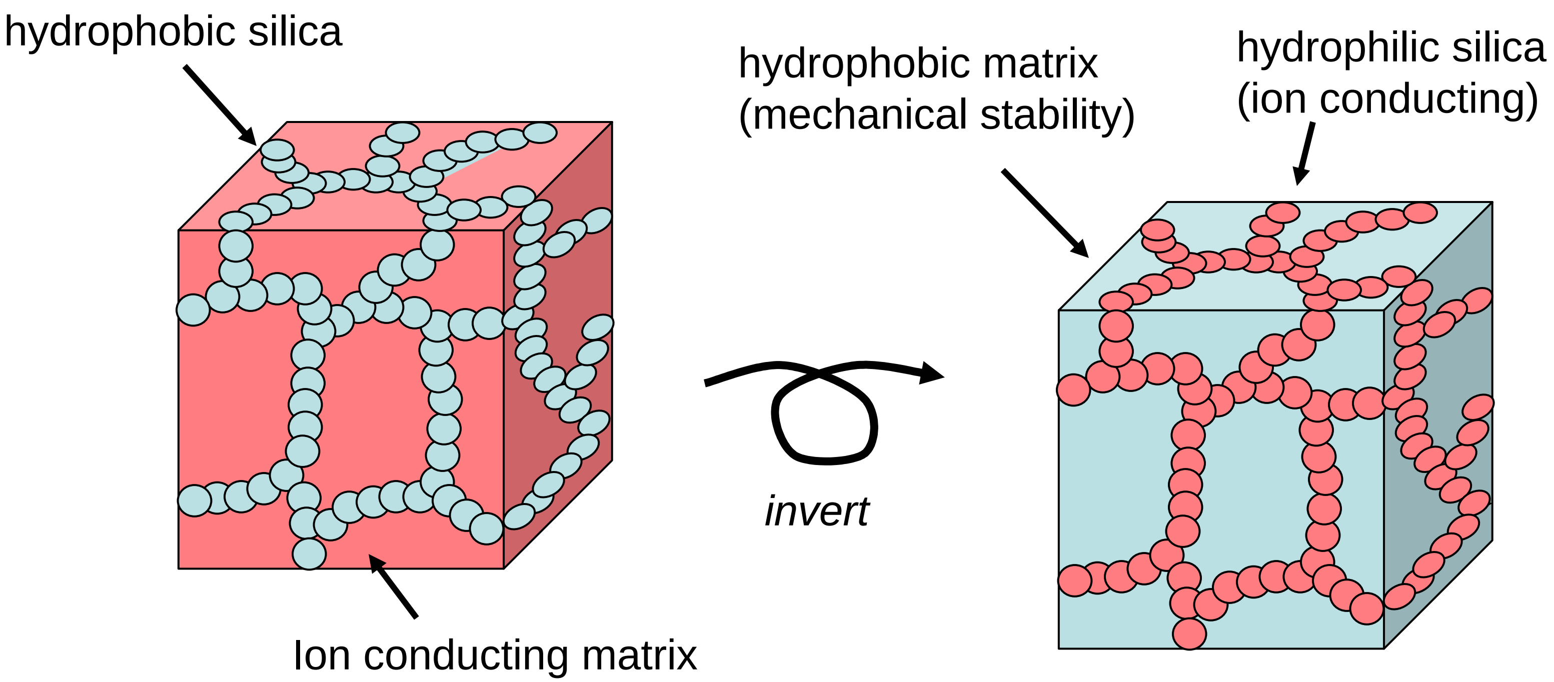


Faure S, Cornet N, Gebel G, Mercier R, Pineri M, Silicon B. *Proceedings of Second International Symposium on New Materials for Fuel Cell and Modern Battery Systems*, Montreal, Canada, July 6-10, **1997**. P. 818.

Random incorporation of sulfonic acid groups causes uncontrolled swelling in H_2O

Distribution as blocks (a la Nafion) controls swelling

Particle in polymer approach



Hydrophobic particles (alkyl terminated) dispersed in a hydrophilic ion-conducting electrolyte.

Network formation enhances mechanical properties with insignificant effects on conductivity

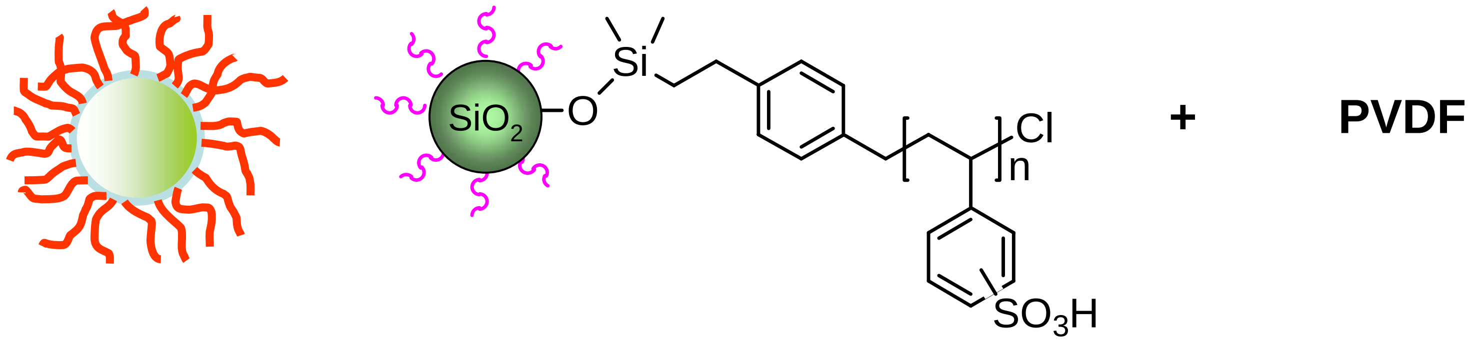
Hydrophilic particles (sulfonic acid terminated) dispersed in a hydrophobic matrix (PVDF).

Dimensionally stable hydrophobic polymer provides mechanical stability and is uninvolved in transport

Khan, A. S.; Baker, G. L.; Colson, S.; *Chem. Mater*, **1994**, *6*, 2359-2363

Particles with polystyrene brushes

Composite membranes made from poly(styrene sulfonic acid) grown from nano-sized silica surface and PVDF:



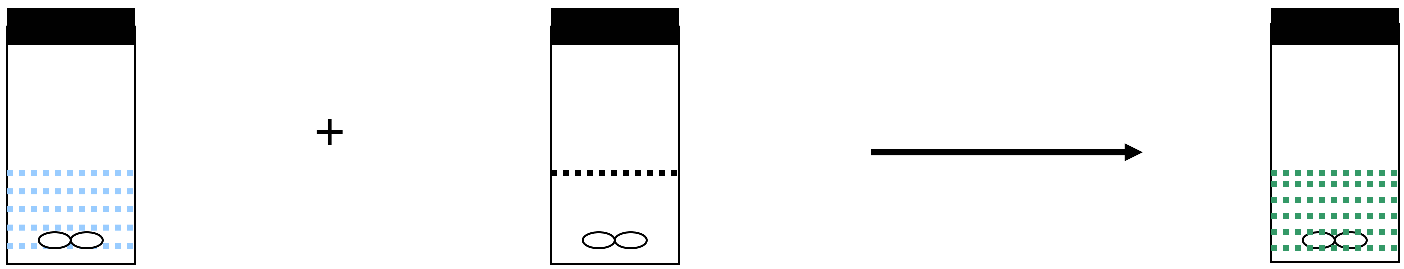
Nano sized particle provides high surface area

Homogeneous membranes, comparable conductivity compared to Nafion.

de-coupled mechanical properties from proton transport

Easy solution to swelling issues.

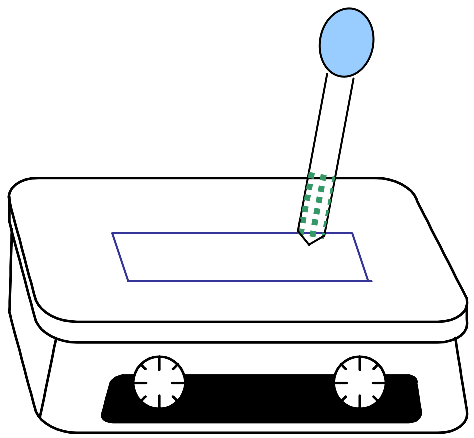
Membrane fabrication



Particles in DMF

PVDF in DMF

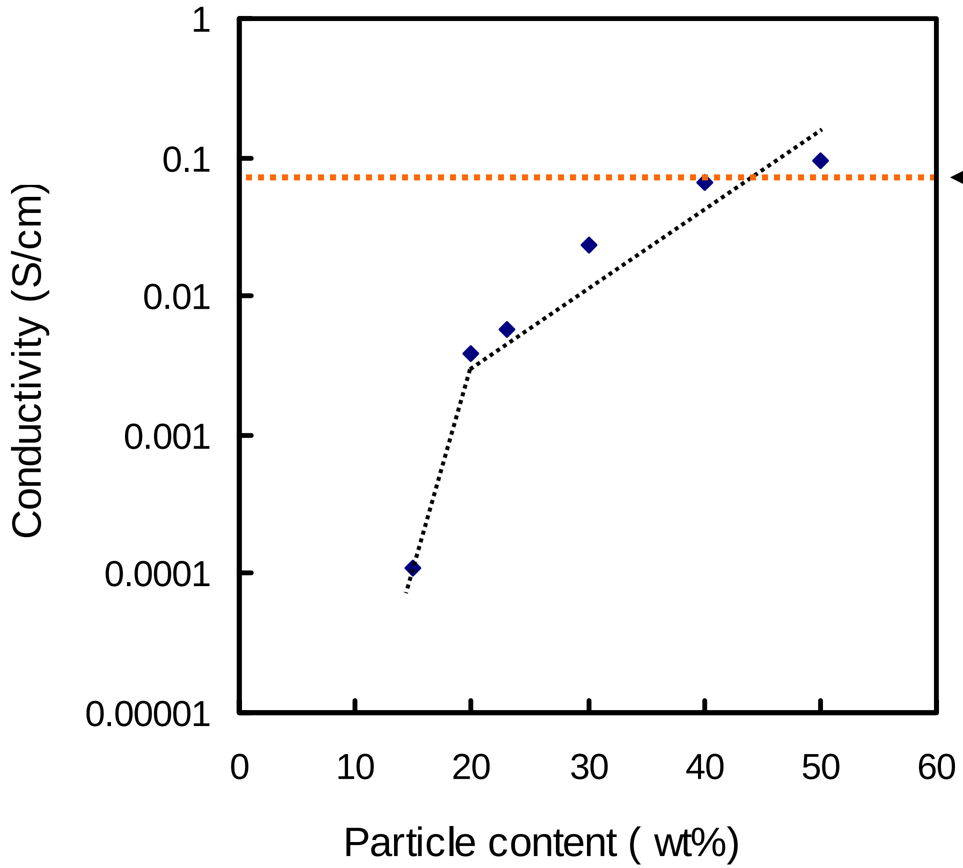
Combined mixture, stirred overnight at room temperature



Mixtures were cast on glass slide and dried at ~50 ºC

Cast membrane

Particle content vs conductivity



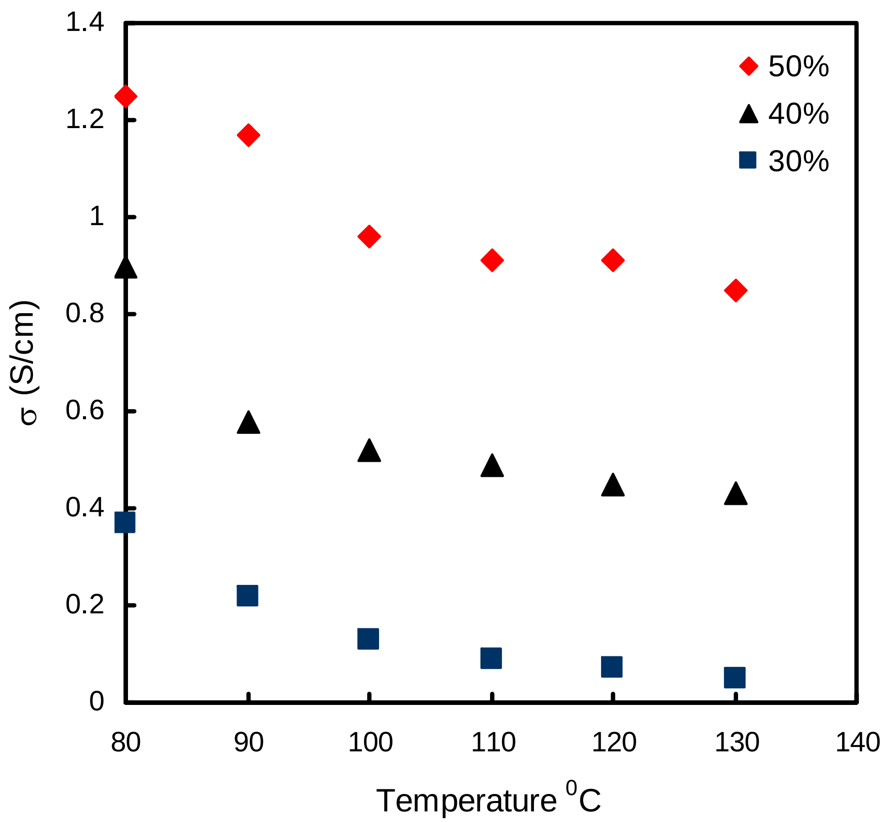
Nafion 117 measured under the same conditions: 0.08 S/cm

The conductivity data suggest a percolation threshold at ~20% particle content.

Need to push the particle content to lower loadings while maintaining conductivity.

Measurements taken at room temperature, 100% relative humidity

Membrane conductivity vs. temperature



50% particles

40% particles

30% particles

Compatible with high temperatures

Still need to push the particle content to lower loadings

Membranes were soaked with 8M H_3PO_4,

measurements were taken under 0.3 atmosphere pressure humidity

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