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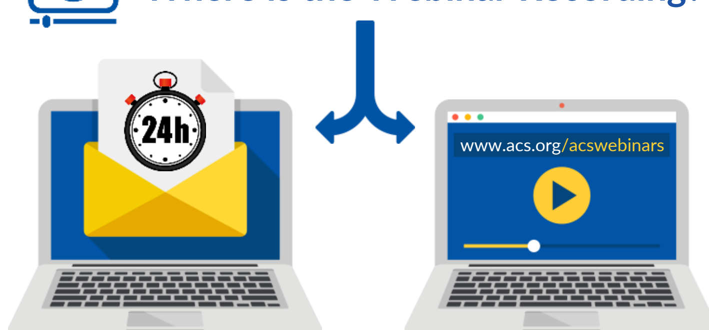

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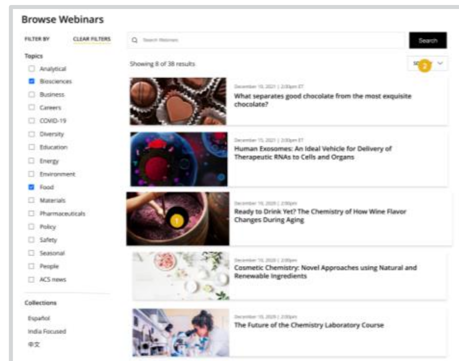

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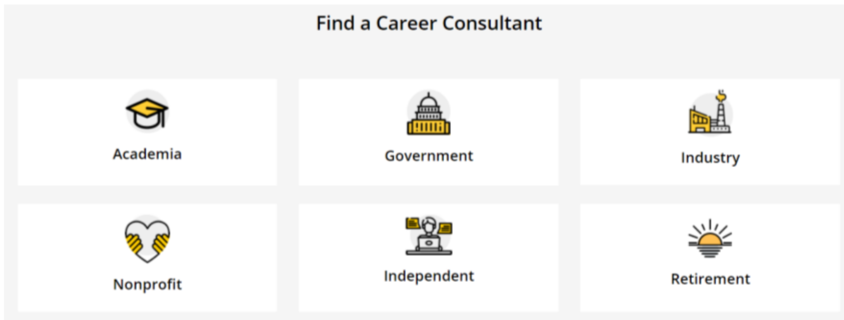

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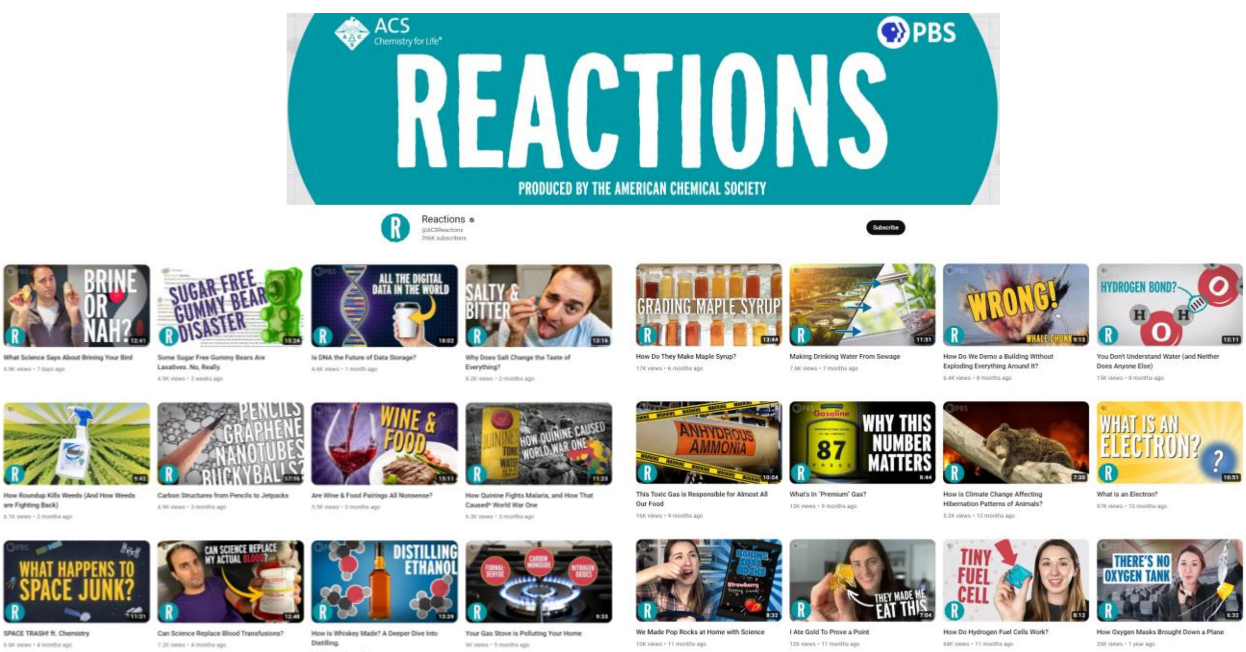

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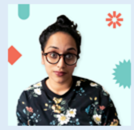

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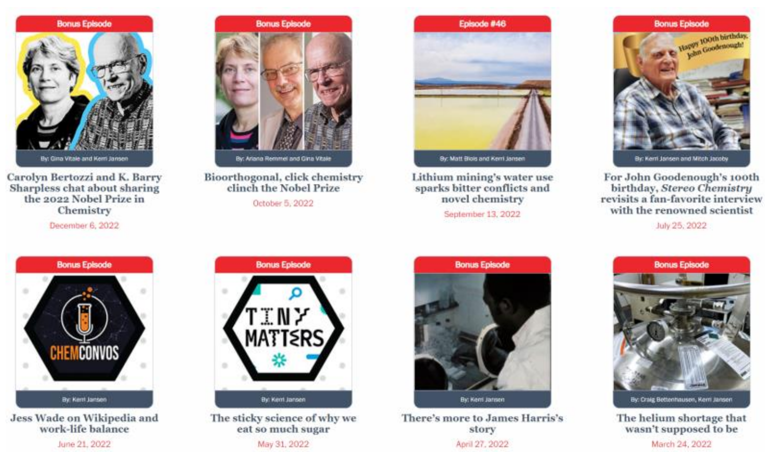

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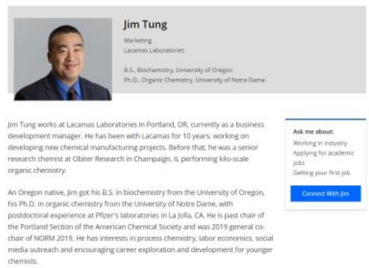

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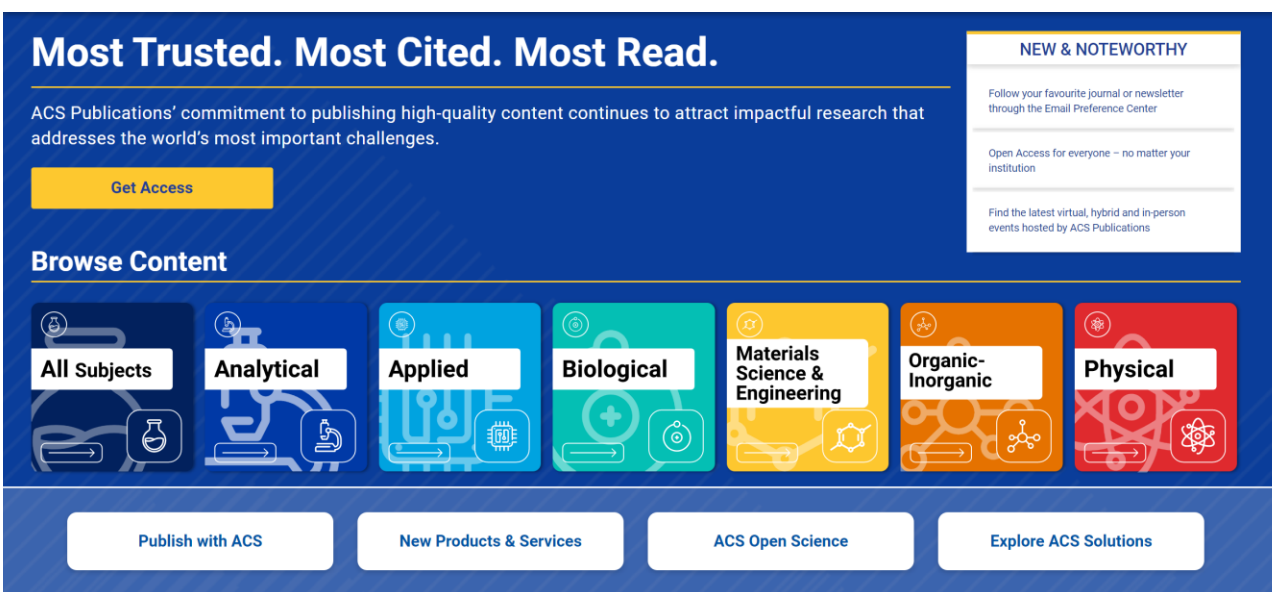

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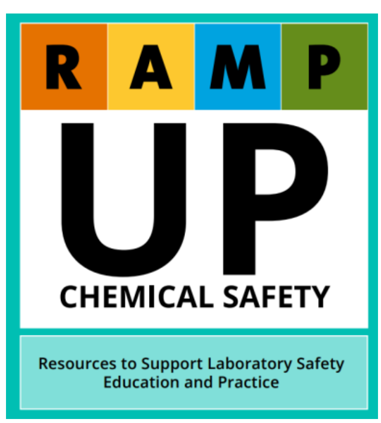

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Advancing ACS' Core Value of Diversity, Equity, Inclusion and Respect

Resources

Inclusivity Style Guide
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Diversity**
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Inclusion**
Builds a culture of belonging by actively inviting the contribution and participation of all people. Every person's voice adds value, and ACS strives to create balance in the face of power differences. In addition, no one person can or should be called upon to represent an entire community.

Respect
Ensures that each person is treated with professionalism, integrity, and ethics underpinning all interpersonal interactions.

https://www.acs.org/diversity

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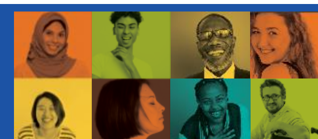

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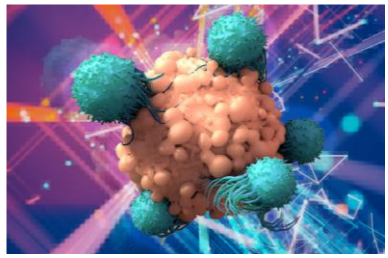

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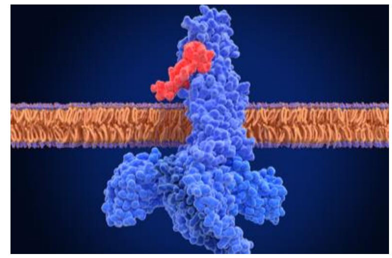

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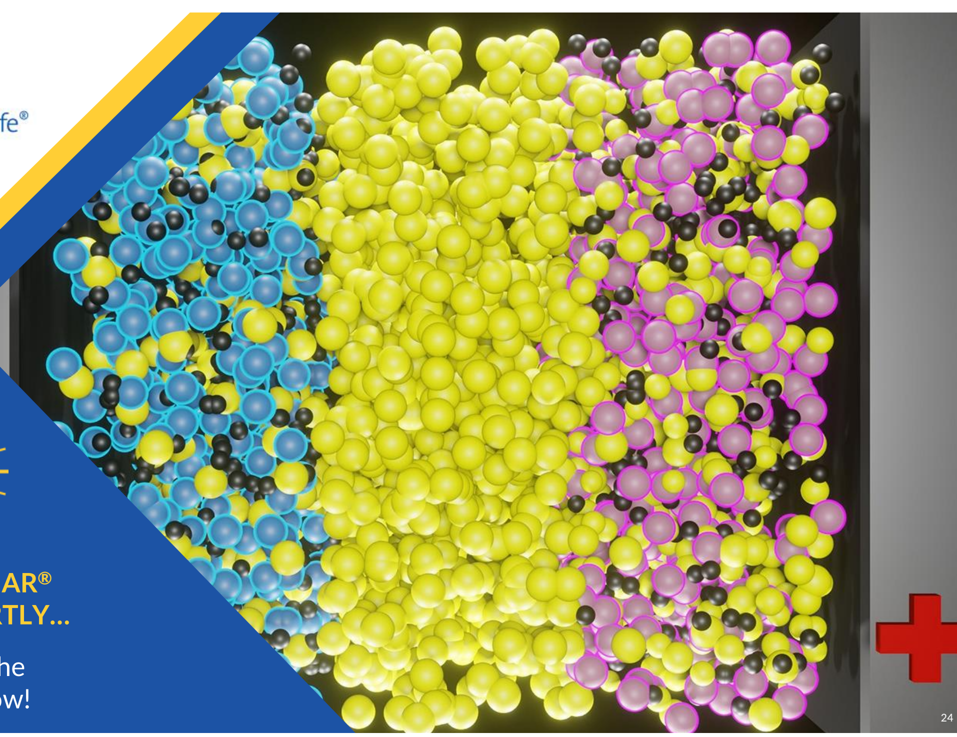

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Better Ion Transport through Polymer Chemistry:

Polymer Electrolytes and Ion-conducting Membranes

ALEXEI SOKOLOV, PhD

ORNL/UT Governor's Chair, Professor of Chemistry and Physics, Chemical Sciences Division, University of Tennessee

MICHAEL HICKNER, PhD

Craig A. Rogerson Endowed Professor, Department of Chemical Engineering and Materials Science, Michigan State University & Associate Editor, ACS *Applied Energy Materials*

CHELSEA CHEN, PhD

R&D Staff Polymer Scientist, Oak Ridge National Laboratory

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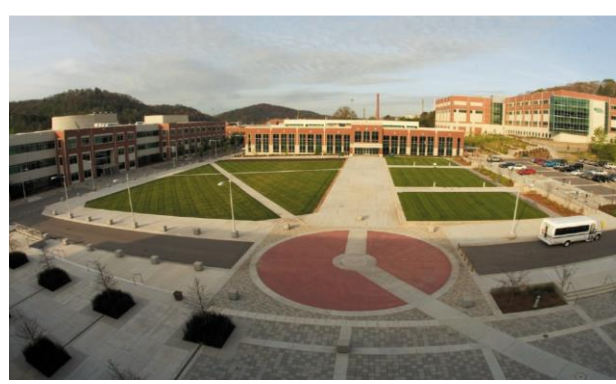
Polymer Electrolytes: from Fundamentals of Ion Transport to Solid State Batteries

Alexei Sokolov

University of Tennessee Knoxville and Oak Ridge National Laboratory, USA



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Polymer Electrolytes are Critical for Many Technologies


Regular batteries for mobile electronics and EVs


Flow batteries for long duration energy storage to provide more efficient use of renewable energy


Fuel cells and Electrolyzers

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Advantages of Solid State Batteries

Next breakthrough in battery technology is expected with **Solid State Batteries**. They will be

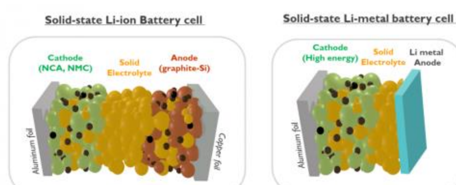
- ***Safer***
- ***Have higher energy density***
- ***Enable electrochemistry not accessible with liquid electrolytes***

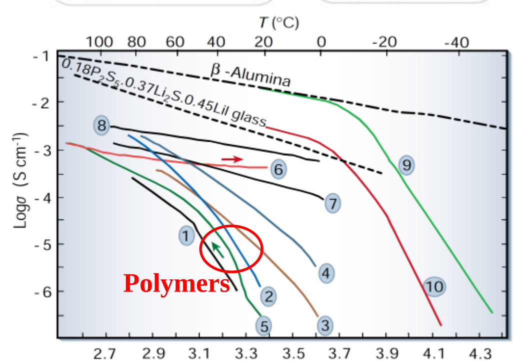
Polymer electrolytes would provide the best solution for solid state batteries:

- ***Good mechanical properties and flexibility***
- ***Good adhesion to electrodes***
- ***Ability to withstand changes of electrode volume during charge/discharge processes***
- ***Easy processing on large surface area***

The Major Problems of Current Polymer Electrolytes

- Low ionic conductivity at ambient T; far below the required level $\sigma \sim 10^{-3}$ S/cm.
- Transport number for Li+ in many cases is low, need for a single ion conductors





Polymers have lower conductivity than liquid electrolytes or superionic ceramics [J.M. Tarascon, M. Armand, **Nature 414**, 359 (2001)].

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Major Mechanisms of Ion Transport

In simplified approximation, conductivity is defined by ion charge **q**, concentration **n** and diffusion **D**

$$\sigma_{NE} = \frac{q^2 n}{kT} D = \frac{q^2 n}{kT} \frac{\lambda^2}{6\tau}$$

D can be expressed through a jump length **λ** and rate **1/τ**. Assuming $\lambda \sim$ 1-3 A, and n ~ 1-3 nm^{-3}, we estimate **required ion jump rate $1/\tau \sim 10^9$-10^{10} 1/s, to achieve required $\sigma \sim 10^{-3}$ S/cm**

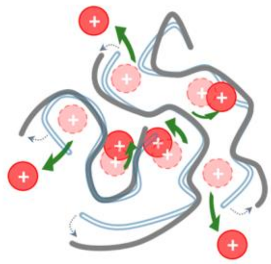
Two Major Mechanisms

Liquid-like

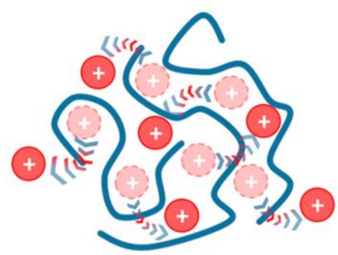
Ions jump with segmental motions.

Requires segmental relaxation time at ambient T: **$\tau \sim 10^{-9}$-10^{-10} s**

The major direction – reduce Tg of the polymer.



Solid-like



Ions jump over energy barrier E in a frozen structure.
$\tau \sim \tau_0 * \exp(E/kT)$

Requires energy barrier **E ~ 20 - 30 kJ/mol**

V. Bocharova, A.P. Sokolov **Macromolecules 53**, 4141 (2020)

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Walden Plot

Ionic conductivity is defined by the charge *q*, concentration n_f and diffusion *D* of free ions:

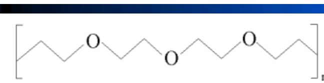
$$\sigma = n_f \frac{q^2 D}{kT}$$

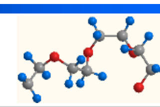
For the liquid-like mechanism the diffusion coefficient D is defined by the viscosity η and/or the structural relaxation time τ_α:

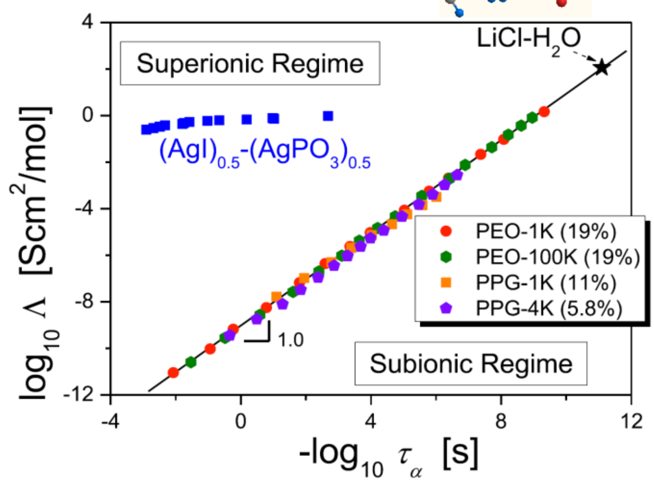
$$D \propto \frac{T}{\eta} \propto \frac{1}{\tau_\alpha}$$

This leads to the Walden rule that relates molar conductivity, $\Lambda = \sigma/n$ to inverse viscosity $1/\eta$ or the rate of structural relaxation $1/\tau$.

$$\Lambda\eta \propto \Lambda\tau_\alpha = \text{Const}$$







Walden rule works surprisingly well for PEO and PPG with salt.

Y. Wang, et al., **Polymer 55**, 4067 (2014)

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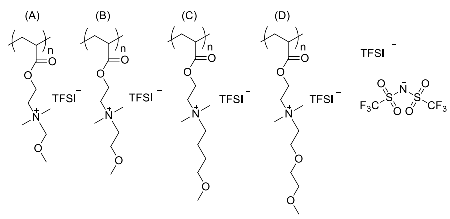
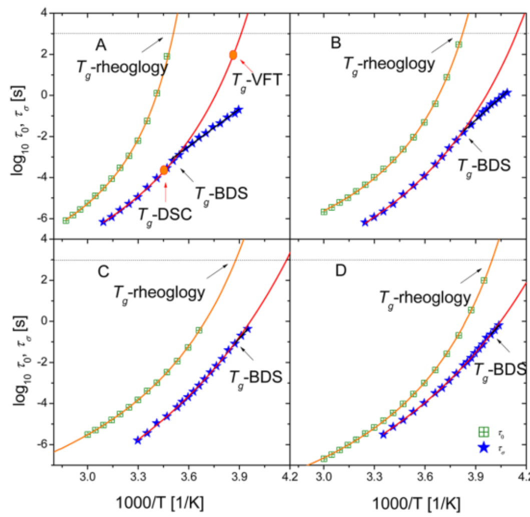
Comparing segmental and conductivity relaxation time



In many polymer electrolytes the rate of ion hopping is much faster than the rate of segmental relaxation.



Comparison of the segmental τ (rheology) to conductivity τ (dielectrics) reveals clear decoupling that is material dependent.

F. Fan, **Macromolecules 48**, 4461 (2015)

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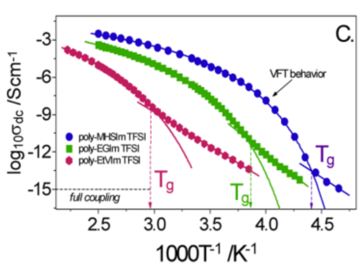
Activation energy below Tg



Activation energy has 2 contributions: (i) coulombic interactions and (ii) elastic force:

$$E_\sigma(T<T_g)=\frac{q^2}{4\pi\varepsilon_0\epsilon R}+E_{el}(T)$$

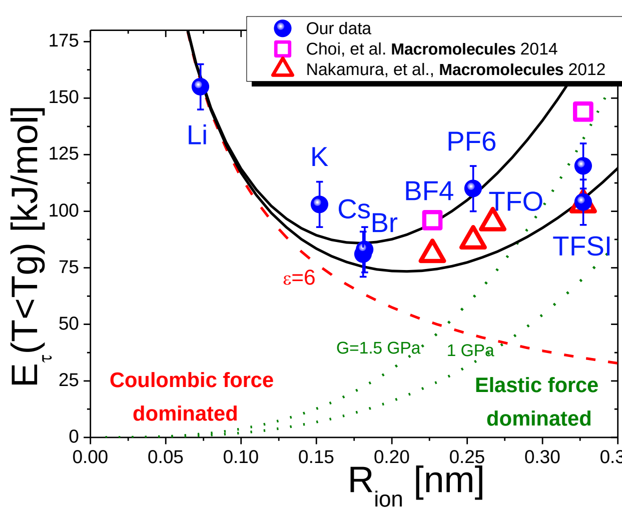
Elastic E_{el} has different presentations:

$$E_{el}(T)=4\pi G_\infty(T)\,l\,(R_{ion}-R_D)^2$$

Anderson-Stuart model, l – ion jump length, R_D – open space

$$E_{el}(T)=\alpha G_\infty(T)\frac{4}{3}\pi R_{ion}^3$$

Shoving model, with α ~1.



Analysis shows good agreement with this model even on a quantitative level. Coulombic force dominates for small ions, e.g. Li, Na, while elastic for large ions, e.g. TFSI.

E.W. Stacy, et al., **Macromolecules 51**, 8637 (2018).

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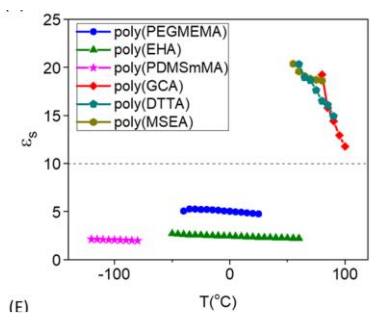
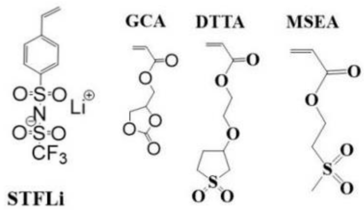
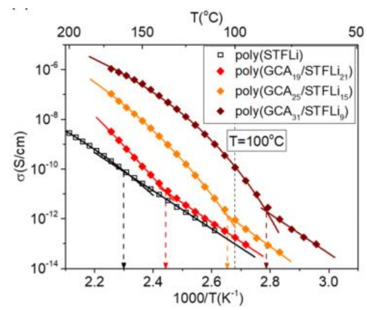
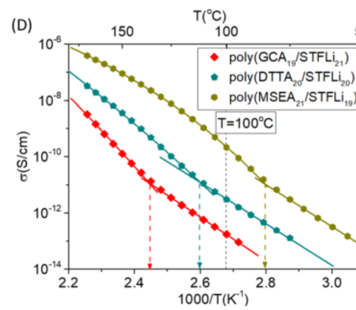
No role of macroscopic dielectric constant









Copolymerization styrene-TFSI with monomers having high dielectric constant did not decrease the energy barrier for conductivity below Tg.

Increase in conductivity was only through a drop in copolymer Tg.

Thus, simply increasing macroscopic dielectric constant does not improve significantly the conductivity

S. Zhao, et al., **Appl. Mat. Interf. 13**, 51525 (2021)

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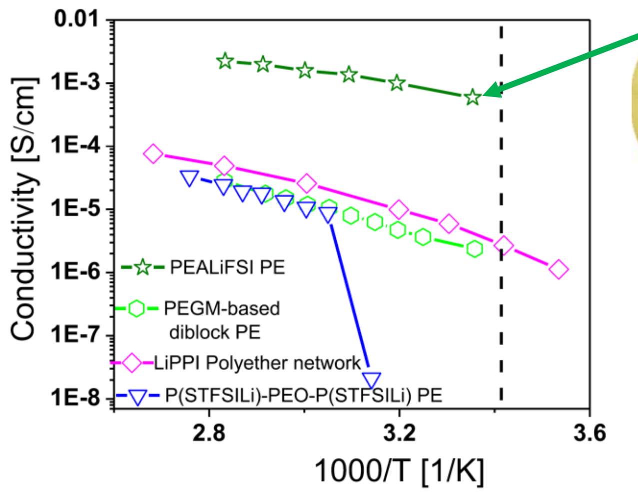
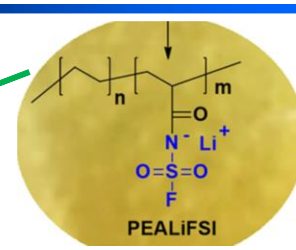
Recent Achievements in PolyILs Li+ Conductivity





[F. Ahmed, et al., **ACS Appl. Mat. Interf. 11**, 34930 (2019)]

Dry PolyILs are approaching the required level. Developments of anions with strongly delocalized charge might help in reducing electrostatic energy barrier for small cations (Li or Na).

V. Bocharova, A.P. Sokolov **Macromolecules 53**, 4141 (2020)

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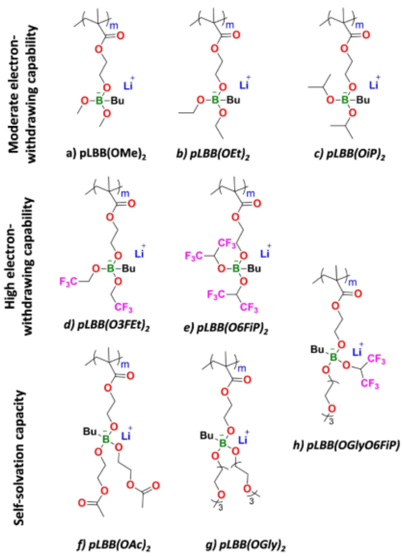
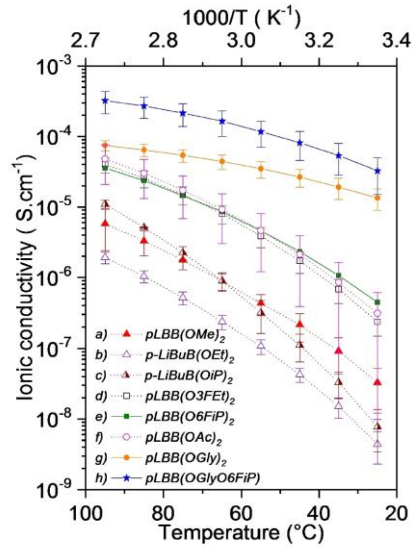
Designing Borate-based Polyanions





Modifying borate anions enabled single Li^+ ion conductivity σ ~ 10^{-4} S/cm at room temperature
[G. Guzman-Gonzalez, et al., **Angew. Chem. 134**, e202114024 (2022)]

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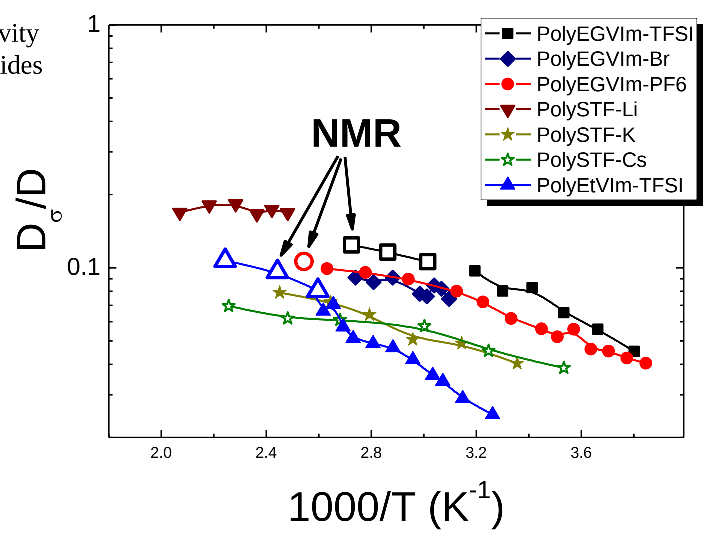
Ion diffusion and Charge diffusion

We can measure ion D from NMR or conductivity relaxation, while Nernst-Einstein relation provides estimate of charge D_σ from conductivity σ:

$$\sigma = \frac{nq^2}{kT} D_\sigma$$

The ratio of these diffusion coefficients is called ionicity or inverse Haven ratio

$$H^{-1} = \frac{D_\sigma}{D} = \frac{\sigma_{exp}}{\sigma_{NE}}$$



Analysis reveals that ionic conductivity in PolyILs is ~10 times lower that it should be according to the ion diffusion

E.W. Stacy, et al., **Macromolecules 51,** 8637 (2018).

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Audience Survey Question

ANSWER THE QUESTION ON THE INTERACTIVE SCREEN IN ONE MOMENT

Why is conductivity in Polymerized Ionic Liquids so much lower than expected from ion diffusion?

- Diffusion of ion pairs
- Correlated motions of mobile ions
- Not all ions contribute to conductivity
- All of the above

* If your answer differs greatly from the choices above **tell us in the chat!**

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Conductivity and Ion – Ion correlations

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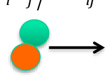
Diffusion presents a self-correlation function $D^*(\omega) = \frac{1}{3}\int_0^\infty \langle \vec{v}_i(0)\vec{v}_i(t)\rangle \exp(-i\omega t)\,dt$

While conductivity depends on all ion-ion correlations

$$\sigma_{DC} = \frac{1}{3Vk_BT}\int_0^\infty \langle \vec{J}(0)\cdot\vec{J}(t)\rangle\,dt, \quad \text{where} \quad \langle \vec{J}(0)\cdot\vec{J}(t)\rangle = \langle \textstyle\sum_i q_i\vec{v}_i(0)\cdot\sum_j q_j\vec{v}_j(t)\rangle.$$

Only assuming no ion-ion correlations, $\langle v_i v_j\rangle = d_{ij}$, we get Nernst-Einstein relation.

Often diffusion of ion pairs is assumed: 

In general, one can present conductivity as 4 terms: $\sigma = \sigma_{NE} + \sigma_{+-} + \sigma^d_{++} + \sigma^d_{--},\ where\ \sigma_{NE} = \sigma^s_+ + \sigma^S_-$,

Based on momentum conservation argument, Schönert proposed a model **[JPC 88**, 3359 (1984)**]** that expresses distinct correlation terms through the measured conductivity, σ_{exp}:

$$\sigma^d_{++} = \sigma_{exp}\left(\frac{z_+m_-}{z_+m_- - z_-m_+}\right)^2 - \sigma^s_+, \qquad \sigma^s_+ = \frac{e^2n}{kT}x_+z_+^2D_+,$$

$$\sigma^d_{--} = \sigma_{exp}\left(\frac{z_-m_+}{z_-m_+ - z_+m_-}\right)^2 - \sigma^s_-, \qquad \sigma^S_- = \frac{e^2n}{kT}x_-z_-^2D_-,$$

$$\sigma_{+-} = -2\sigma_{exp}\frac{z_+z_-m_+m_-}{(z_+m_- - z_-m_+)^2}.$$

Here **z** is the charge, **m** is the mass and **x** is the molar fraction of cation (+) and anion (-); **n** is the total concentration of ions.

According to this model cation-anion term always increases conductivity

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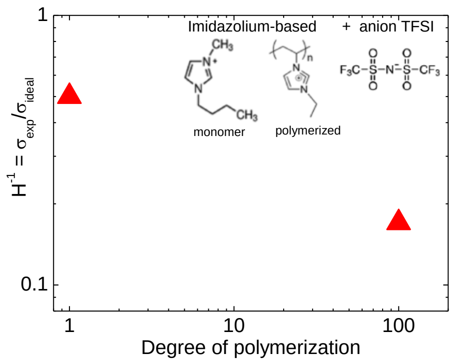
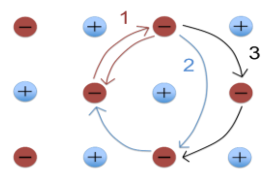
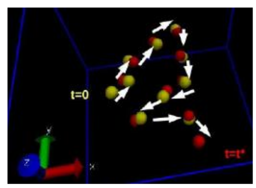
Inverse Haven Ratio in ILs and PolyILs



The inverse Haven ratio decreases with increase of the cation degree of polymerization. ***This clearly excludes ion pairs as the major mechanism reducing ionicity or inverse Haven ratio.***



The only plausible explanation is a correlated motion of mobile ions, a kind of 'backflow', that contributes to ion diffusion, but no charge transport [E.W. Stacy, et al., **Macromolecules 51**, 8637 (2018)].



MD simulations by Paddison and co-workers indeed revealed the correlated mobile ion motion in PolyILs [Liu, et al., **J.Phys.Chem. B** 125, 372 (2021)].

Gainaru, et al., **J.Phys.Chem. B 120**, 11074 (2016)

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Ion diffusion and Charge diffusion

Extending the model to polymers, e.g., poly-cation with N monomers, monomer mass M_+, and mobile anion with mass m_-:

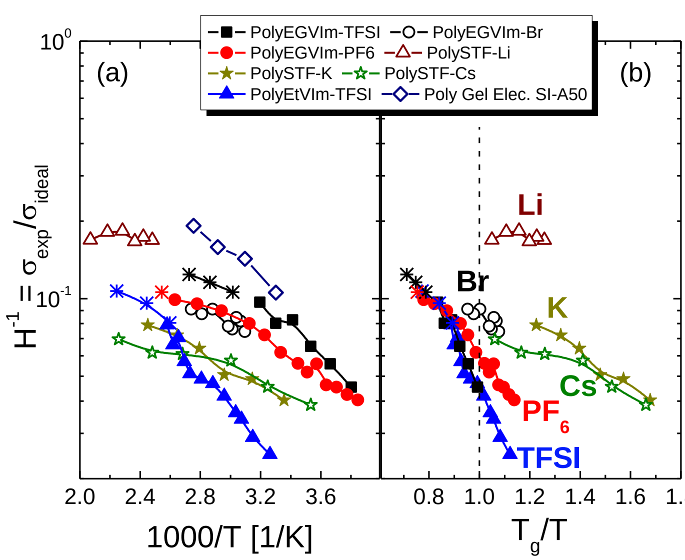
$$\sigma^d_{++} = \sigma_{exp}\left(\frac{m_-}{M_+ + m_-}\right)^2 - \sigma^s_+,$$

$$\sigma^d_{--} = \sigma_{exp}\left(\frac{M_+}{M_+ + m_-}\right)^2 - \sigma^s_-,$$

$$\sigma_{+-} = 2\sigma_{exp}\frac{m_- M_+}{(M_+ + m_-)^2}.$$

Indeed mobile ions correlations provide the main suppression of conductivity

I. Popov, et al., **J. Phys. Chem. C 124,** 17889 (2020)



Experimental data revealed that H^{-1} decreases with increase of the mobile ion size.

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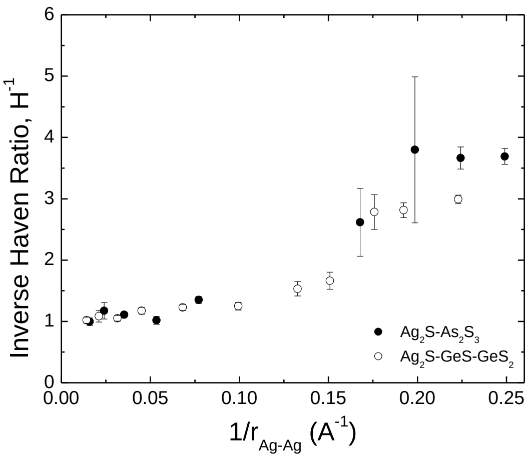
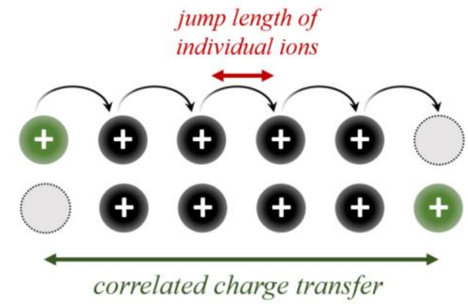
Ion-Ion correlations in 'superionic' glasses

There are many examples of 'superionic' glasses and crystals where $\mathbf{H^{-1} > 1}$ (i.e. the Haven ratio is smaller than 1). This means that ion-ion correlations enhance conductivity.





Charge diffusion faster than ion diffusion is possible due to collective chain-like ion jumps. Apparently, this mechanism requires short distance between mobile ions and formation of ion channels

Inverse Haven ratio in superionic glasses increases with the decrease of the distance between mobile ions [Bychkov, **Sol.St.Ionics 180**, 510 (2009)]. These data correspond to $\mathbf{H^{-1} \sim 4}$.

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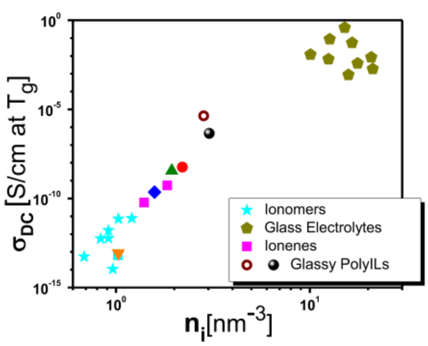
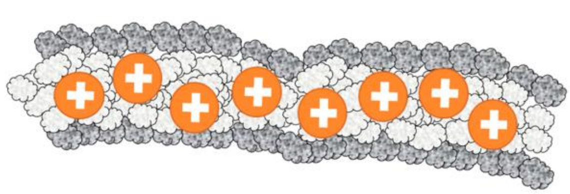
Enhancing Conductivity through ion-ion correlations

Thus, in comparison to superionic systems PolyILs are losing in conductivity by more than 20 times due to the ion-ion correlations alone.



Analysis of literature also reveals a strong increase in conductivity at Tg with increase of ions concentration.



Formation of one-dimensional ion channels with high local ion concentration can significantly improve ionic conductivity in polymer electrolytes.

V. Bocharova, A.P. Sokolov **Macromolecules 53**, 4141 (2020)

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Recent results on zwitterionic polymer

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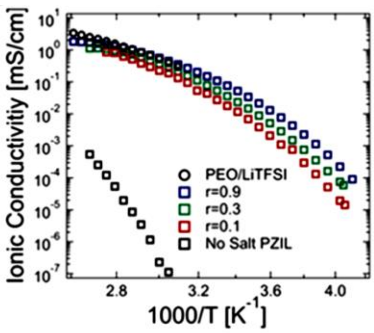

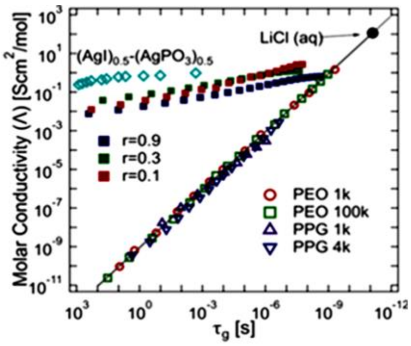

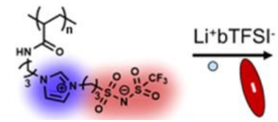

Recent studies [S.D. Jones, et al., **ACS Centr Sci 8**, 169 (2022)] revealed rather high conductivity and extremely strong decoupling from segmental dynamics in zwitterionic polymers with Li-TFSI salt. These polymers form ionic channels, and this might be the major reason for this high conductivity.

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In situ Polymerization: SPE doped with plastic crystal

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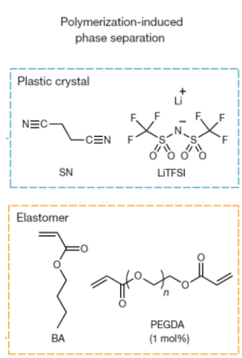
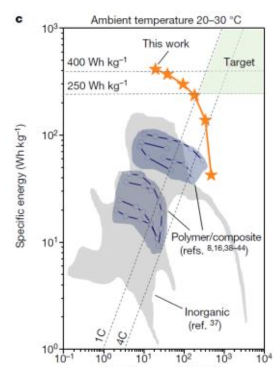
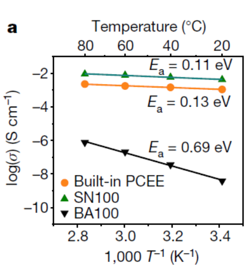
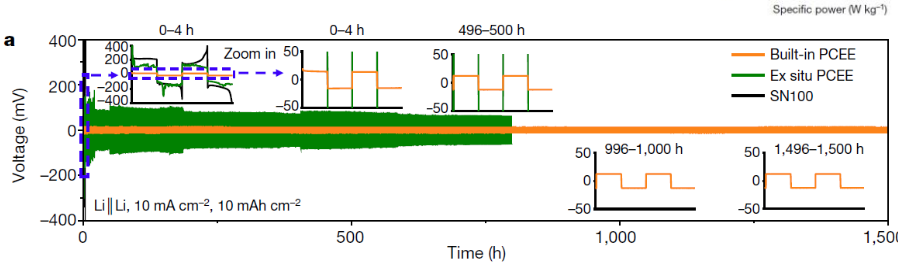


In situ polymerization and crosslinking of PMMA-based polymer plasticized with plastic crystal (succinonitrile) and added Li-TFSI provided high conductivity, **σ ~ 1.1*10^{-3} S/cm, and t$^+$ ~ 0.75 at room temperature** [M.J. Lee, et al., **Nature 601**, 217 (2022)].

This polymer electrolyte demonstrates stable cycling in symmetric Li/Li cell up to 1500 cycles with very high current density 10 mA/cm^2.







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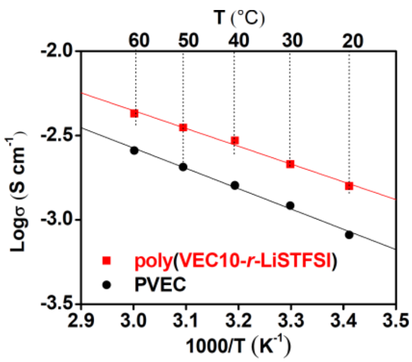
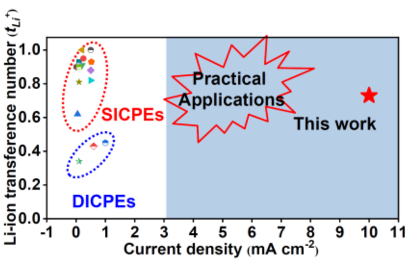
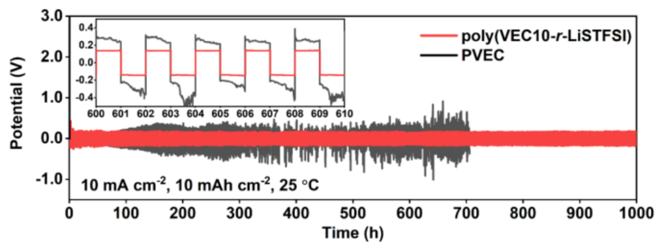
Our recent progress with polymers for solid state battery







- We recently developed a polymer with cation transport number t^+ ~ 0.73, room temperature conductivity > 1 mS/cm, and wide electrochemical stability window.
- This polymer shows high stability even at very high current density 10 mA/cm^2 after 1000 hours cycling in symmetric Li/Li cell.
- The latter indicates good suppression of dendrites growth by this polymer.

X. Shan, et al., **ACS Energy Lett. 7**, 4342 (2022).

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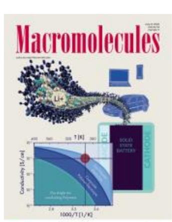
Conclusions

- Decoupling ion transport is the best way to improve conductivity in dry polymers
- Energy barrier for the decoupled ion conductivity of small cations (e.g. Li, Na) is dominated by electrostatic interactions.
- Designing polymer electrolytes either (i) with strongly delocalized charge on polymerized anions, or (ii) with concentrated ion channels might strongly increase ion conductivity
- Controlling ionic correlations can provide additional increase of conductivity by about 10-50 times.



Suggested Literature:
1) E. W. Stacy, et al., **Macromolecules 51**, 8637(2018).
2) V. Bocharova, A.P. Sokolov, **Macromolecules 53**, 4141(2020).
3) X. Shan, et al., **ACS Energy Letters 7,** 4342 (2022).

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College of Engineering
MICHIGAN STATE UNIVERSITY

Mechanically and Chemically Robust Polymers Containing Acidic or Basic Groups

Michael A. Hickner
Craig A. Rogerson Endowed Professor
Chemical Engineering and Materials Science
Michigan State University
Associate Editor, ACS Applied Energy Materials
mhickner@msu.edu

ACS Webinar
Better Ion Transport Through Polymer Chemistry: Polymer Electrolytes and Ion-conducting Membranes

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Hickner Research Group @ MSU

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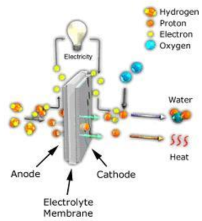
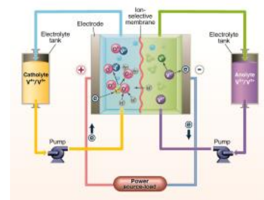
Membranes in Energy Applications

Fuel Cells



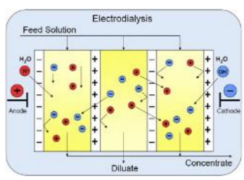
J. Am. Chem. Soc. **2013**

Flow Batteries



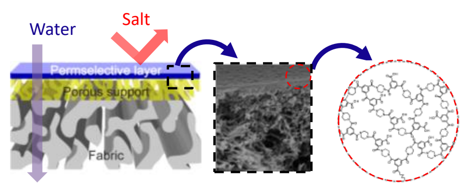
ACS Appl. Mater. Interfaces **2013**

Electrodialysis



Environ. Sci. Technol. Lett. **2014**

Reverse Osmosis



ACS Macro Lett. **2016**

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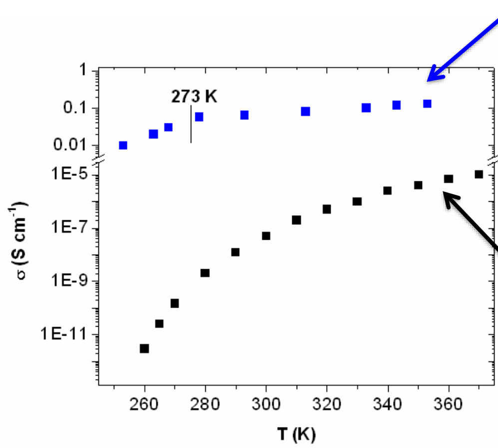
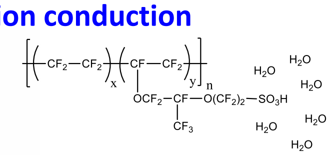
Aqueous vs non-aqueous ion conduction



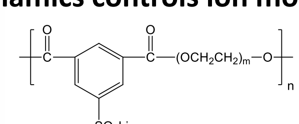
Hickner *Mater. Today* **2010**.

Nafion – water-mediated ion conduction



Holdcroft, *et al.*, *J. Phys. Chem. B* **2006**.
Kreuer, et al., *Chem. Rev.* **2004**.

PEO-Li – polymer segmental dynamics controls ion motion



Colby and Runt *Chem. Mater.* **2006**.

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Audience Survey Question

ANSWER THE QUESTION ON THE INTERACTIVE SCREEN IN ONE MOMENT

Why is the conductivity of aqueous membranes generally larger than polymer-based ionic conductors?

- Sodium and lithium are larger than protons and diffuse more slowly
- There is well-developed nanophase morphology in proton-conducting membranes
- Water rotation and diffusion are more rapid than polymer dynamics
- All of the above

* If your answer differs greatly from the choices above **tell us in the chat!**

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Why is the conductivity of aqueous membranes generally larger than polymer-based ionic conductors?

- Sodium and lithium are larger than protons and diffuse more slowly?
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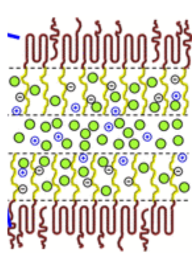
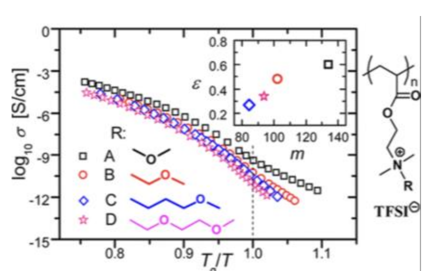


Chen, et al.
Nano Lett. **2014**, 14, 7.



Fan, et al.
Macromolecules **2015**, 48, 13.

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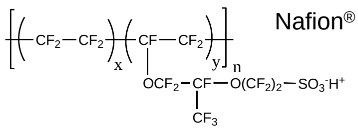
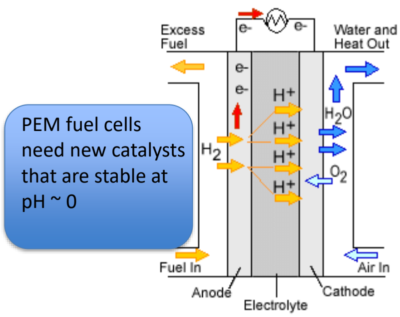
Polymer electrolyte membrane fuel cells

Proton Exchange Membrane (PEM)

Nafion®





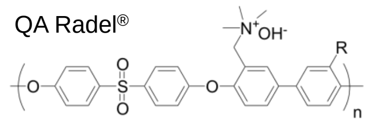
$H_2 \rightarrow 2\,H^+ + 2\,e^-$

$\frac{1}{2}\,O_2 + 2\,e^- + 2\,H^+ \rightarrow H_2O$

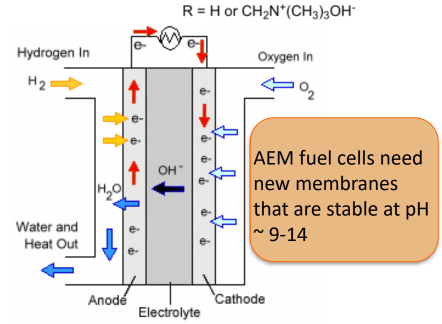
$\mathbf{H_2 + \frac{1}{2}\,O_2 \rightarrow H_2O}$

Anion Exchange Membrane (AEM)

QA Radel®



R = H or $CH_2N^+(CH_3)_3OH^-$



$H_2 + 2\,OH^- \rightarrow 2\,H_2O + 2\,e^-$

$\frac{1}{2}\,O_2 + H_2O + 2\,e^- \rightarrow 2\,OH^-$

$\mathbf{H_2 + \frac{1}{2}\,O_2 \rightarrow H_2O}$

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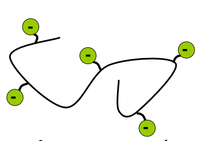
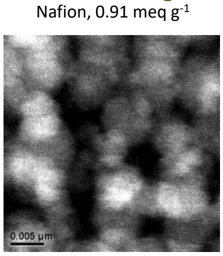
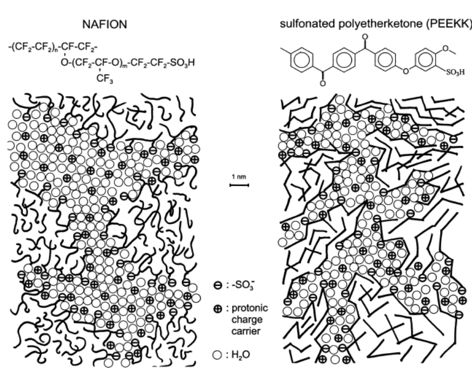
Membrane structure and function



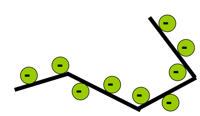
Nafion, 0.91 meq g^{-1}



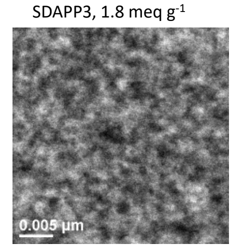


- wide channels
- more separated
- less branched
- good connectivity
- small $-SO_3^-$ / $-SO_3^-$ separation
- pK_a ~ -6

- narrow channels
- less separated
- highly branched
- dead-end channels
- large $-SO_3^-$ / $-SO_3^-$ separation
- pK_a ~ -1



SDAPP3, 1.8 meq g^{-1}



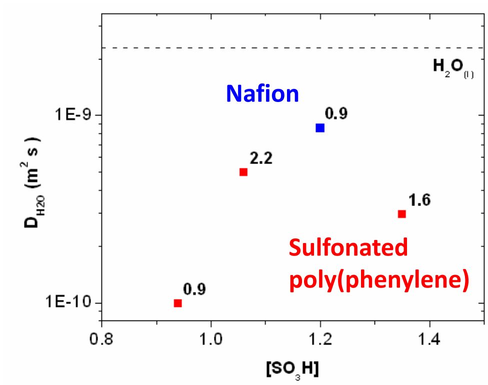
Kreuer, *J. Membrane Sci.* **2001**.

Fujimoto, et al. *Macromolecules* **2005**.
Hickner, et al. *Polymer* **2006**.

54

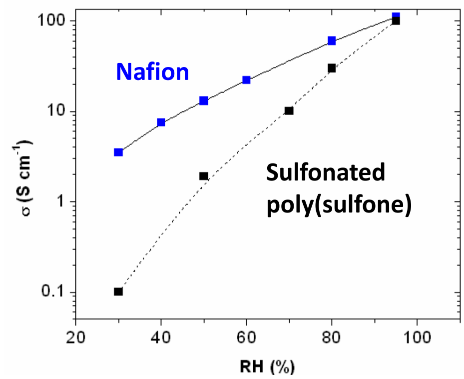
Small ionic domains lead to lower water diffusivity

Low water diffusion in aromatic PEMs can be leveraged for low crossover methanol fuel cell and battery membranes.



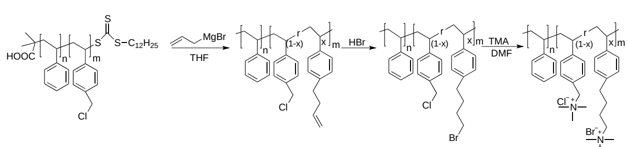
Fujimoto, C. H., *et al., Macromolecules* **2005**.
Hickner, M. A., *et al., Polymer* **2006**.

Why is conductivity lower in aromatic PEMs? Morphology, water diffusivity, other?

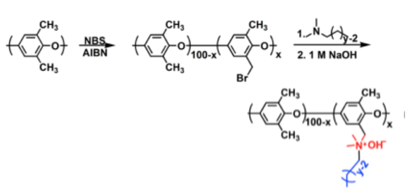


Roy, A., *et al., J. Membr. Sci.* **2009**.

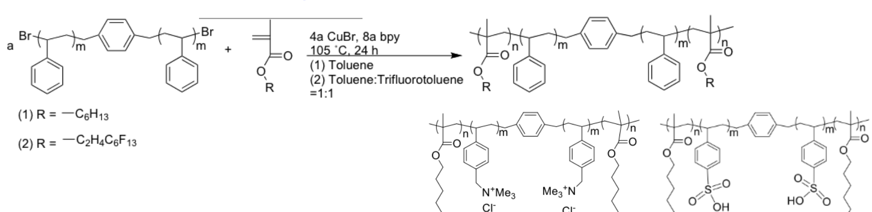
New Membranes Through Polymer Synthesis



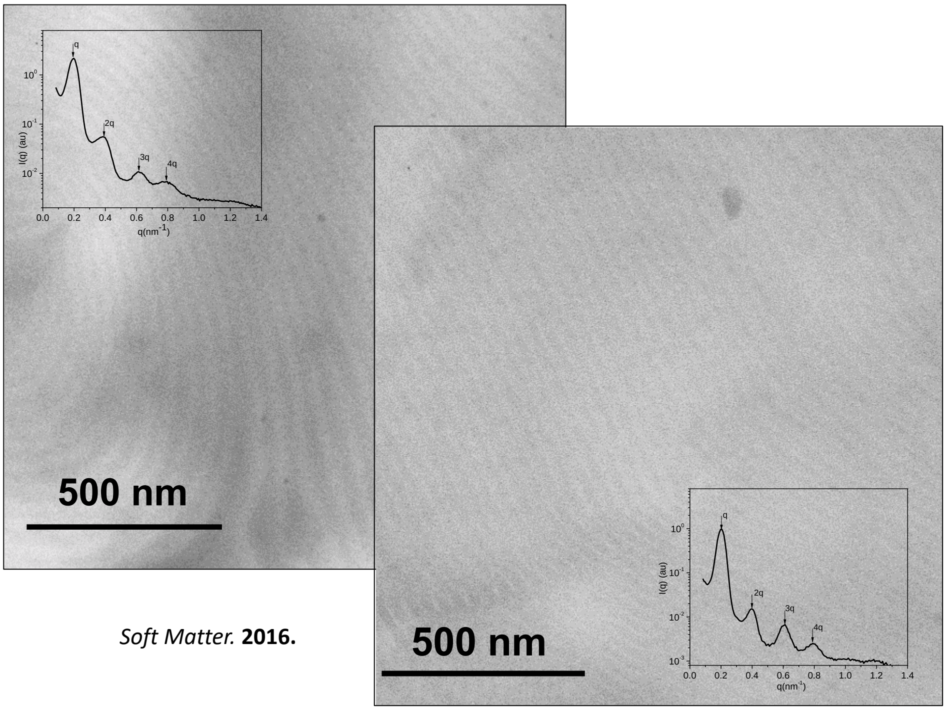
Wang, Hickner, *Soft Matter.* **2016.**



Li, Hickner, et al., *J. Am. Chem. Soc.* **2013**.
Zha, Disabb-Miller, Tew, Hickner, *J. Am. Chem. Soc.* **2012**.



Disabb-Miller, Hickner, et al., *Macromolecules* **2013**.
Moore, Saito, Hickner, *J. Mater. Chem.* **2010**.



Soft Matter. **2016.**

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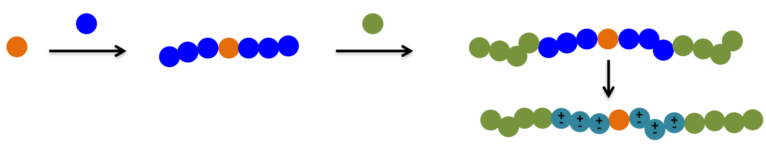
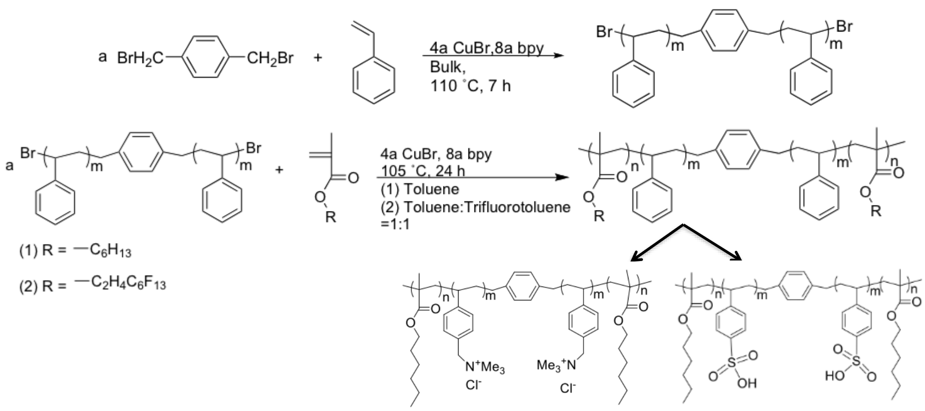
Synthesis of multifunctional block copolymers





Disabb-Miller, M. L., Z. D. Johnson, M. A. Hickner, "Ion Motion in Anion and Proton-Conducting Triblock Copolymers," *Macromolecules* **2013**, 46(3), 949–956.

58

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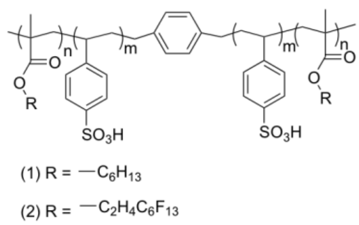
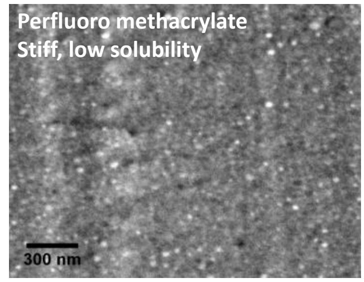
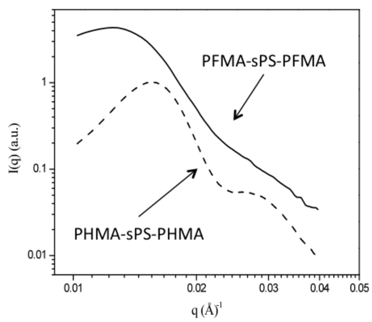
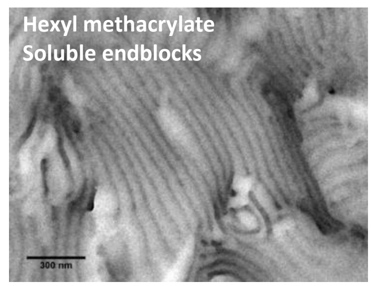
Block copolymer assemblies to form ionic channels









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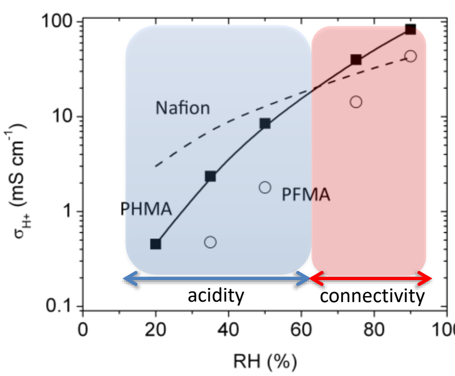
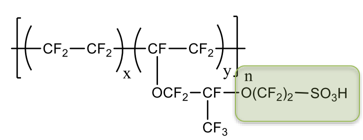
Morphological connectivity and headgroup acidity in PEMs

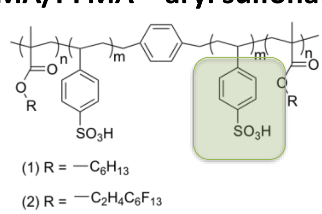


Need superacid polymers for high conductivity at low relative humidity

Nafion – perfluoro sulfonate



PHMA/PFMA – aryl sulfonate



Saito, T., H. D. Moore, M. A. Hickner, "*Macromolecules* **2010**, 43 (2), 599-601.

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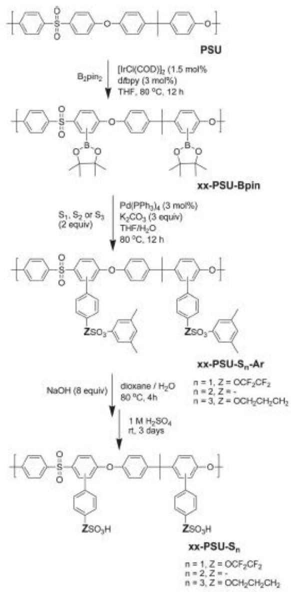
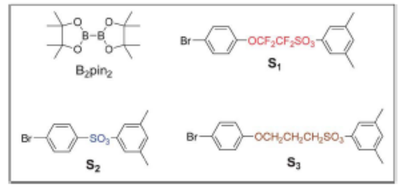
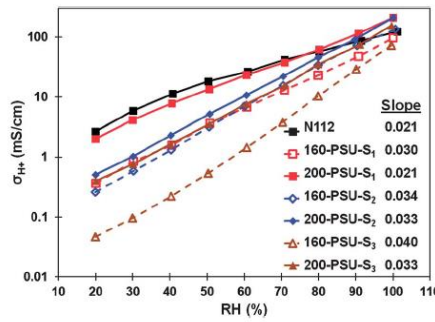
60

Poly(sulfone) superacid membranes







Chang, Y., G. F. Brunello, J. Fuller, M. Hawley, Y. S. Kim, M. Disabb-Miller, M. A. Hickner, S. S. Jang, C. Bae *Macromolecules* **2011**, 44(21), 8458–8469.

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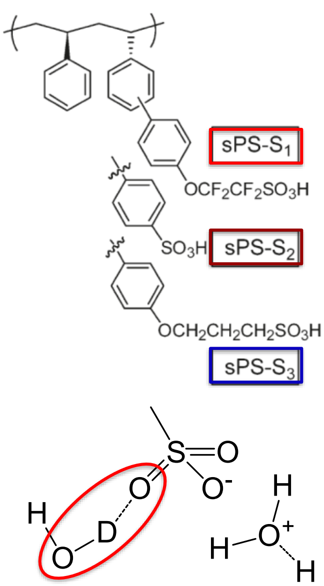
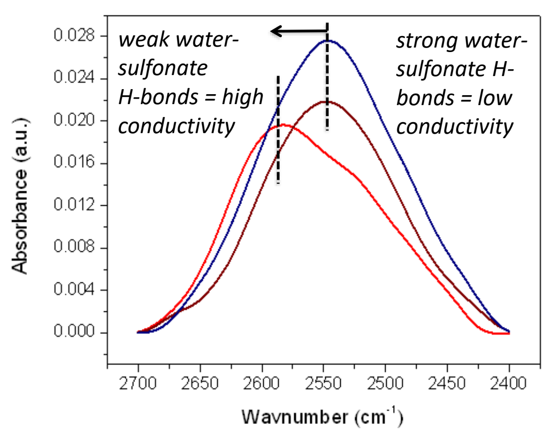
Hydration in superacidic polymers



Increased acidity of the superacid weakens the H-bond between sulfonate and water causing a red shift in the O-D stretch



Black, S., Y. Chang, C. Bae, M. A. Hickner, *J. Phys. Chem. B* **2013**, 117 (50), 16266–16274.

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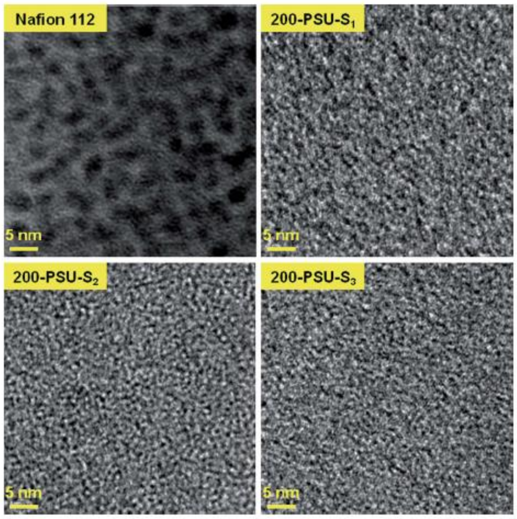
Poly(sulfone) superacid membranes



Much smaller morphological size in PSU-based membranes, but similar conductivity to Nafion.

Morphology is important, but superacid groups are more important in these samples for high conductivity at low RH.

Chang, Y., G. F. Brunello, J. Fuller, M. L. Disabb-Miller, M. E. Hawley, Y. S. Kim, M. A. Hickner, S. S. Jang, C. Bae, "Acidity Effects in Poly(sulfone)–based Proton Exchange Membranes," *Polym. Chem.* **2013**, 4, 272–281.

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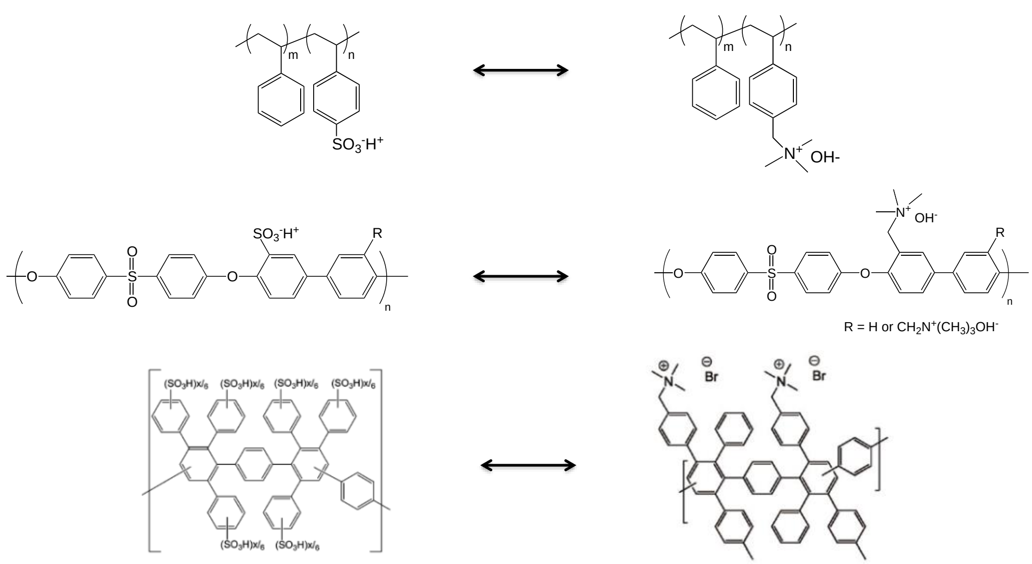
Many of the strategies reported for PEMs can be used for AEMs



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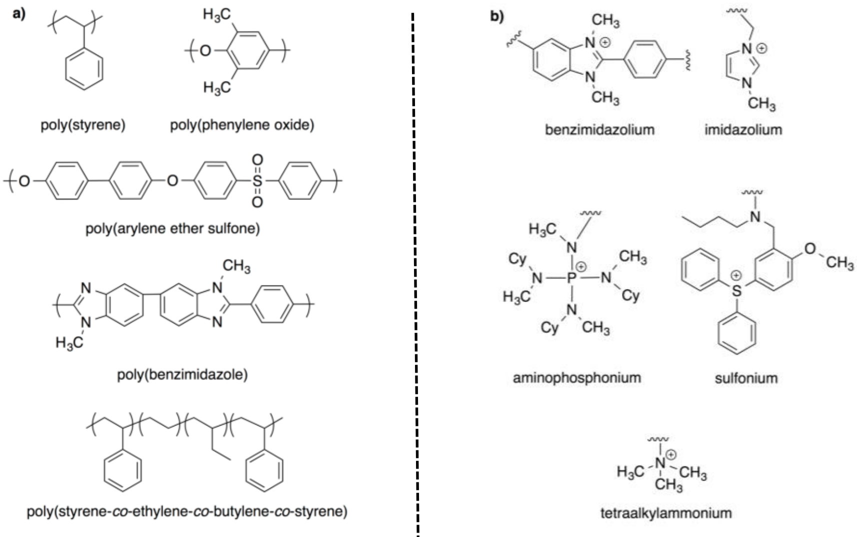
Chemical structures of polymer backbones and cations common to anion exchange membranes



Nuñez, Capparelli, Hickner, *Chem. Mater.* **2016**, 28, 2589−2598.

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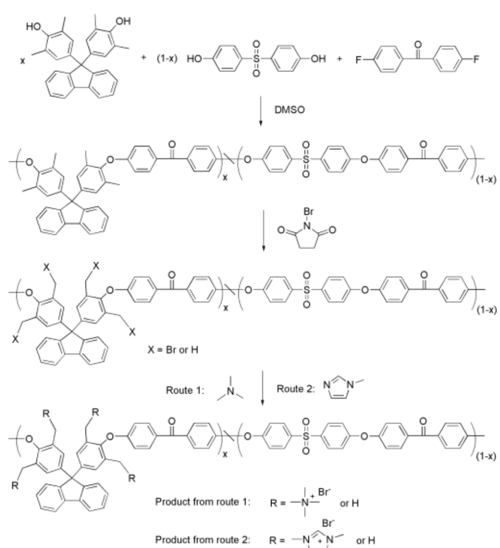
Need to evaluate ionic group and backbone stability



1. Bromination of benzylic methyl groups

2. Quaternization with different cationic moieties

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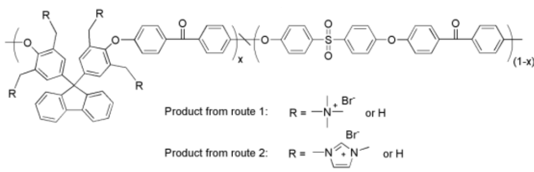
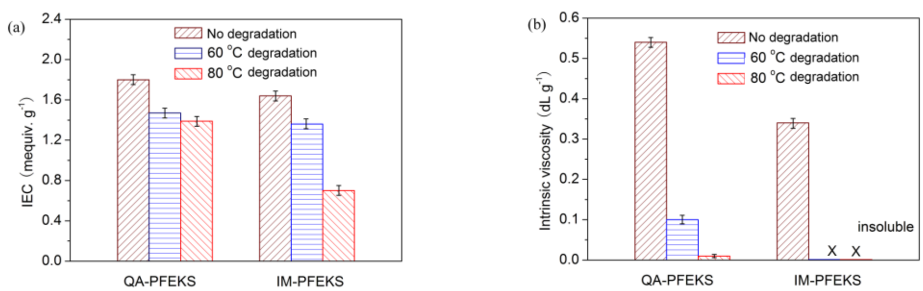
Need to evaluate ionic group and backbone stability



	λ		Conductivity (mS cm^{-1})	
	OH-	HCO3-	OH-	HCO3-
QA-FEKS	18.2	11.1	22.3	5.1
IM-PFEKS	14.8	9.9	17.1	3.9



Chen, D., M. A. Hickner, "Degradation of Imidazolium and Quaternary Ammonium Functionalized Poly(fluorenyl ether ketone sulfone)s for Anion Exchange Membranes," *ACS Appl. Mater. Int.* **2012**.

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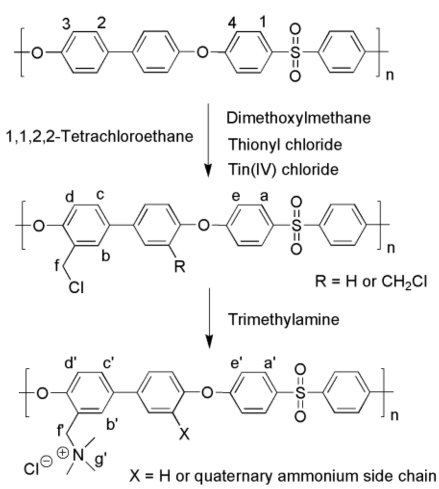
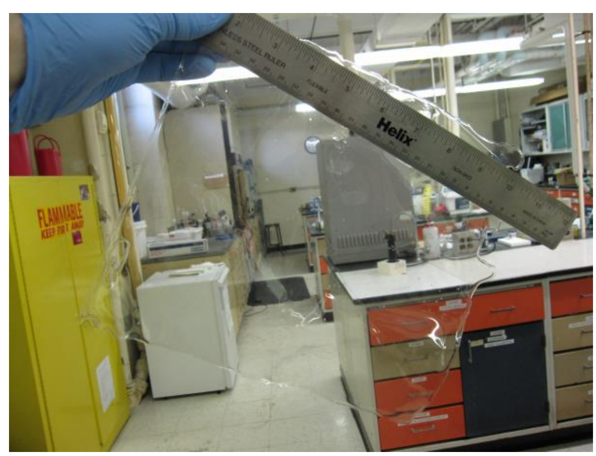
Route to scale-up with commercial starting materials





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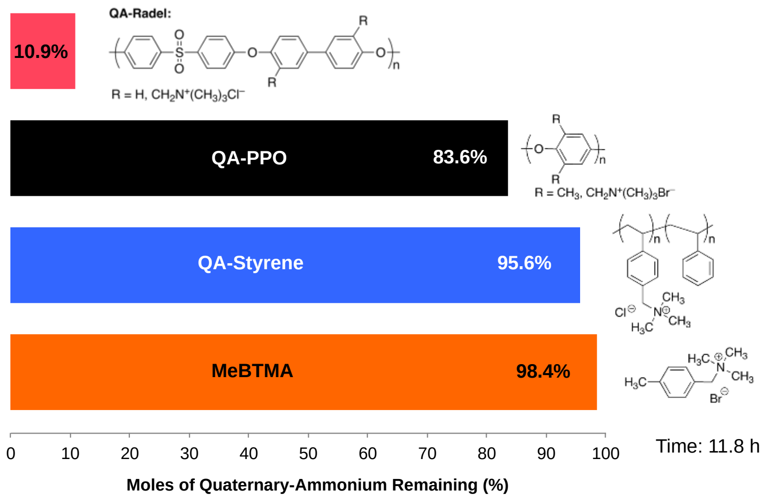
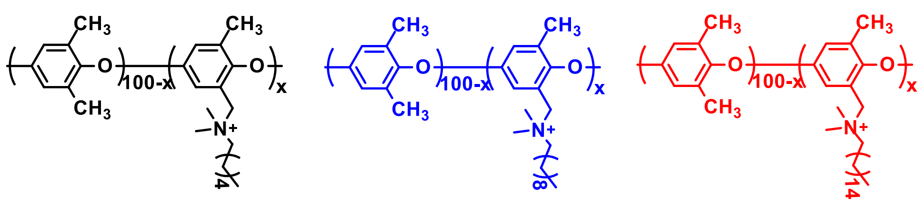
Stability ranking of AEMs



Nuñez, S. A. & Hickner, M. A. "Quantitative 1H NMR Analysis of Chemical Stabilities in Anion-Exchange Membranes," *ACS Macro Lett.* **2013**, 2, 49–52.

PPO-based AEMs

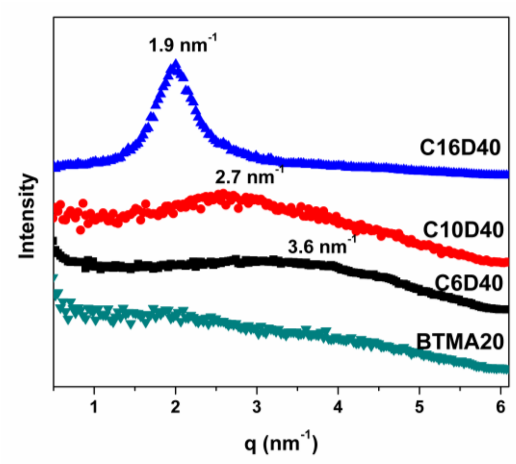


Short	Medium	Long
C6 Dx	**C10 Dx**	**C16 Dx**

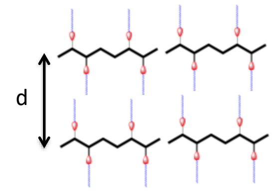
C denotes side chain length.
D denotes functionalization, e.g. 40 = 0.4 cationic groups per repeat unit.

Li, N., Y. Leng, M. A. Hickner, C.-Y. Wang, "Highly Stable, Anion Conductive Comb-shaped Copolymers for Alkaline Fuel Cells," *J. Am. Chem. Soc.* **2013**, 135 (27), 10124–10133.

Phase separation observed with longer alkyl side chains



d-spacing
C16D40 3.3 nm
C10D40 2.3 nm
C6D40 1.7 nm



Roughly correspond to extended side chain lengths.

No separation observed for benzyltrimethyl ammonium (BTMA) cations – as seen in other aromatic AEMs.

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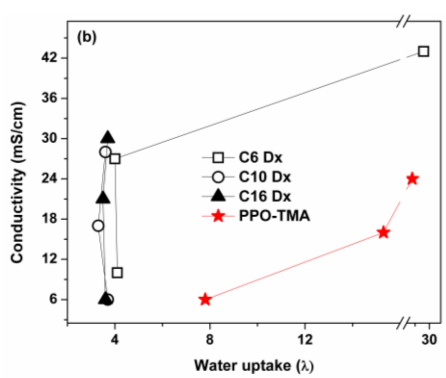
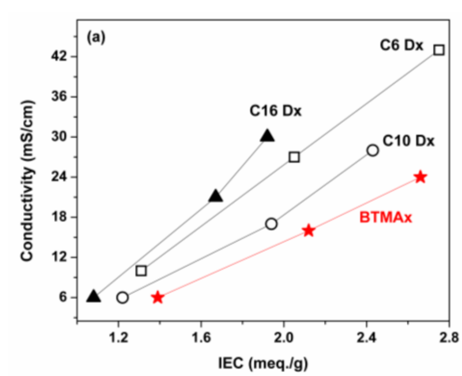
Low lambda and higher conductivity with long side chains





OH^- conductivity in liquid water at 25 °C

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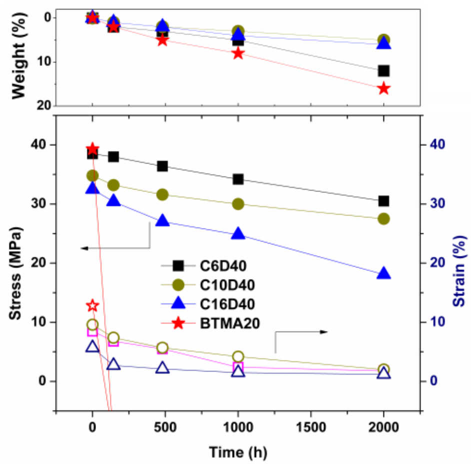
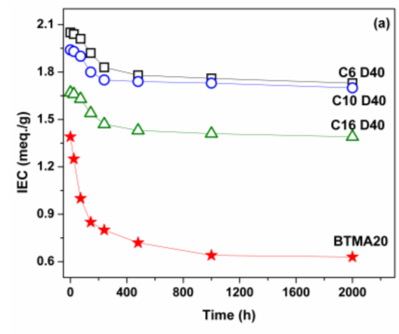
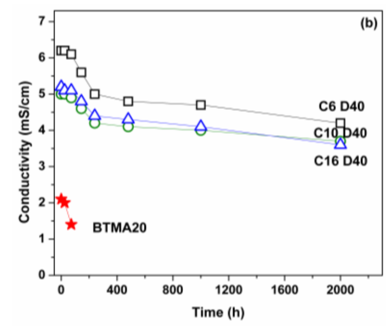
1 M NaOH at 80 ° C degradation







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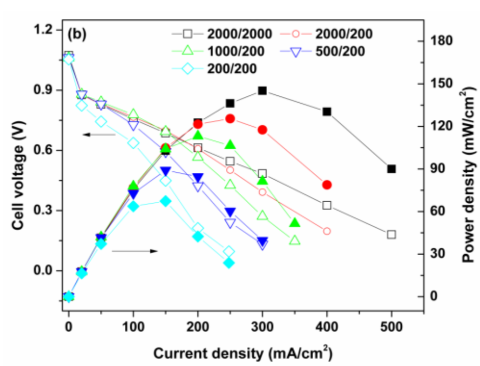
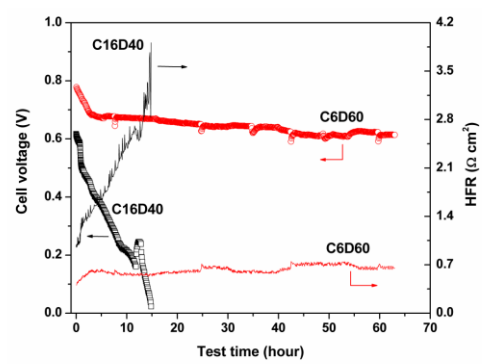
Fuel cell power density and stability are reasonable but more development is needed

50 °C, air, Pt catalysts





100 mA/cm² constant current

Still work to be done to optimize the fuel cell MEA construction and operating conditions

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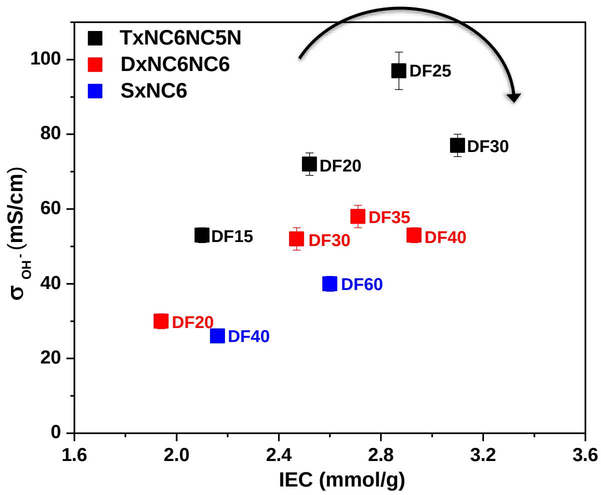
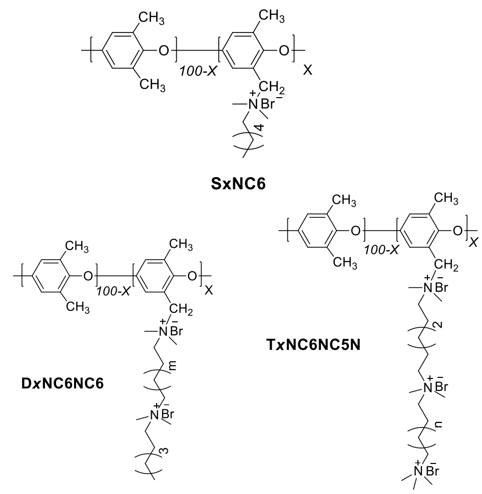
OH^- conductivity with increasing cation number



Overswelling decreases conductivity due to ion dilution.



Zhu, Pan, Wang, Han, Zhuang, Hickner *Macromolecules* **2016**.

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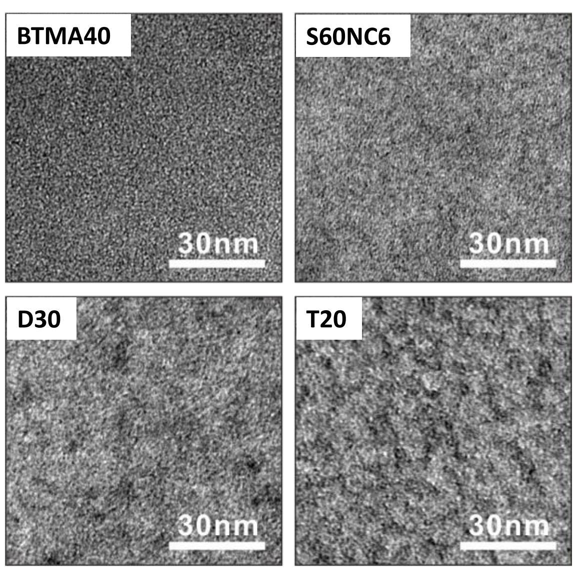
Microscopy confirms structured AEMs with addition of side chains



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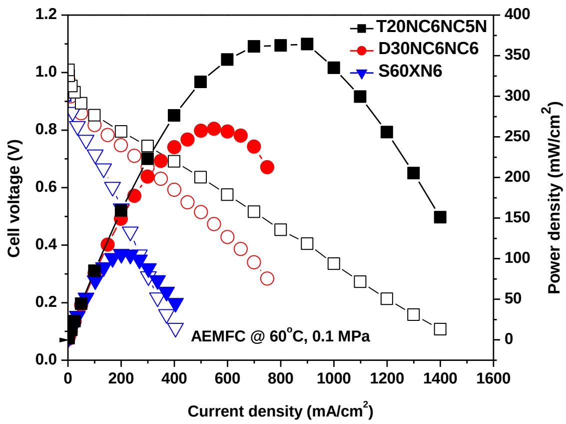
H_2/O_2 fuel cell performance

Triple cation side chain AEMs show reasonable fuel cell performance



Many demonstrations of fuel cell performance with power densities between 150-500 mW/cm^2.

There appears to be an optimization barrier to obtain higher power densities.

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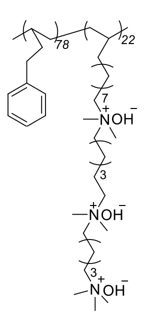
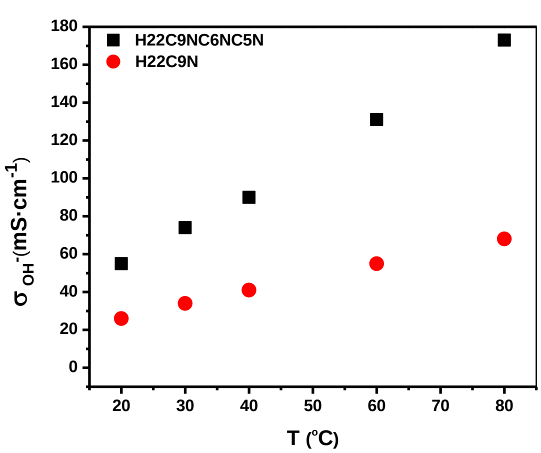
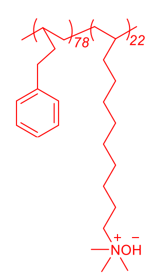
Robust liquid water conductivity







Zhu, Yu, Peng, Zimudzi, Saikia, Kwasny, Song, Kushner, Fu, Tew, Mustain, Yandrasits, Hickner *Macromolecules* **2019**.

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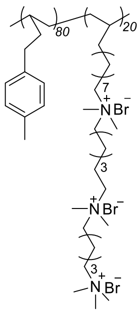
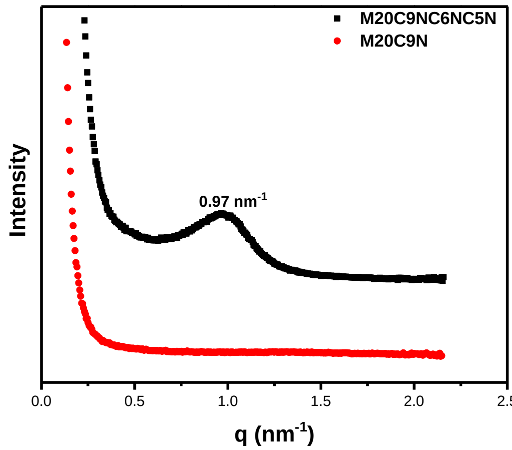
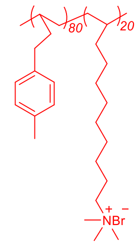
Graft-type cations lead to phase separation



M20C9NC6NC5N





M20C9N

Random copolymers with ionic domain separation.

SAXS profiles of membranes reveal ~6.5 nm ionic phase formation.

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Outlook

- We have good control over chemistry, morphology, and other properties in polymeric membranes that absorb water.
- Important to consider the mechanical properties and chemical stability of the material.
- What is the speed limit for ion transport in these systems?
- How do we match perfluorinated materials’ chemical resistance for long-term operation?

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Thank you!

Michael Hickner
mhickner@msu.edu

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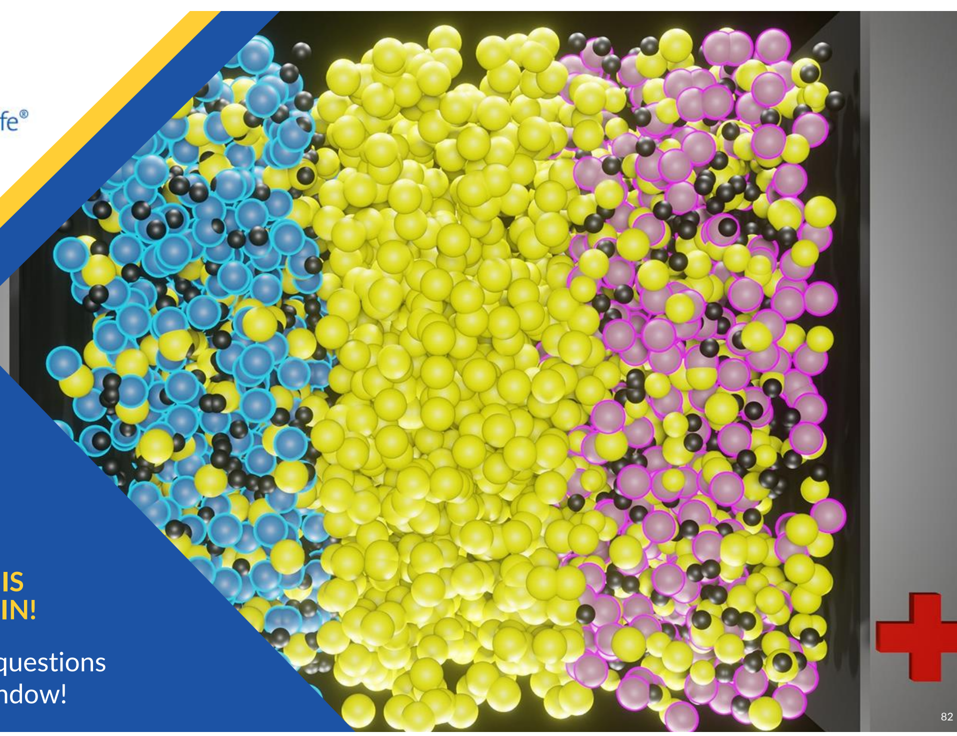

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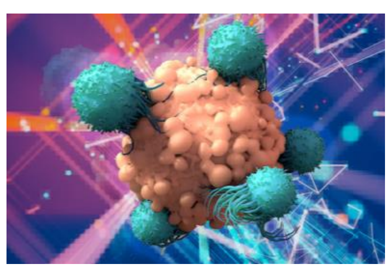

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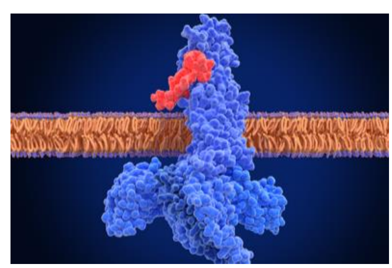

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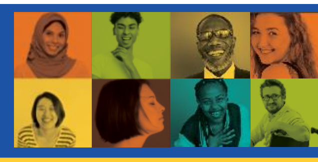

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