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Counterion Effects on Ion Mobility and Mobile Ion Concentration of Doped Polyphosphazenes and Polyphosphazene Ionomers

Robert J. Klein[†,1], **Daniel Welna**[‡,2], **Arlin Weikel**[2],
Harry Allcock[2], **Ralph Colby**[1], **James Runt**[1]

[1]Department of Materials Science and Engineering
[2]Department of Chemistry
Pennsylvania State University

[†]Presently at Materials and Processing Sciences Center,
Sandia National Laboratories, NM
[‡]Presently at Air Force Research Laboratory,
Wright-Patterson Air Force Base, OH

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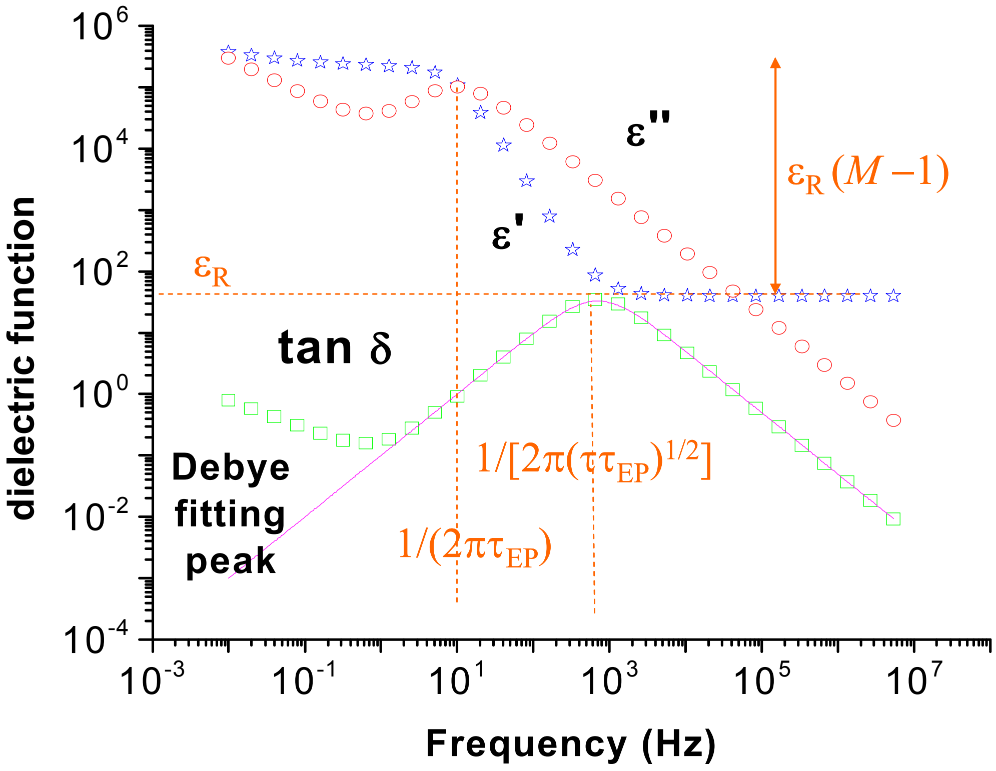
Dielectric measurement of electrode polarization[1]

- Clearly visible in dielectric constant, dielectric loss, and their ratio tan δ
- Macroscopic relaxation created by ions crossing the sample to create concentration gradient

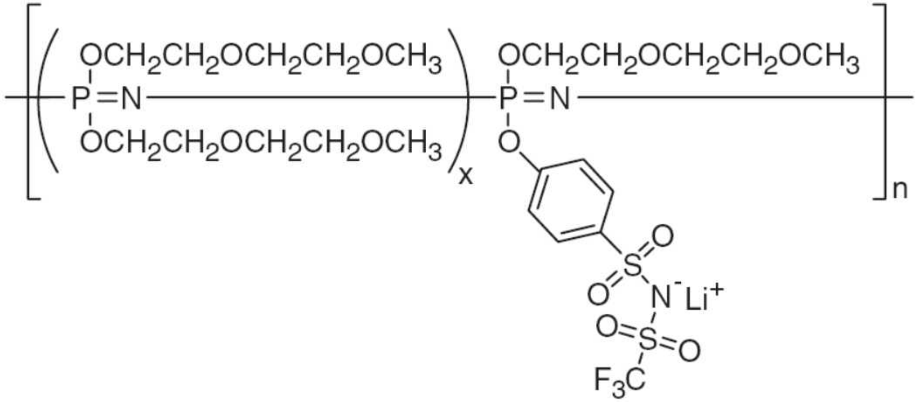


Model for ideal EP

[1] Klein, Zhang, Dou, Jones, Colby, Runt, *Journal of Chemical Physics* 2006

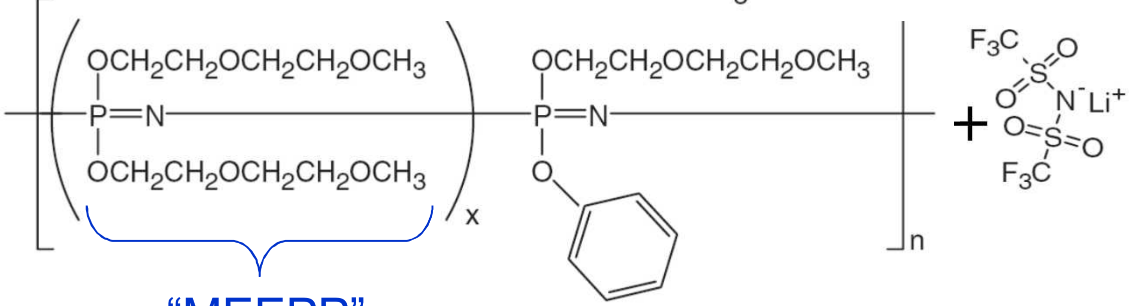
MEEP-based chemistry

- Two poly(methoxyethoxy-ethoxy phenoxyphosphazene)-based species[1]
  - **Ionomer (*MI*)** has covalently-attached anion
  - **Polymer + salt (*M+S*)** contains dissolved salt



9 % Li / MEE groups

17 % Li / MEE groups



"MEEPP"

10 % Li / MEE groups

15 % Li / MEE groups

[1]Allcock, Welna, Maher *Solid State Ionics* 2006

Polymer properties*

- T_g highly dependent on ion concentration, due to physical intermolecular bonds, especially prominent in ionomers[1-3]
- Total ion concentration ≈ 4 x 10^{20} cm^{-3}, 1 % of common p.e. mixtures

Sample	ions/$(EO)_3$ mol %	T_g (°C)	M_n (kg/mol)	PDI	$[Li^+]$ ions/cm^3
MI-17	17	−32	150	2.8	5.4×10^{20}
MI-9	9	−45	150	2.8	3.0×10^{20}
M+S-15	15	−69	130	2.7	4.8×10^{20}
M+S-10	10	−73	130	2.7	3.4×10^{20}
MEEPP		–85			

*Polymer properties from: Allcock, Welna, Maher *Solid State Ionics* 2006

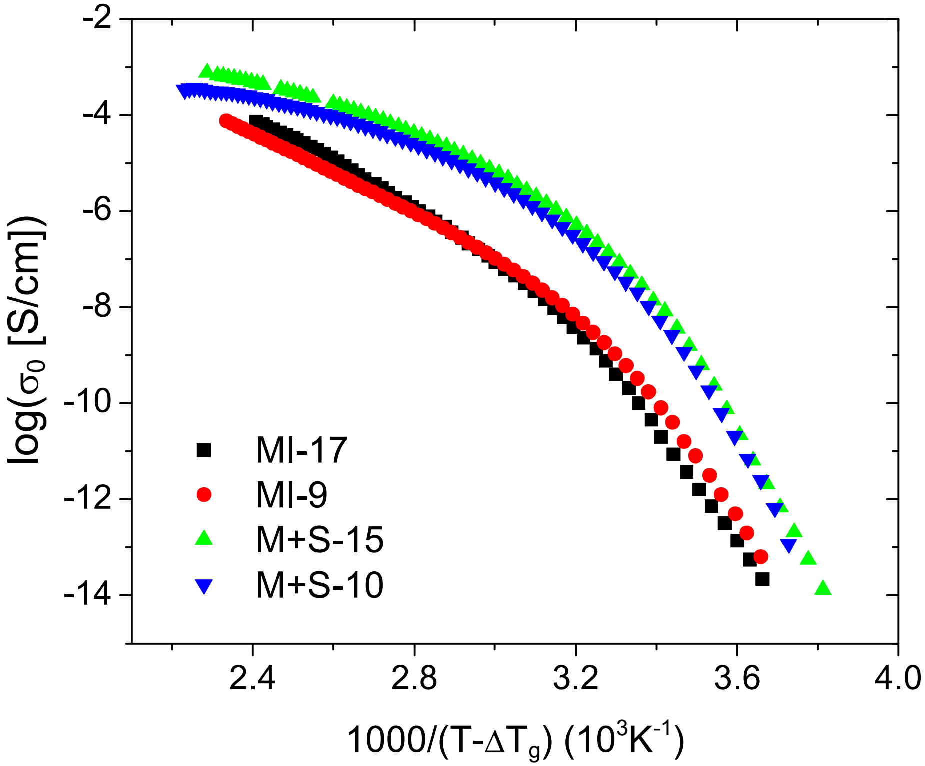
[1] Lemaitre-Auger, Prud'homme *Electro Acta* 2001

[2] Gray, pp.95-123 in *Solid Polymer Electrolytes* 1991

[3] Dou, Zhang, Klein, Runt, Colby *Chem Mater* 2006

Conductivity of MI and M+S

- Vogel-Fulcher-Tamman (VFT)-like functionality, therefore ion motion coupled with polymer segmental motion
- Normalizing by ΔT_g collapses curves[1-3]



[1] Zhang, Dou, Colby, Runt *JNCS* 2005

[2] Besner et al. *Macrom* 1992

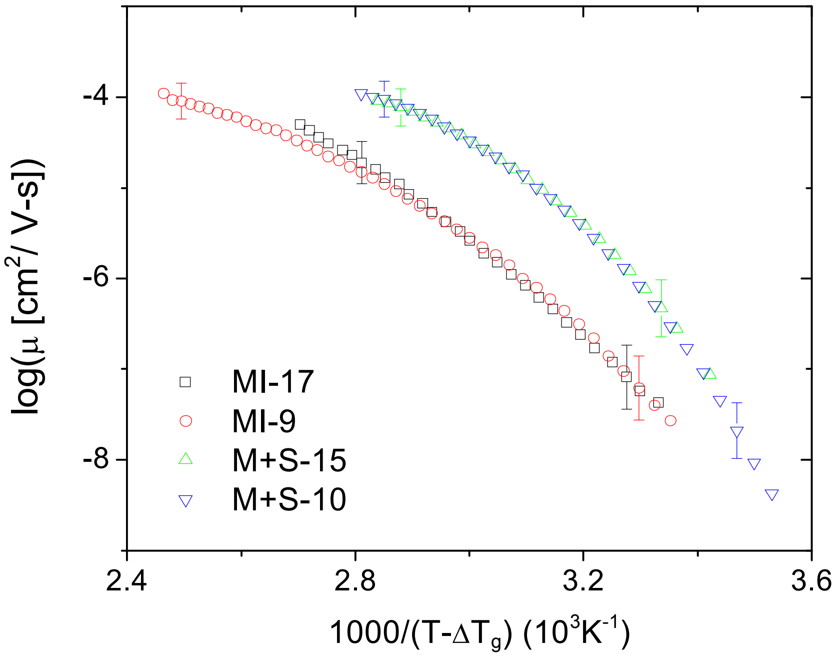
[3] Yoshizawa et al. *Electro Acta* 2000

$$\mu = \frac{qL^2}{4M\tau_{EP}kT}$$

Ion mobility

- Well-modeled by VFT relation[1]
- Normalizing by ΔT_g collapses curves
- After T_g shift, $\mu^{M+S} / \mu^{MI} \approx 10$

$$\mu = \mu_\infty \exp\left(\frac{-B}{T - T_0}\right)$$



[1] VFT relation has origins in Dynamic Bond Percolation Model, free-volume theories, viscosity universalities

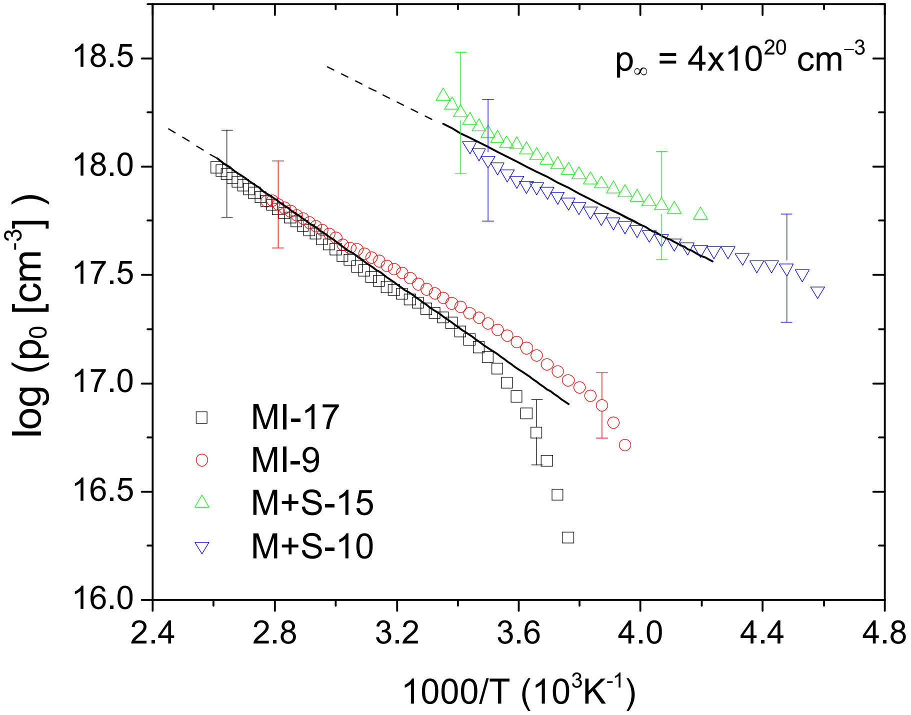
$$p_0 = \frac{\sigma_0}{q\mu}$$

Mobile ion concentration

- Even for M+S, p_0 is a very small fraction of the total ion concentration (0.3 % for M+S and 0.05 % for MI, at 20 °C)
- Follows Arrhenius relation

$$p_0 = p_\infty \exp\left(\frac{-E_a}{RT}\right)$$

- $p_0^{M+S} / p_0^{MI} \approx 10$ ($n_0 = p_0$ at any condition)



Fitting parameters

- Segmental pseudo-activation energy coefficient $B_{MI} / B_{M+S} \approx 1.5$
- Ion pair activation energy $E_a^{MI} / E_a^{M+S} \approx 1.4$

sample
MI-17
MI-9
M+S-15
M+S-10

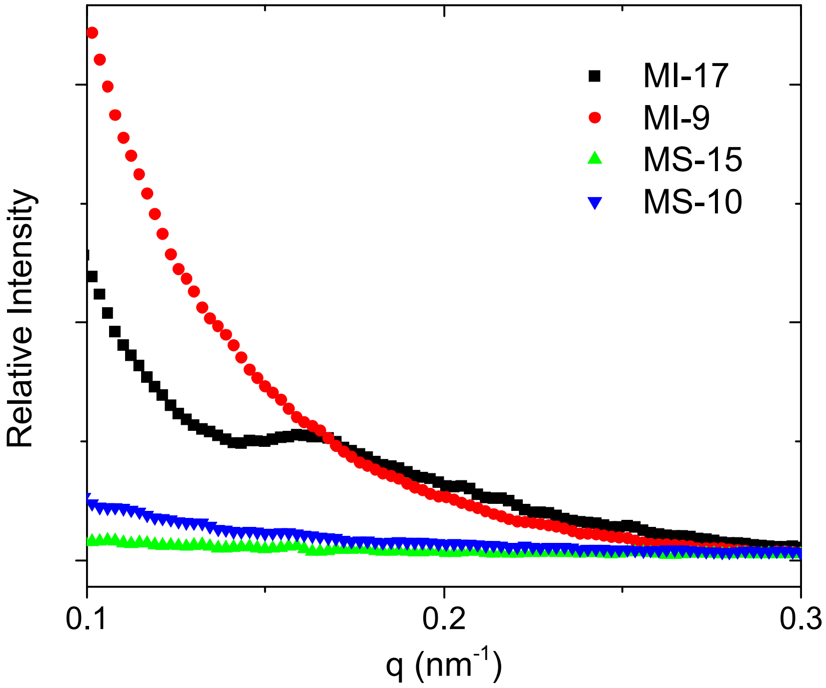
In context of Doolittle-Cohen free volume theory, $B = \frac{f^*}{\alpha_f}$ ← thermal expansion coefficient

and since chemical structure of MI ≈ M+S,

free volume required for ionic hop $f^*_{MI} / f^*_{M+S} \approx 1.5$

Structural evidence

- Small angle x-ray scattering (SAXS)
  - "Ionomer scattering peak" for MI-17 (d_{avg} = 39 nm)
  - Strong low-*q* upturn for both ionomers, indicating long-range spatial inhomogeneity in ionic arrangement[1,2]



[1] Li, Peiffer, Chu *Macrom* 1993

[2] Grady et al. *Macrom* 1993

Conclusions

a) σ and μ highly dependent on polymer segmental motion, demonstrated by scaling with $T - \Delta T_g$

b) $\mu^{M+S} / \mu^{MI} \approx 10$

c) $f^*_{MI} / f^*_{M+S} \approx 1.5$

d) $p_0^{M+S} / p_0^{MI} \approx 10$

e) $E_a^{MI} / E_a^{M+S} \approx 1.4$

f) Ion clustering in MI but not M+S

Since chemical make-up of MI and M+S are identical with exception of fixed position of anion

→ Location of the anion in the polymer matrix has a crucial effect on both

- μ, which is dynamically restricted by the presence of ionic clusters and enhanced by the diffusion of anions
- p_0, which is sensitive to the local coordination environment

Acknowledgments

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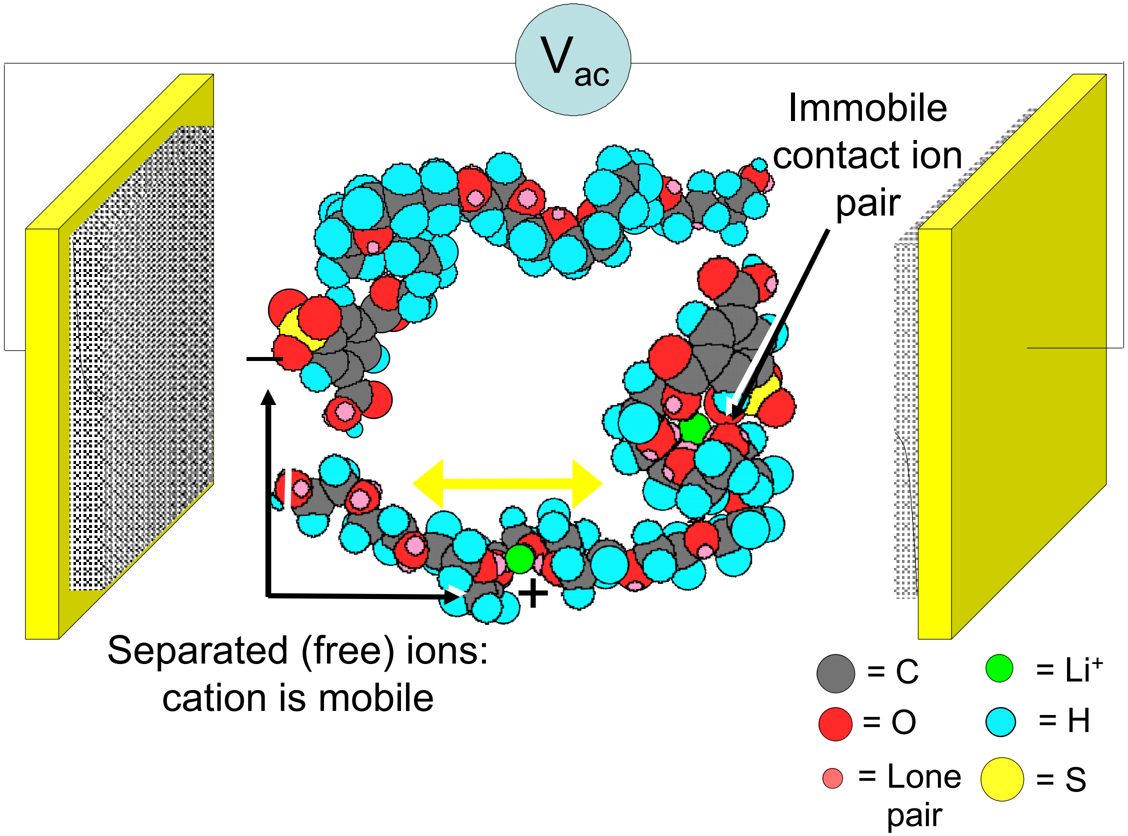
Electrode polarization of ionomer

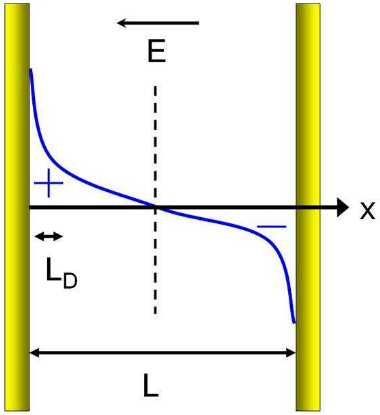
- Electrode polarization ≡ macroscopic relaxation created by ions crossing sample thickness and creating concentration gradient near blocking electrodes



Immobile contact ion pair

Separated (free) ions: cation is mobile

MacDonald-Coelho model



Models electrode polarization by:

- Blocking electrodes
- Neglected ion generation and recombination
- Assumes anions are relatively immobile
- First order in V, p, and E
- Utilizes Poisson's and Einstein relations
- Relates V, p, E, τ, ε^*,ε, P, L, and L_D as complex functions of ω

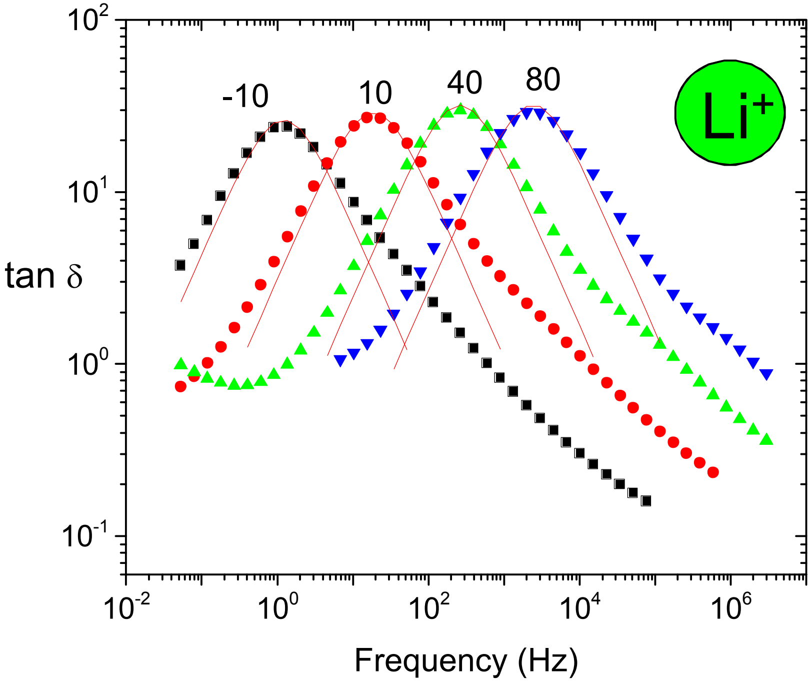
  (voltage, cation conc., electric field, relaxation time, matrix dielectric constant, complex dielectric constant, polarization, thickness, Debye length, radial frequency)

Reduces to a simple relationship for EP based on physical geometry, mobility of mobile ions, and number of mobile ions

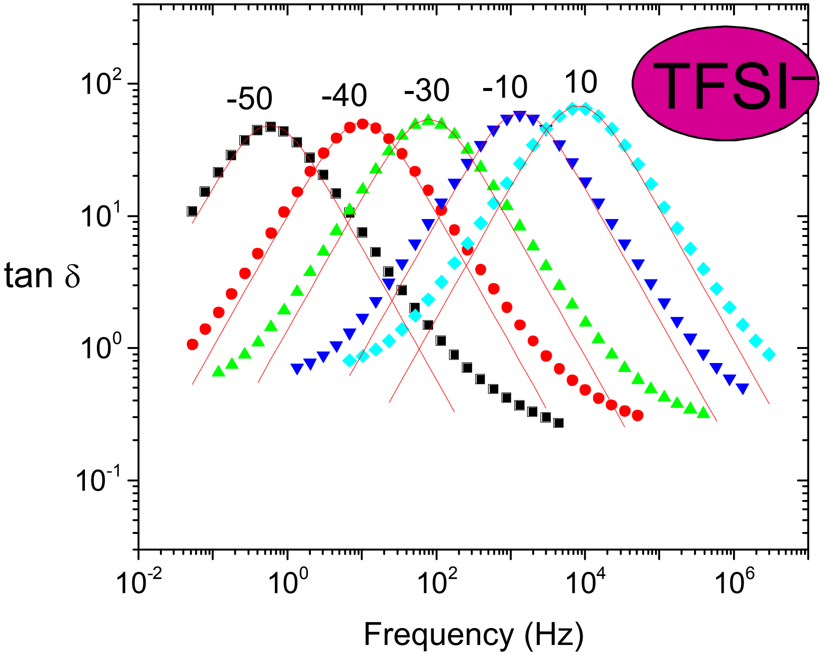
MacDonald *Phys Rev* 1953
Coelho *Rev Phys Appl* 1983
Coelho *J Non-Cryst Solids* 1991

Analysis of electrode polarization

- Fit tan δ (*f*) with EP model: $$\tan\delta = \frac{2\pi f \tau_{EP}}{1+(2\pi f \tau_{EP})^2/M}$$



MI-9



M+S-10

Anion in M+S

- Narrow, unimodal EP peak indicates $\mu_+ = \mu_-$ or $\mu_+ << \mu_-$ or $\mu_+ >> \mu_-$
- Conclude $\mu_+ << \mu_-$ based on:
  - Transference number[1] of Li^+ in PEO:LiTFSI = 0.11, or $\mu_- / \mu_+ = 8$

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

  - Anion in polymer electrolytes often measured to diffuse more quickly[2-3]

[1] Kato et al. *Electro Acta* 2004

[2] Yoshizawa et al. *Electro Acta* 2000

[3] Bando et al. *J Electrochem Soc* 2004

Inductions

- Anion moves significantly faster than cation, supported by refs 1-3
- EO-coordinated Li^+ requires more free volume for diffusion than $TFSI^–$
- "Origin" of ion pairs crucial to conductivity
  - Ionomeric cations originating near EO blocks were shown to be 10 to 100 times less conductive than those originating near a non-conductive block [4,5]
- Inhomogeneous spatial distribution of ions observed for ionomers, but not doped polymer
  - Somewhat counterintuitive, since ion pairs in M+S are simply solvated, but ion pairs in MI are randomly fixed along the chain
- Location of the ion pairs in the polymer matrix has a crucial effect on both
  - μ, which is dynamically restricted by the presence of ionic clusters
  - p_0, which is sensitive to the local coordination environment

[4] Sadoway et al. *J Power Sources* 2001
[5] Ryu et al. J Electrochem Soc 2005

[1] Kato et al. *Electro Acta* 2004
[2] Yoshizawa et al. *Electro Acta* 2000
[3] Bando et al. *J Electrochem Soc* 2004