Recycled & updated

Idea Series

Simulations of materials – focusing on electrolytes for all solid state batteries

Contribution from: Natalie Holzwarth
Department of Physics

Acknowledgements:

Hannah Zhang and Zachary Pipkorn (former WFU undergrads)
Zachary Hood (WFU chemistry alum, Ga Tech Ph. D)
Jason Howard, Ahmad Al-Qawasmeh, Larry E. Rush, and Nicholas Lepley (current and former WFU grad students)
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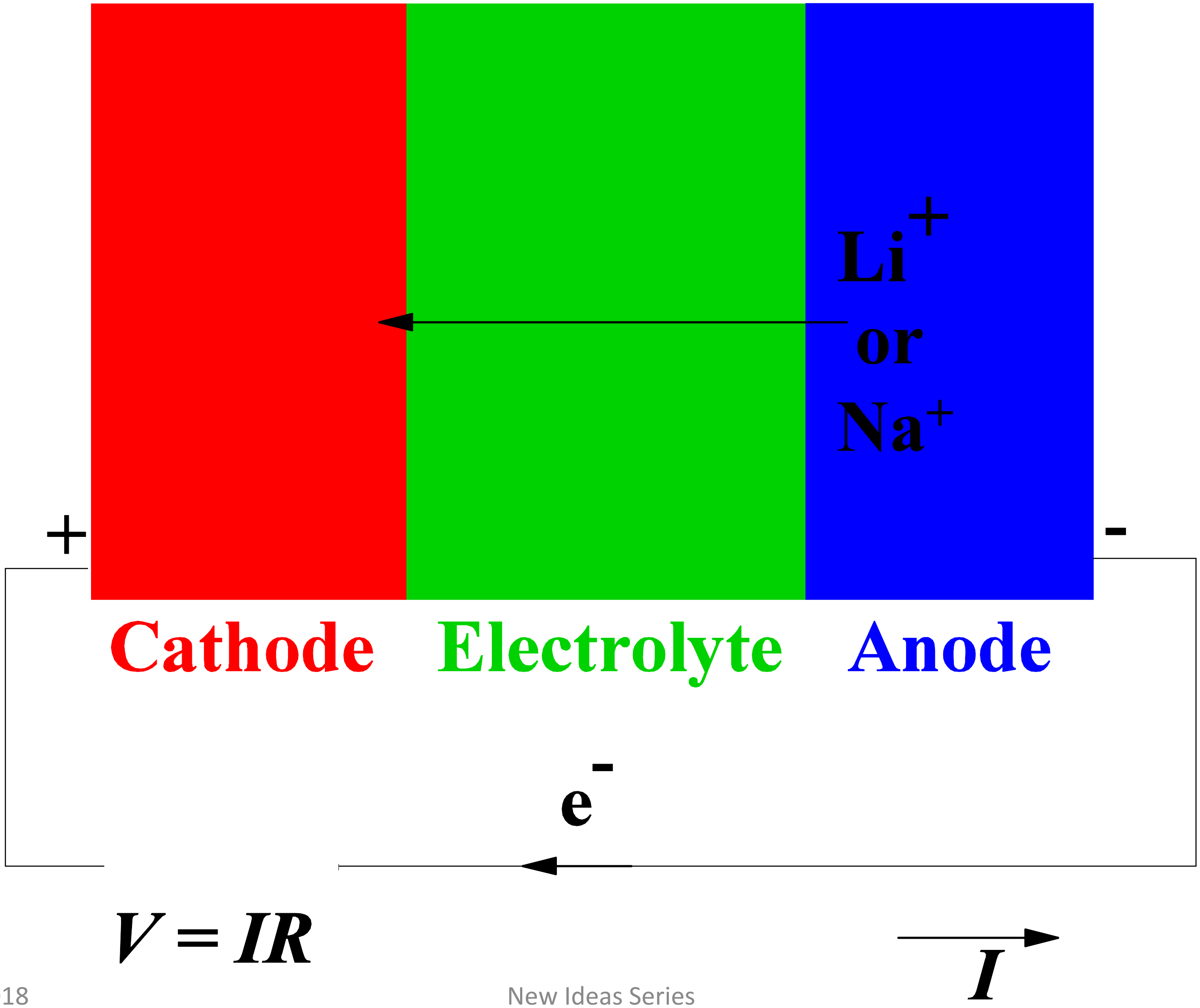
Materials components of a Li or Na ion battery



Development of LiPON electrolyte films at Oak Ridge National Laboratory

WAKE FOREST
UNIVERSITY

SOLID
STATE
IONICS

Solid State Ionics 53–56 (1992) 655–661
North-Holland

Sputtering of lithium compounds for preparation of electrolyte thin films

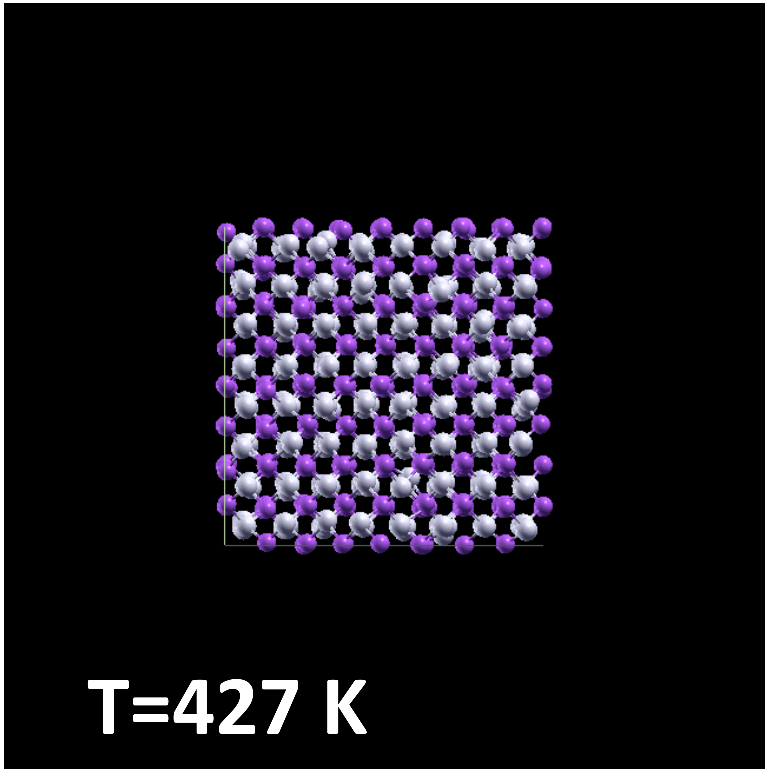
N.J. Dudney, J.B. Bates, R.A. Zuhr and C.F. Luck

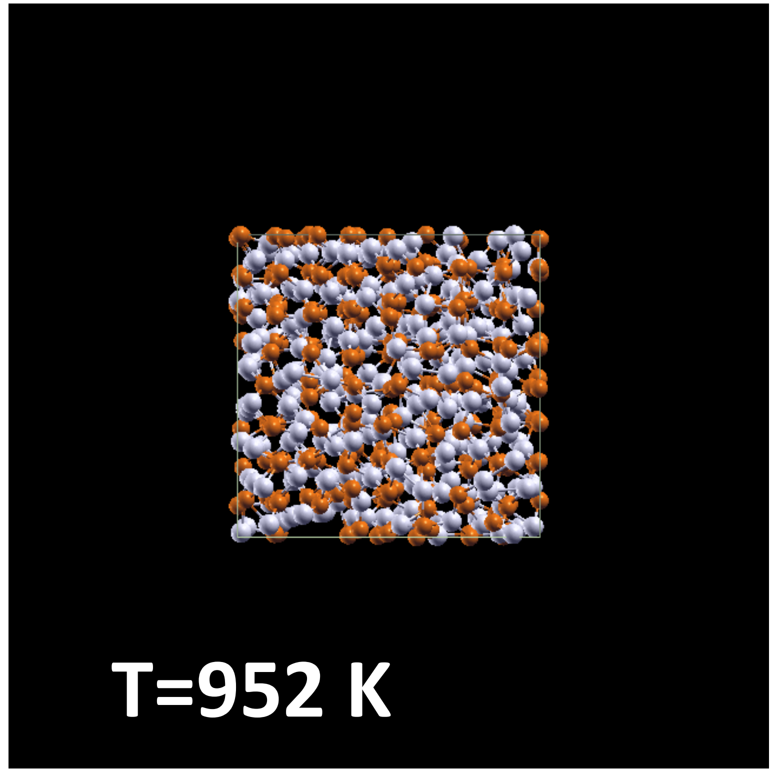
JOURNAL OF SOLID STATE CHEMISTRY 115, 313–323 (1995)

Synthesis, Crystal Structure, and Ionic Conductivity of a Polycrystalline Lithium Phosphorus Oxynitride with the γ-Li_3PO_4 Structure

B. Wang, B. C. Chakoumakos, B. C. Sales, B. S. Kwak, and J. B. Bates

Simulations of ions in electrolyte crystals at two different temperatures.

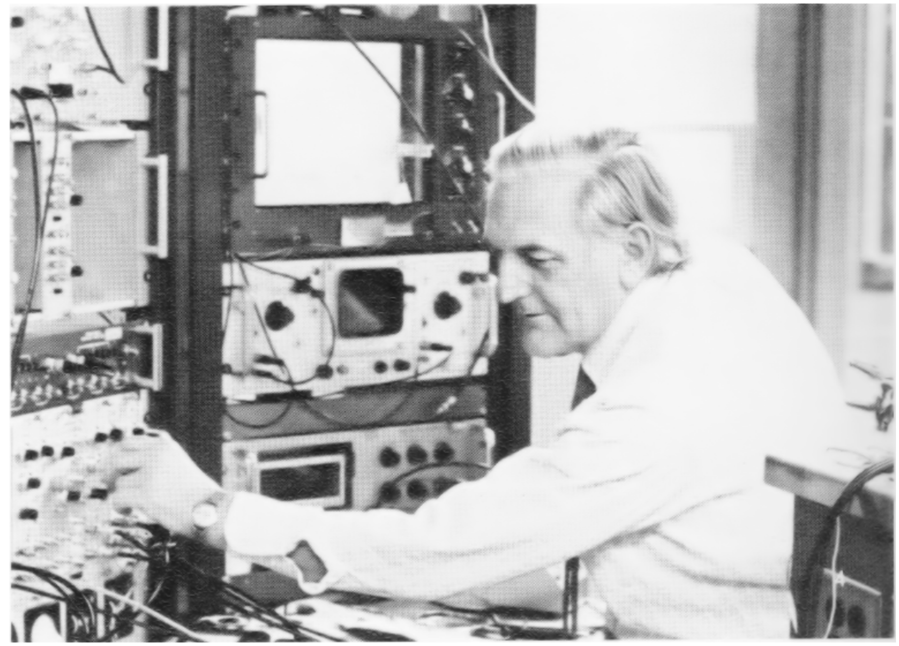




Molecular dynamics simulations of AgI prepared by Zachary Pipkorn in 2015.

Ysbrand Haven – WFU Physics Professor 1965-1983

1975 Howler photo of Professor Haven with his conductivity equipment.



Studied ionic conductivity in well-controlled crystalline samples as a function of temperature, to develop models of basic mechanisms and their relationship to diffusion.

Ionic conductivity in LiI (single crystal form)

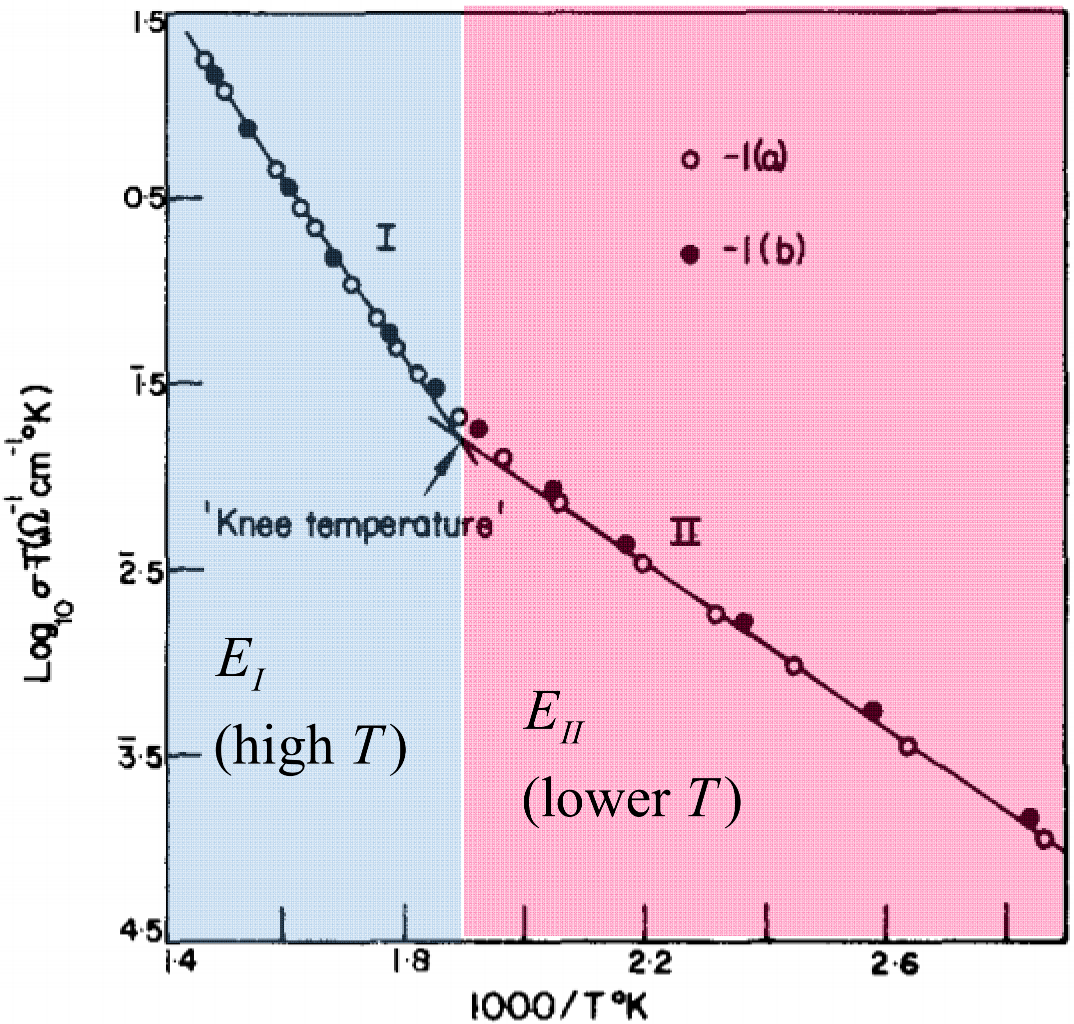


Fig. 2. The intrinsic (I) and extrinsic (II) regions of the ionic conductivity plot for two specimens of as-grown material.

B. J. H. Jackson and D. A. Young, J. Phys. Chem. Solids 30, 1973-1976 (1969)

$$\sigma = \frac{K_I}{T} e^{-E_I/k_B T} + \frac{K_{II}}{T} e^{-E_{II}/k_B T}$$

***E**$_I$* **and** ***E**$_{II}$* **are "activation" energies, characteristic of the hopping processes.**

Relationship between ionic conductivity and diffusion

From statistical mechanics

(Nernst-Einstein relation)

$$\sigma = \frac{N}{V}\frac{q^2}{k_B T} D^{(\mathrm{all})}$$

$$= \frac{1}{H_r}\frac{N}{V}\frac{q^2}{k_B T} D^{(\mathrm{tracer})}$$

Haven ratio: $H_r = \dfrac{D^{(\mathrm{tracer})}}{D^{(\mathrm{all})}}$

Key:

$\sigma \equiv$ DC electrical conductivity

$D \equiv$ Diffusion coefficient

$\frac{N}{V} \equiv$ #mobile ions per unit volume

$q \equiv$ charge of mobile ions

$k_B \equiv$ Boltzmann constant

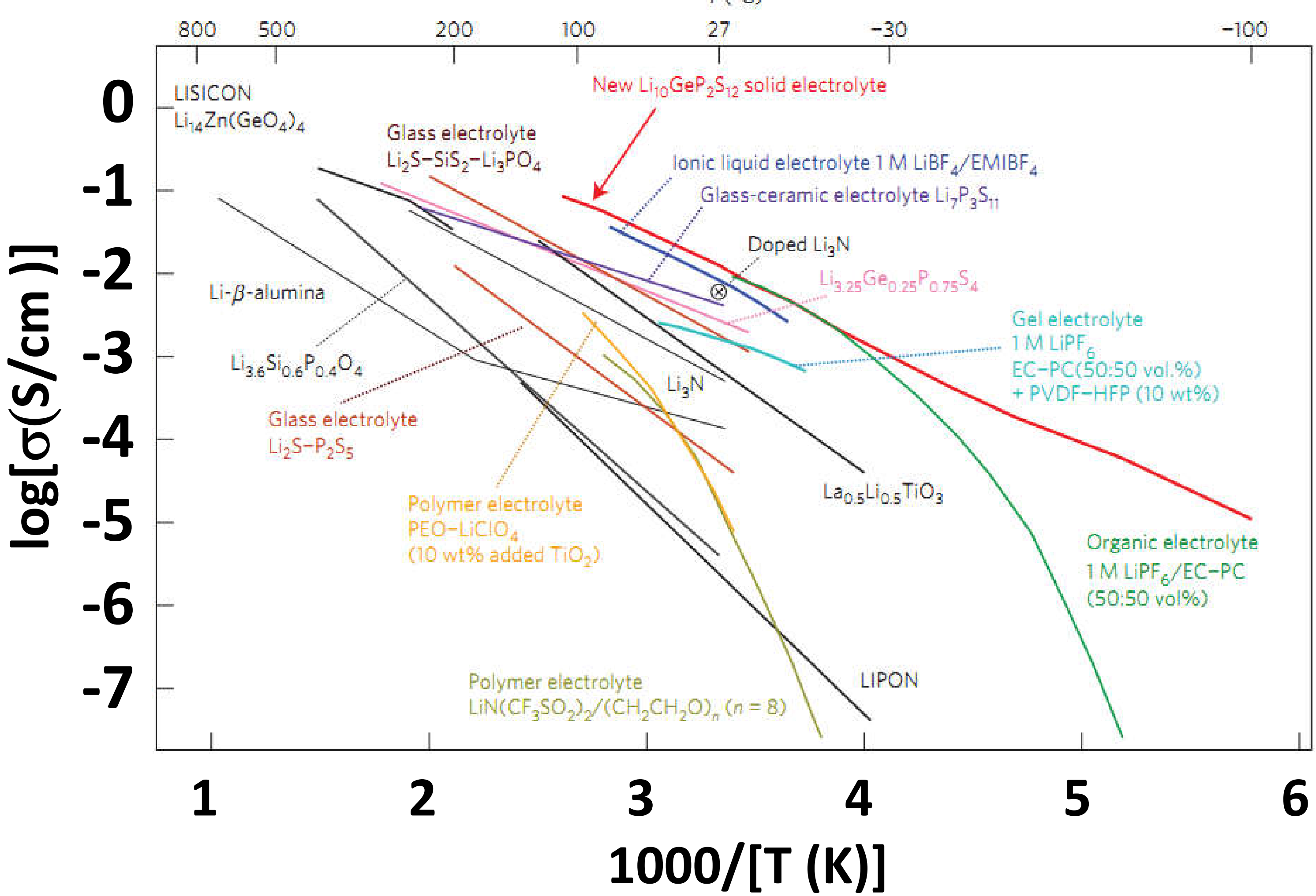
$T \equiv$ temperature in Kelvin

$D^{(\mathrm{tracer})}$: can be measured using nuclear isotopes; represents independent particle motions **accessible by computation**

$D^{(\mathrm{all})}$: measured from the conductivity; includes correlated motions of mobile ions **very difficult to compute**

Recent ionic conductors: --

Paper by N. Kayama, *et. al* in ***Nature Materials* 10**, 682-686 (2011)



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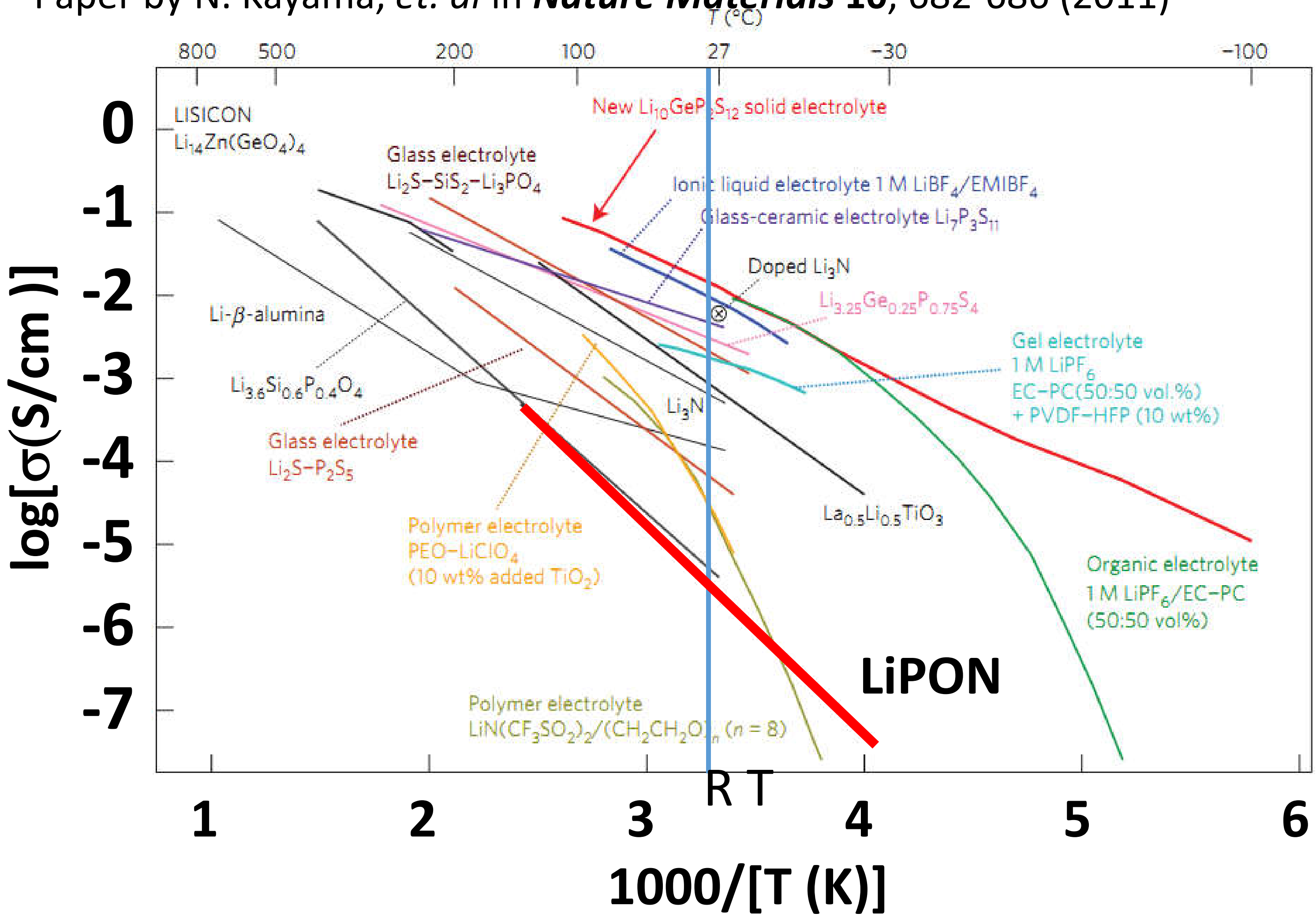

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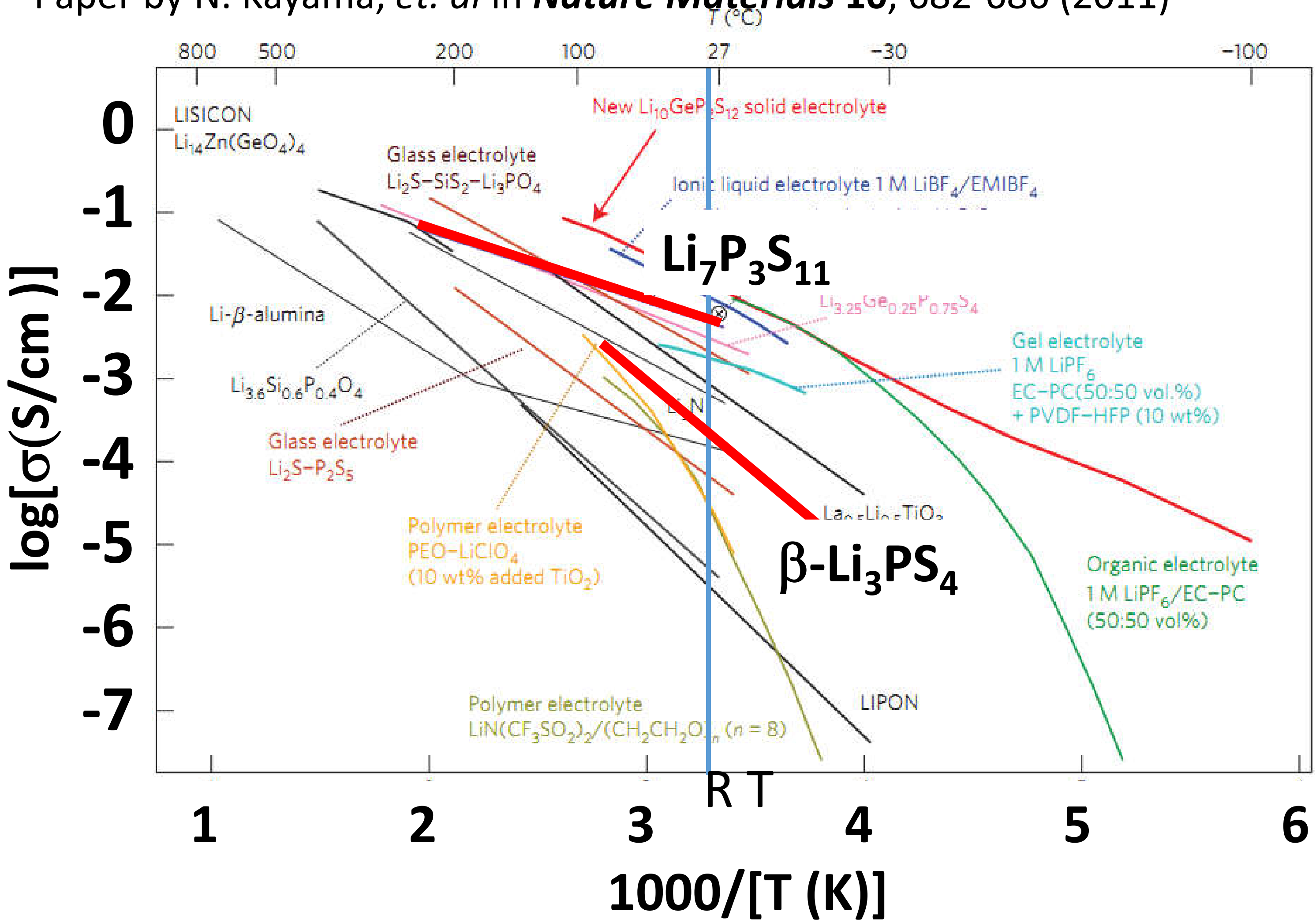

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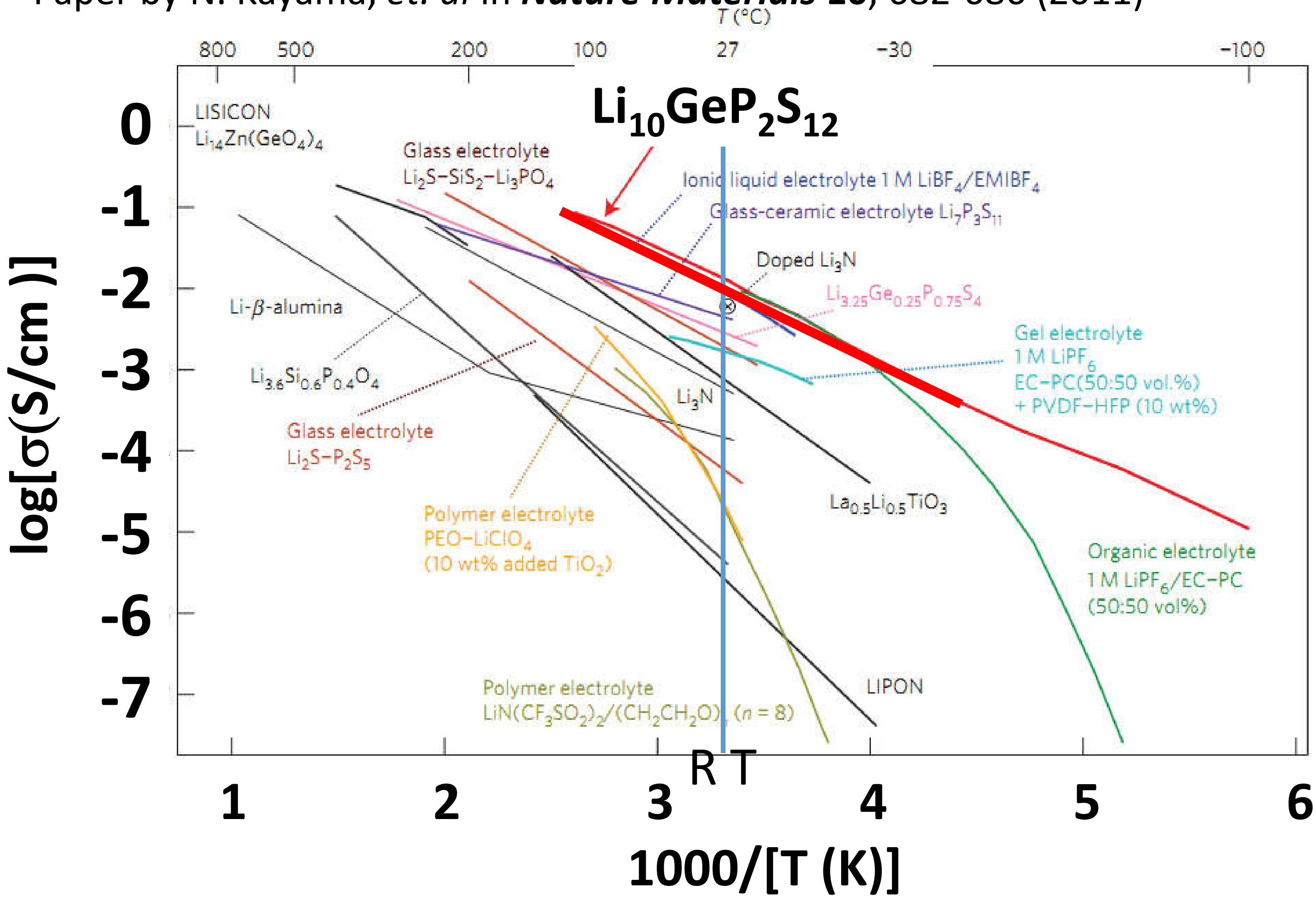
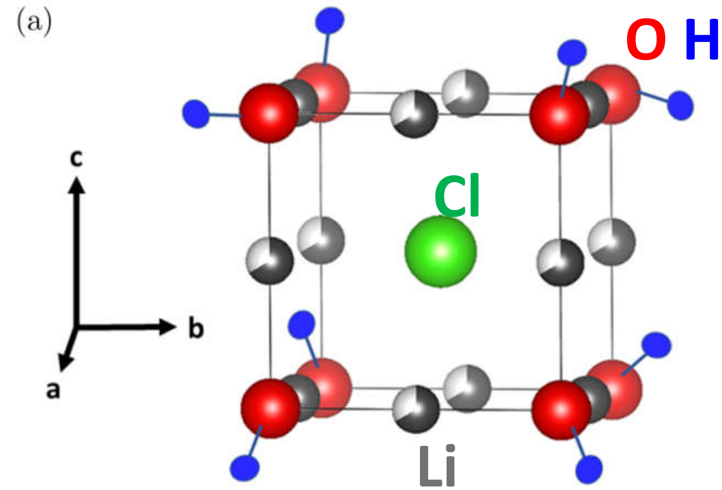
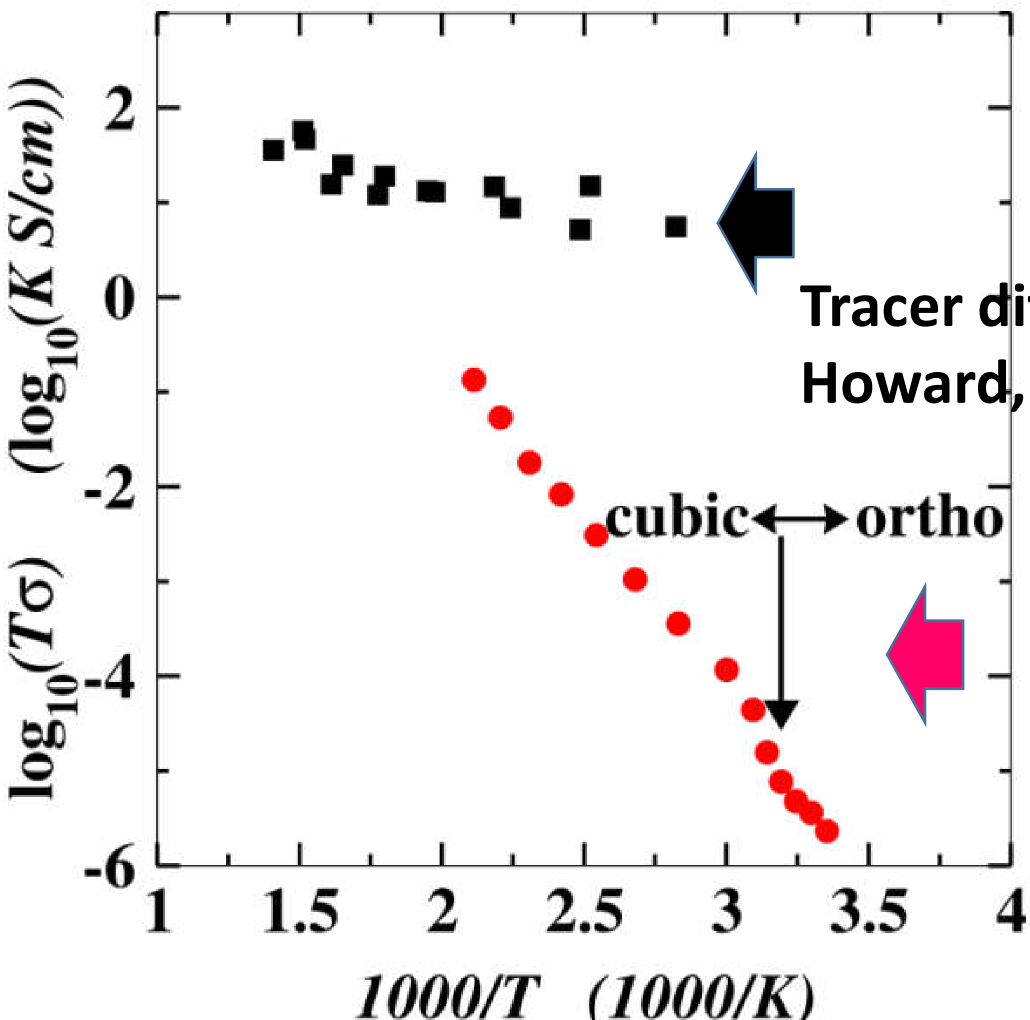


Research from Toyota Motor Company

Ionic conductivity in Li_2OHCl from Howard & co-workers, PRM 1, 075406 (2018)





Tracer diffusion simulations by Jason Howard, suggesting that H_r>>1

Experimental measurements by Zach Hood