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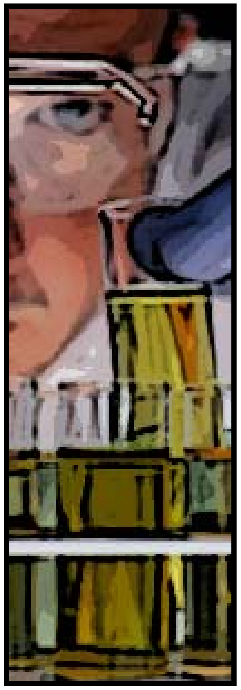

Ionic Liquids, Lithium Salts, Solvents and Water: Phase Behavior and Molecular Interactions

Wesley Henderson

Ionic Liquids & Electrolytes for Energy Technologies (ILEET) Laboratory
Department of Chemical & Biomolecular Engineering
NC State University

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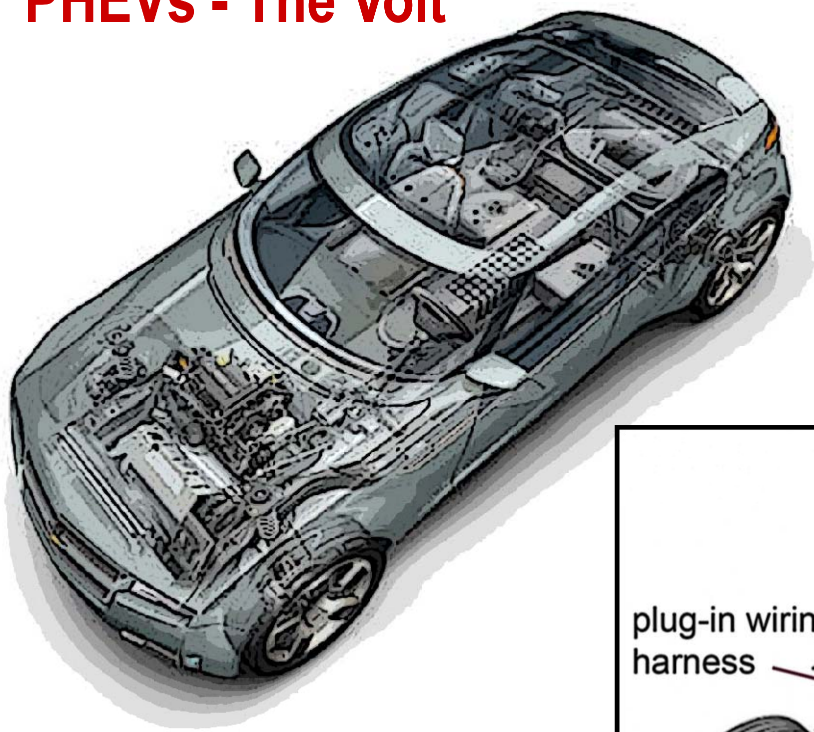
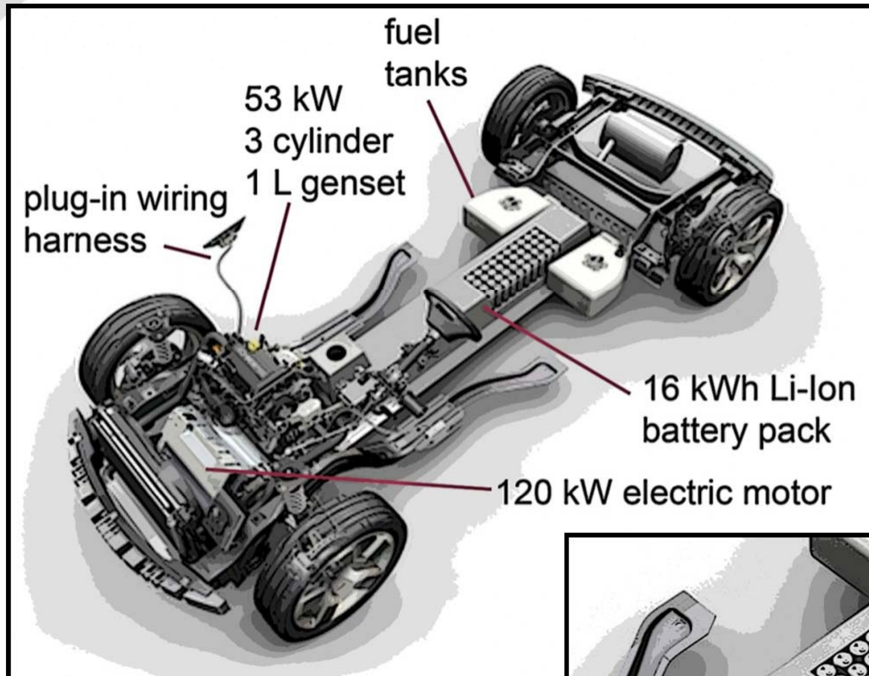
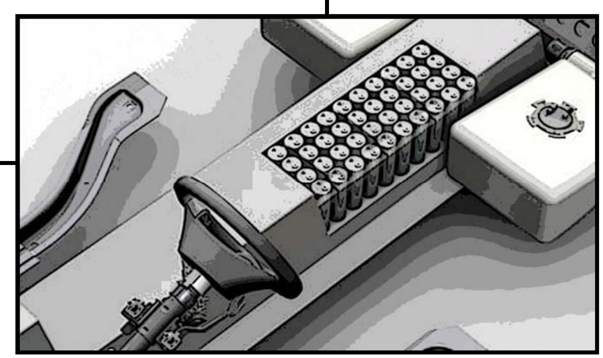
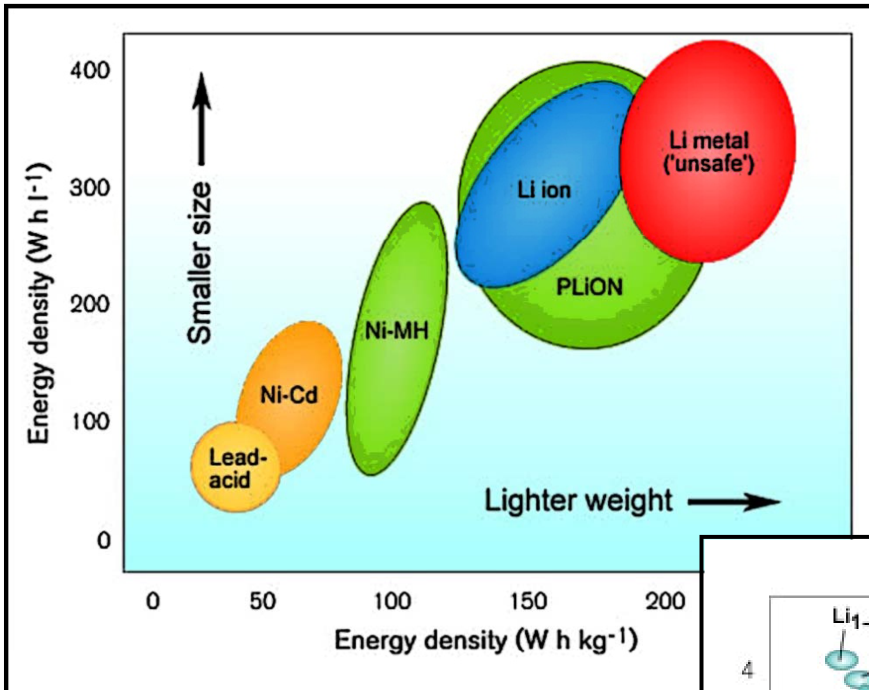
PHEVs - The Volt



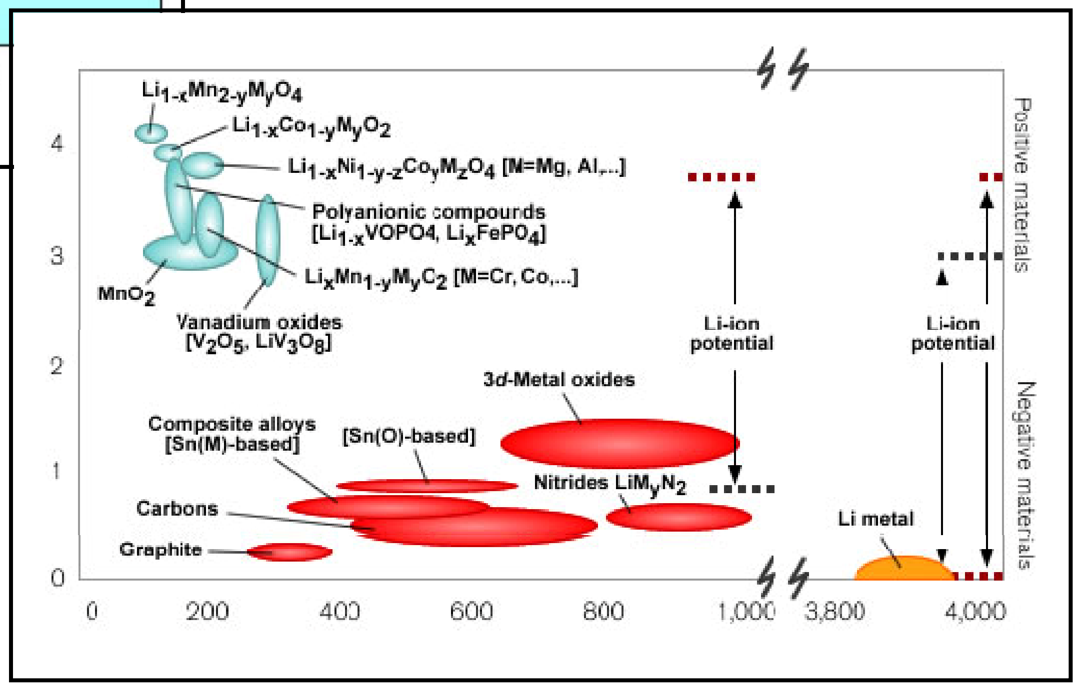




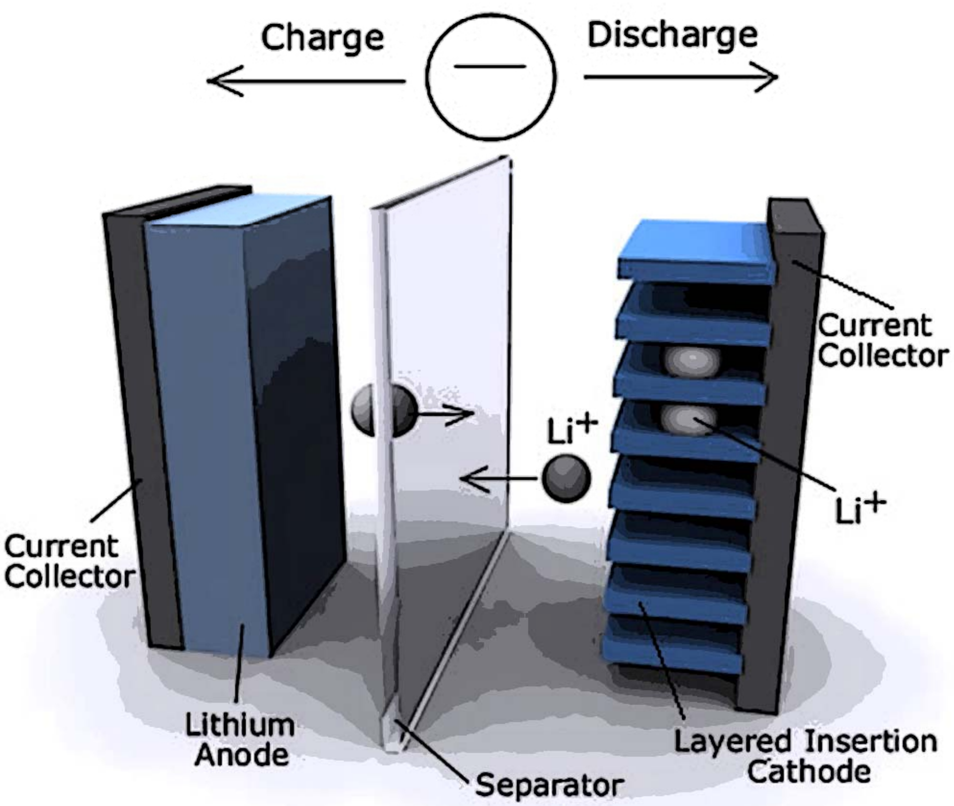
Higher Energy Density Electrodes



Source: http://www.superlatticepower.com/intro.html



Batteries: Better Electrolytes Needed...



- high Li^+ conductivity
- necessary electrochemical stability
- stable with current collectors
- low volatility
- low flammability
- nontoxic
- low cost

Ionic Liquids –
What They Are…And Are Not...

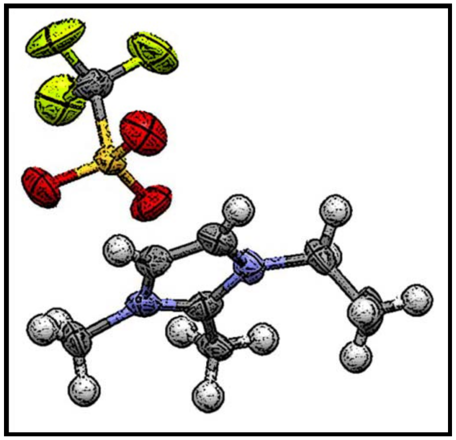
Ionic Liquids (ILs)

Salts, or mixtures of salts (**composed solely of ions**), which are liquids at low temperatures (< 100°C) - often below RT

weak ion coordination & poor packing of the ions…

…typically the cation is organic and anion is inorganic

charge delocalization, steric hindrance & asymmetry



- potentially thousands – millions ILs
- liquid range over 300°C
- hydrophilic or **hydrophobic**
- **outstanding solvents** – inorganic, organic and polymeric materials - readily dissolve H^+X^-, Li^+X^-, etc.
- **high thermally stability**
- **nonvolatile** and **inflammable**
- **high ionic conductivity**
- **high electrochemical stability**

advanced batteries

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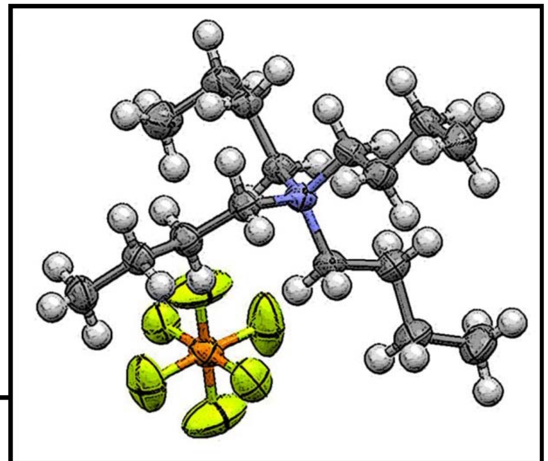
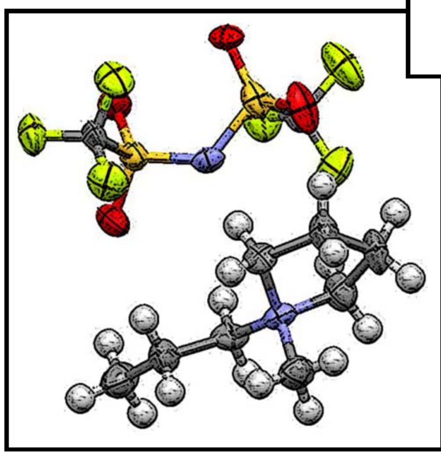
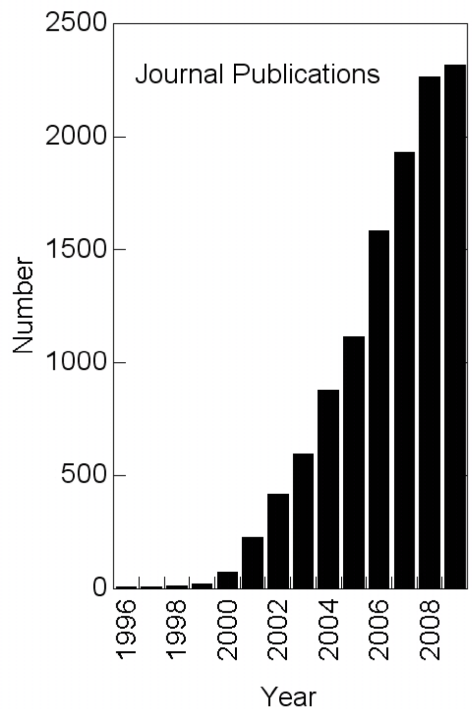
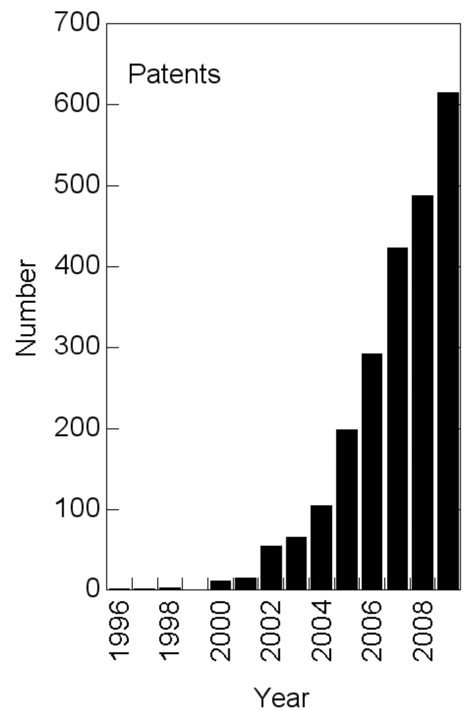
Interest in ILs Has Grown Rapidly

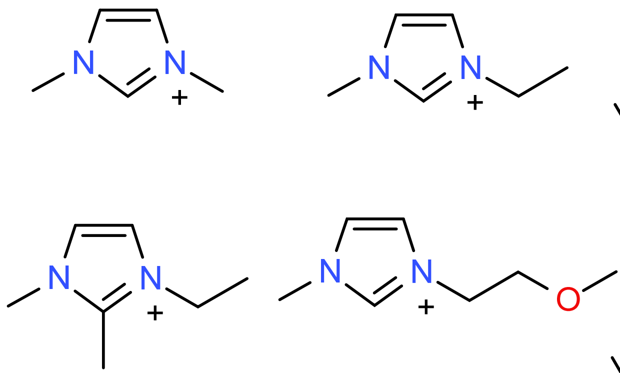


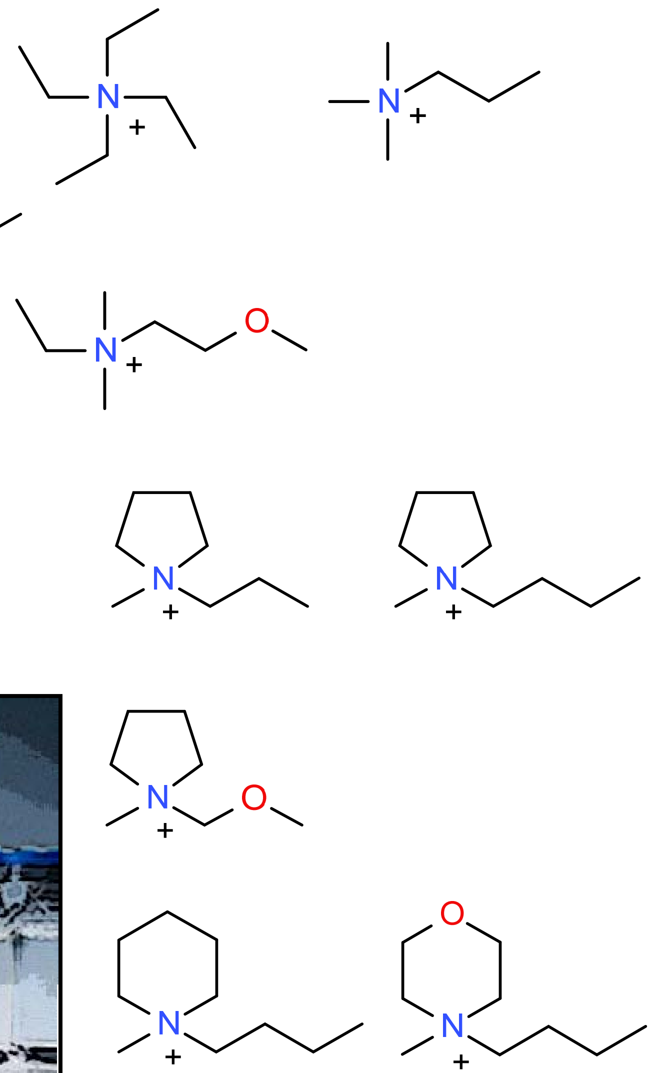


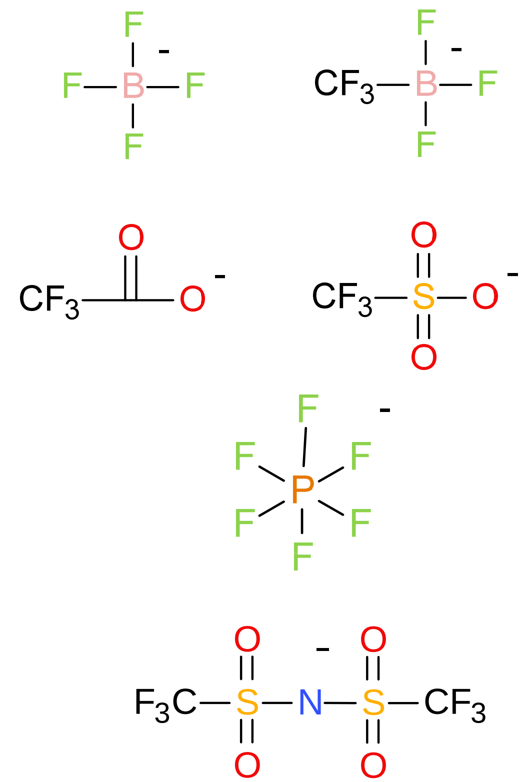




Choice of Ions







Solid-State
Lithium Metal-Polymer Electrolyte
Batteries

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A "Facile Fix" for Polymer Electrolytes

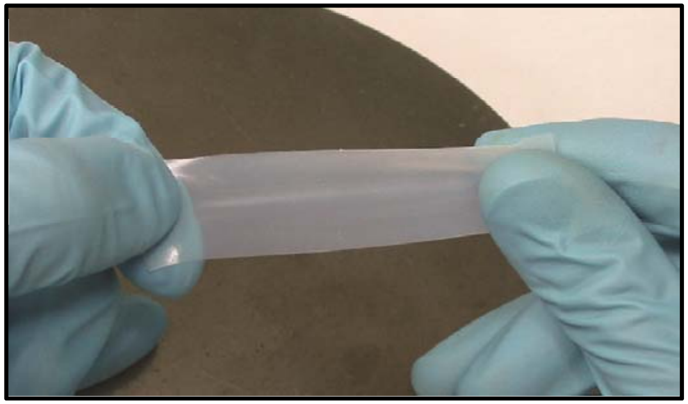
ENEA

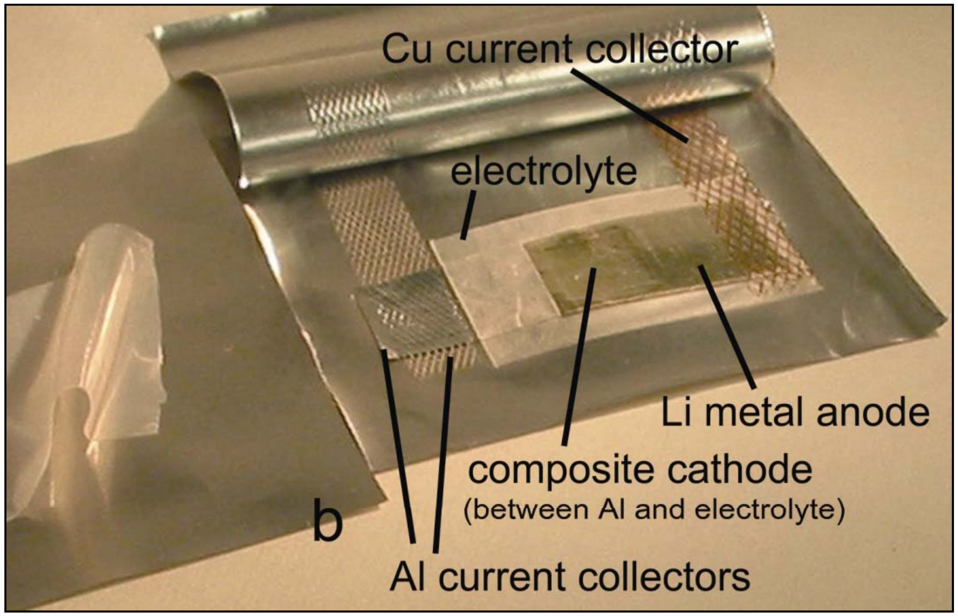
ENTE PER LE NUOVE TECNOLOGIE, L'ENERGIA E L'AMBIENTE

Italian National Agency for New Technologies, Energy and the Environment

$P(EO)_n$-LiTFSI

\+ ionic liquid





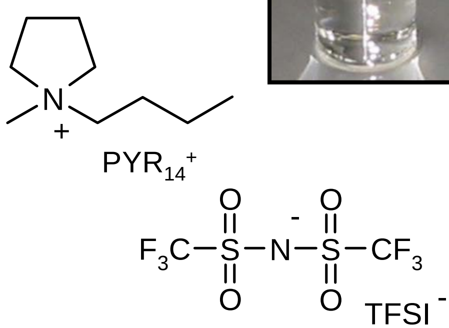
- improved conductivity
- excellent thermal & electrochem. stability
- no volatile components
- tacky, but high mechanical strength
- properties do not change w/ time

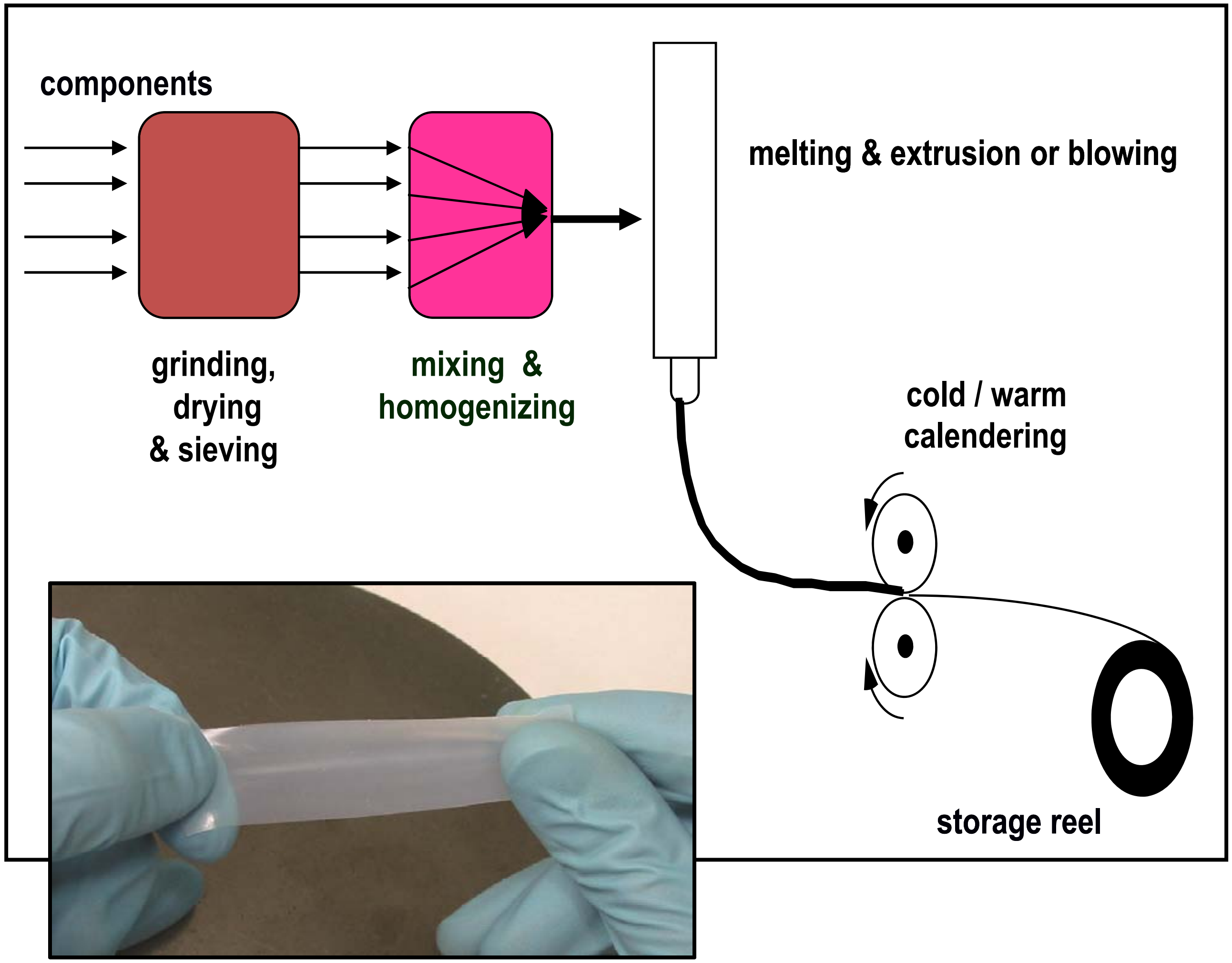
Solid Electrolyte Preparation (No Solvent!)

poly(ethylene oxide) (PEO)

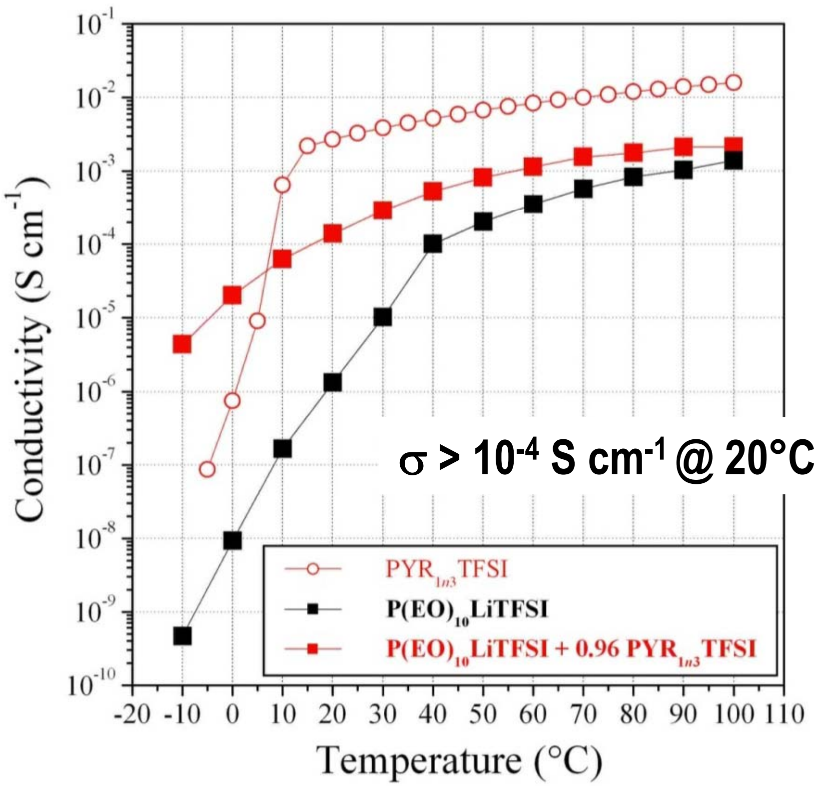
lithium salt (LiX)

IL

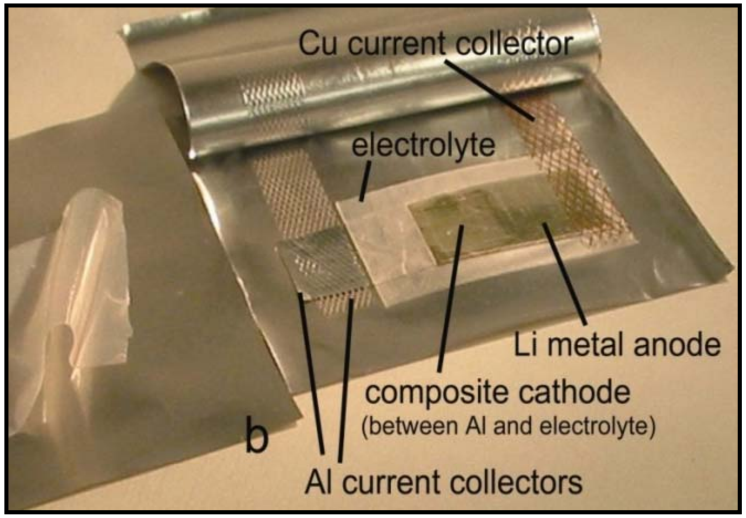




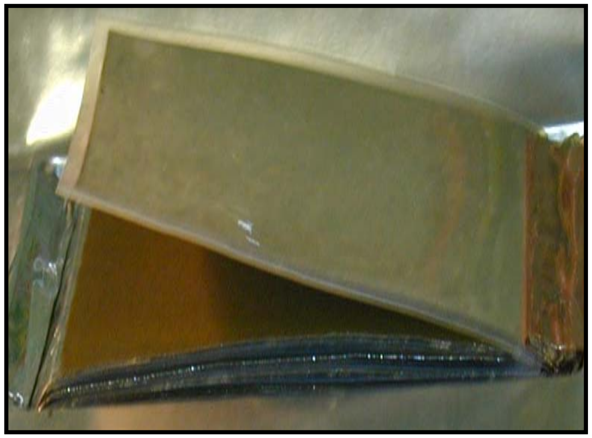
Ionic Conductivity & Solid-State Lithium Batteries



$\sigma > 10^{-4}$ S cm^{-1} @ 20°C



vacuum-sealed, laminated, solid-state cells



0.6 Ah lithium - polymer electrolyte battery prototype

Shin et al. Electrochem. Commun. 2003, 5, 1016
Shin et al. Electrochem. Solid-State Lett. 2005, 8, A125
Shin et al. J. Electrochem. Soc. 2005, 152, A978
Shin et al. Electrochim. Acta. 2005, 50, 3859
Shin et al. J. Power Sources. 2006, 156, 560
Shin et al. J. Electrochem. Soc. 2006, 153, A1649

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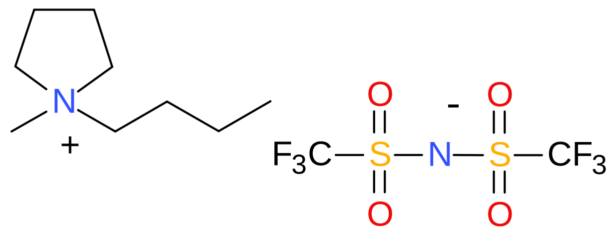
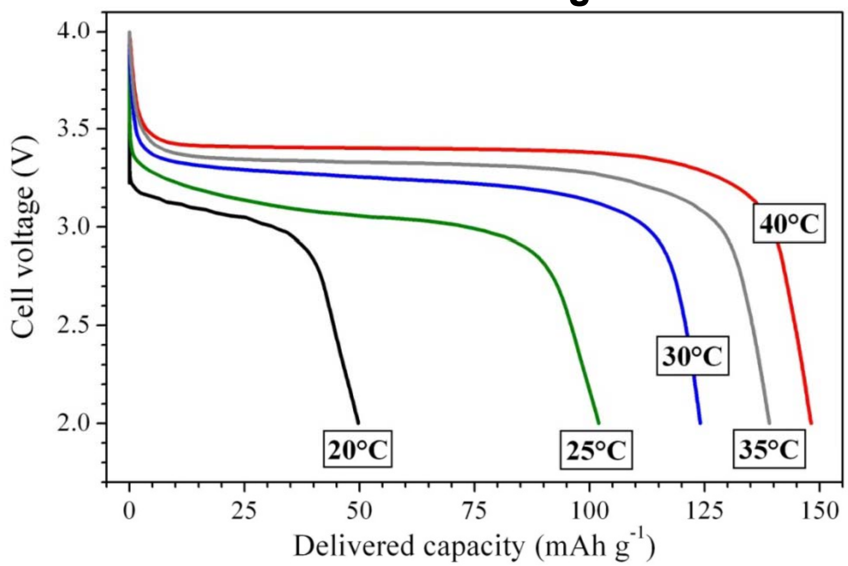
'Low' Temperature Battery Testing

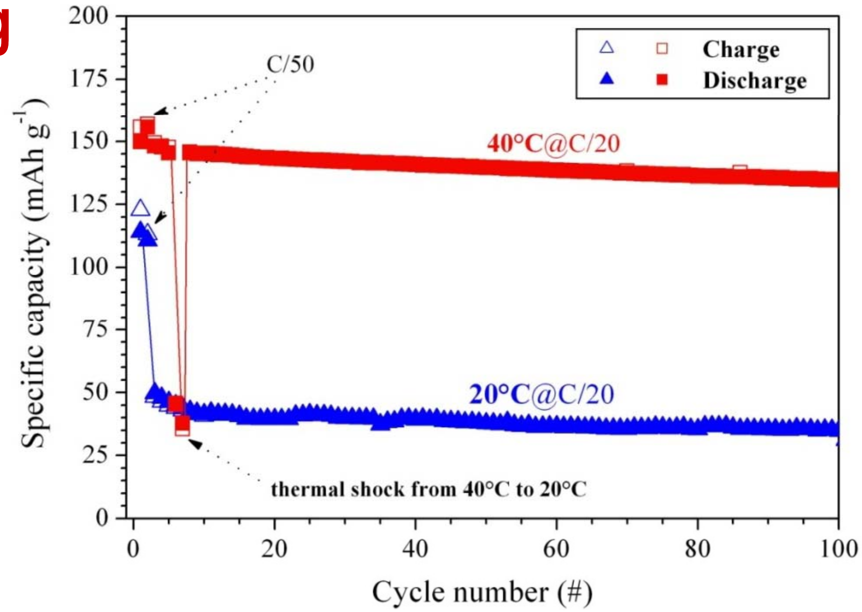


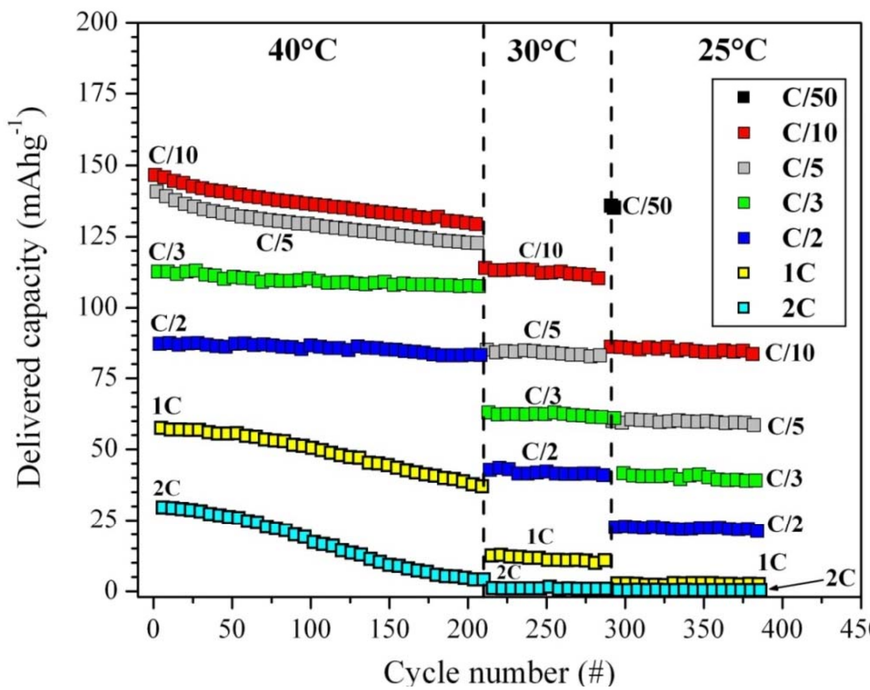
$Li/P(EO)_{10}LiTFSI + 0.96\ PYR_{14}TFSI/LiFePO_4$

C/20 discharge rate

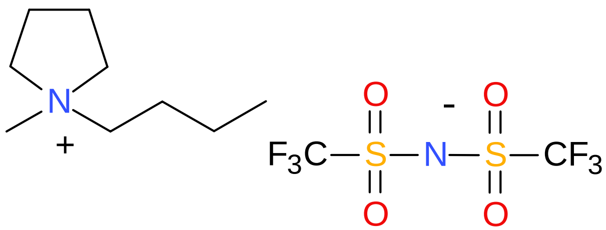


Kim et al. J. Power Sources 2007, 171, 861



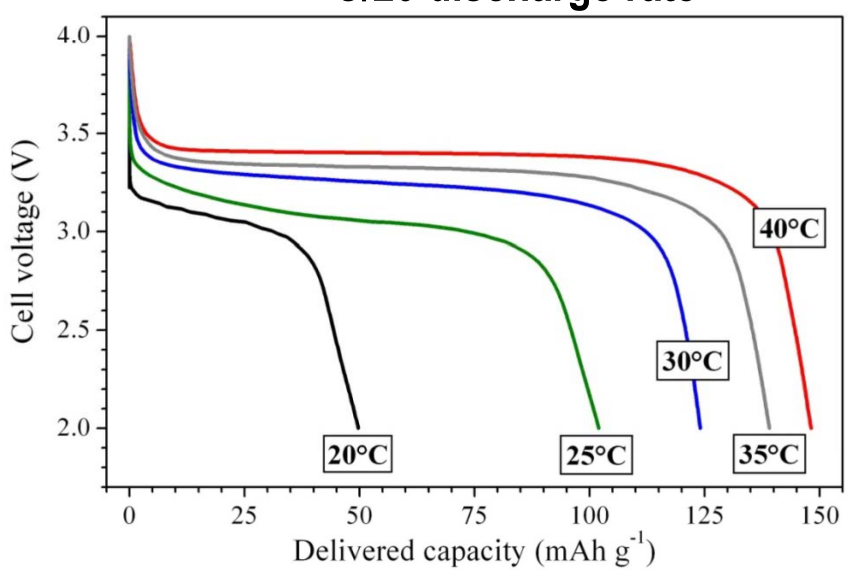


Performance & Ionic Conductivity

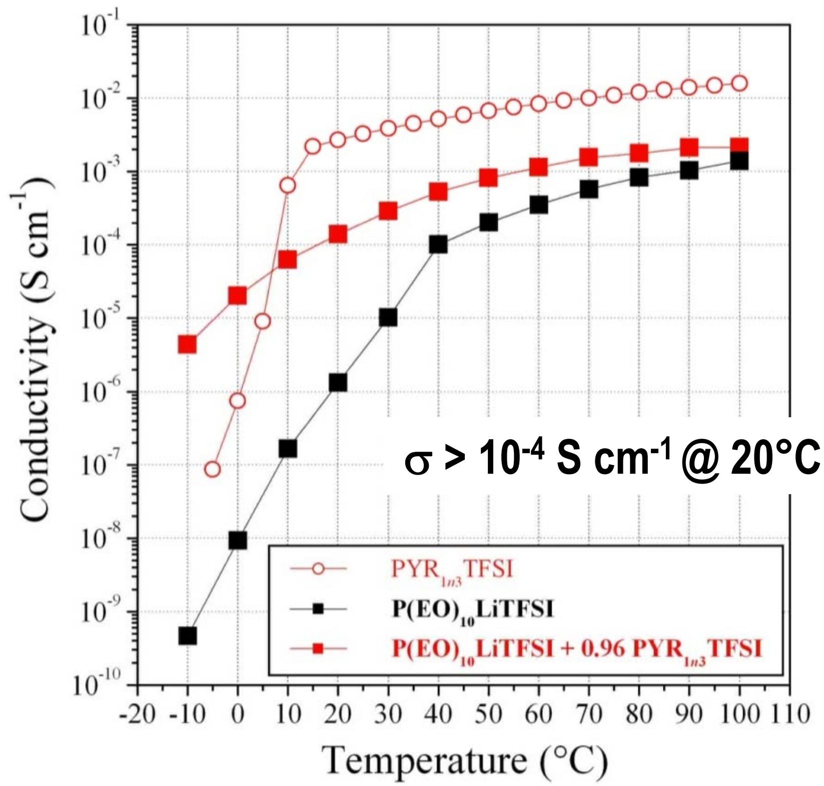


Li/P(EO)$_{10}$LiTFSI + 0.96 PYR$_{14}$TFSI/LiFePO$_4$

C/20 discharge rate



Kim et al. J. Power Sources 2007, 171, 861



σ > 10^{-4} S cm^{-1} @ 20°C

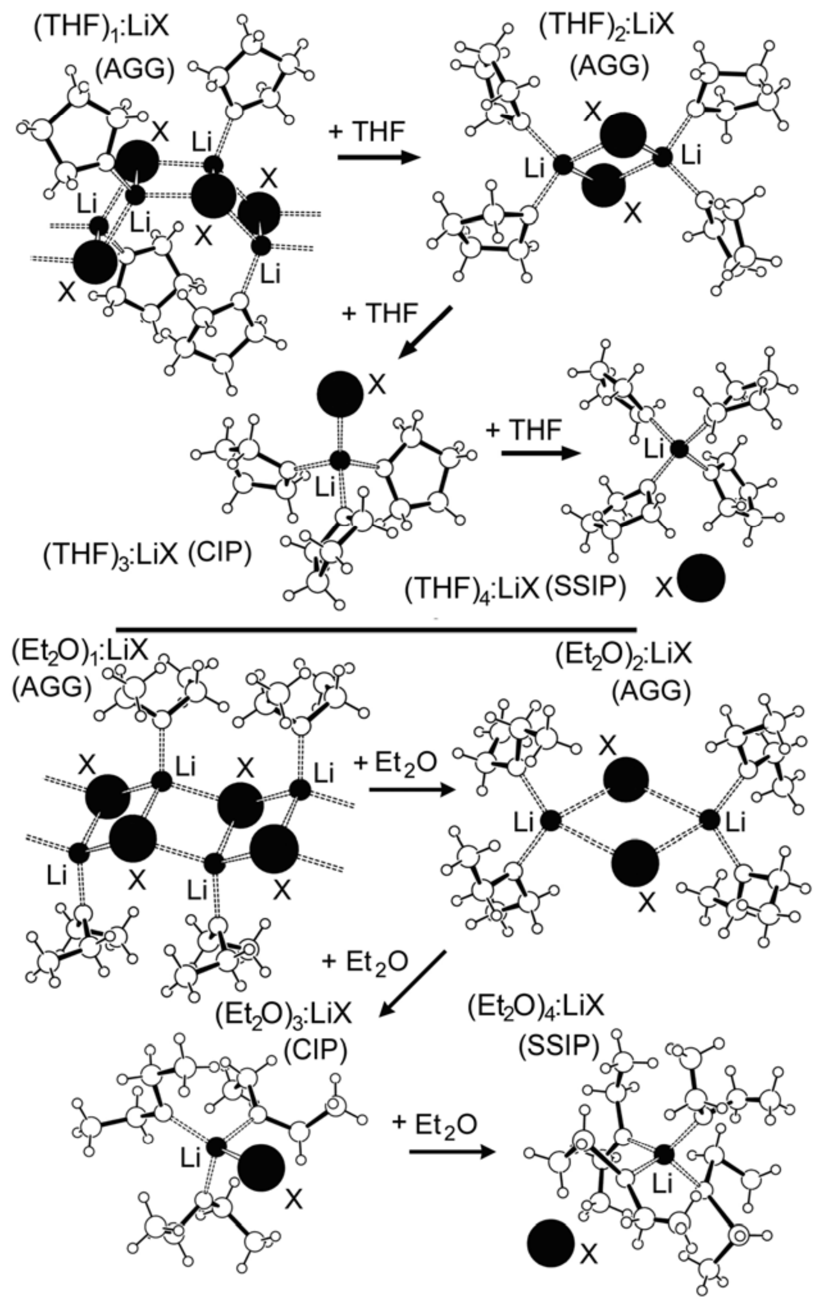
Structure in Ionic Liquids – Solvation & Coordination

Ionic Association

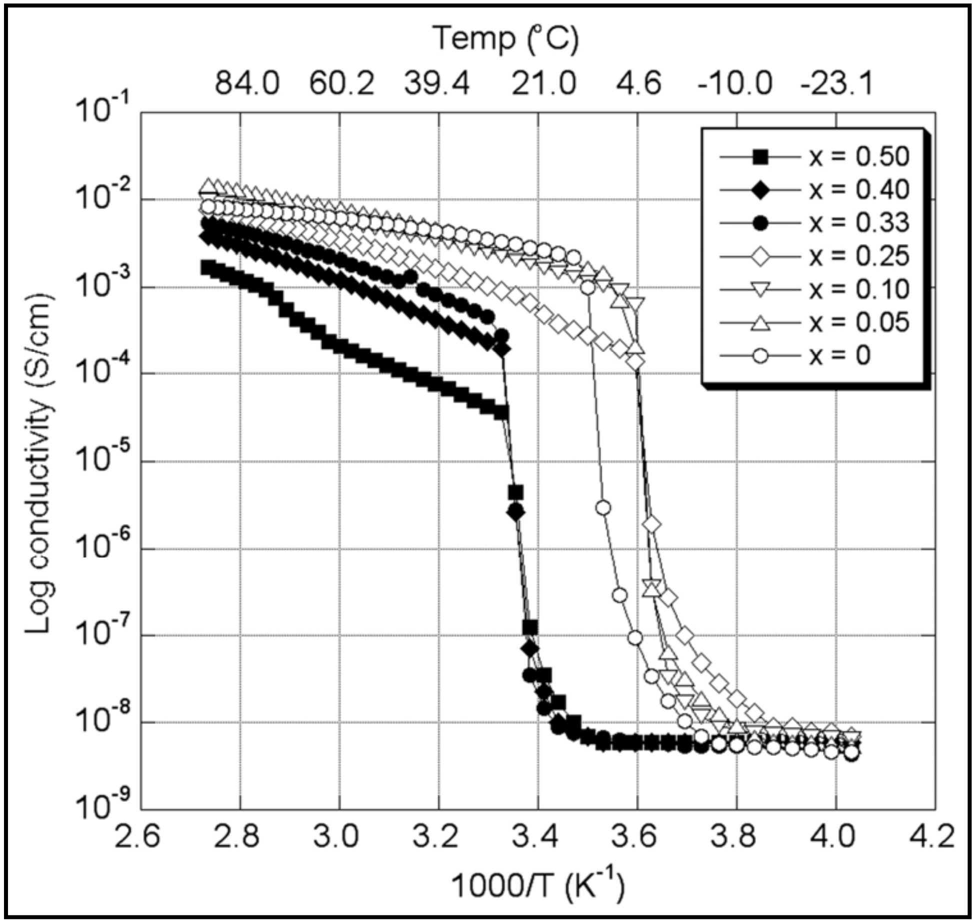
- **Solvent-Separated Ion Pairs (SSIPs)**
  (uncoordinated anions)

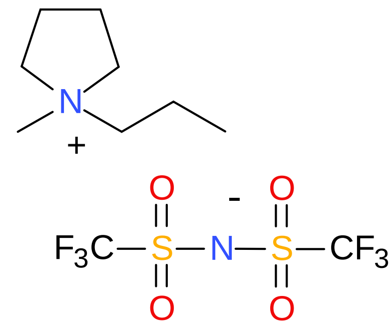
- **Contact Ion Pairs (CIPs)**
  (anion coordinated to 1 Li^+)

- **Aggregates (AGGs)**
  (anion coordinated to 2 or more Li^+)



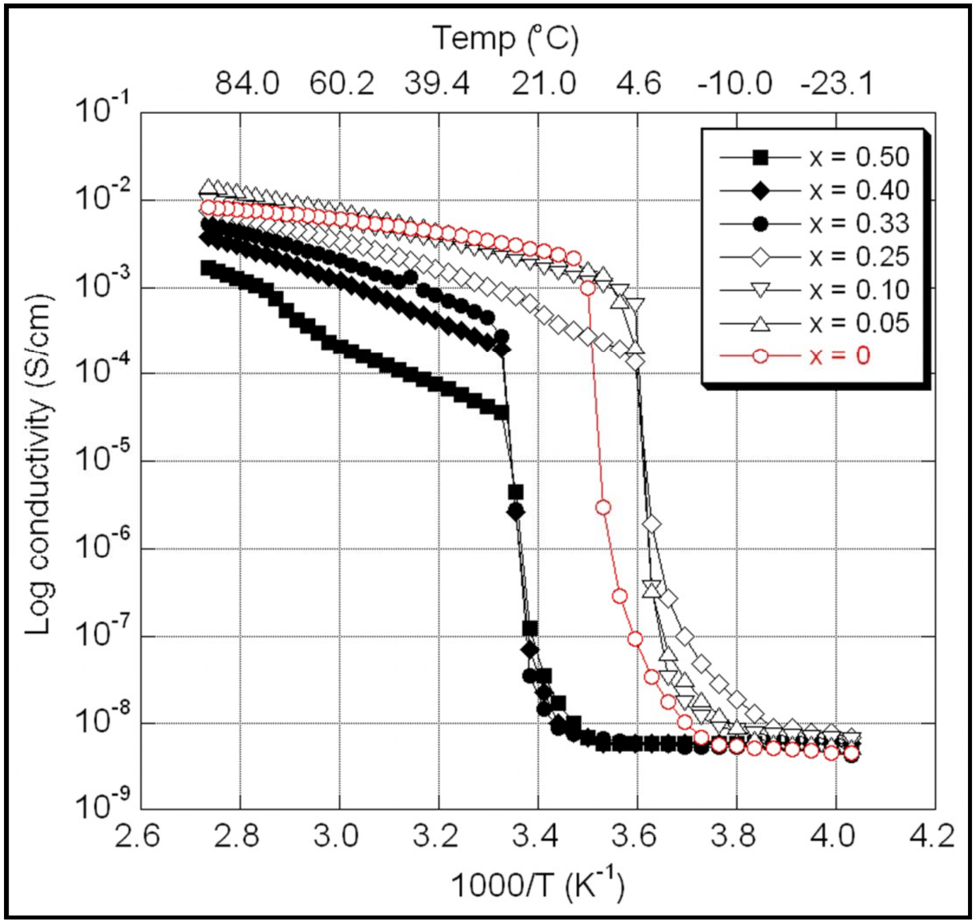
IL-LiX Phase Behavior & Conductivity

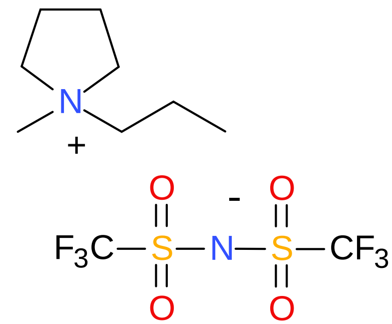




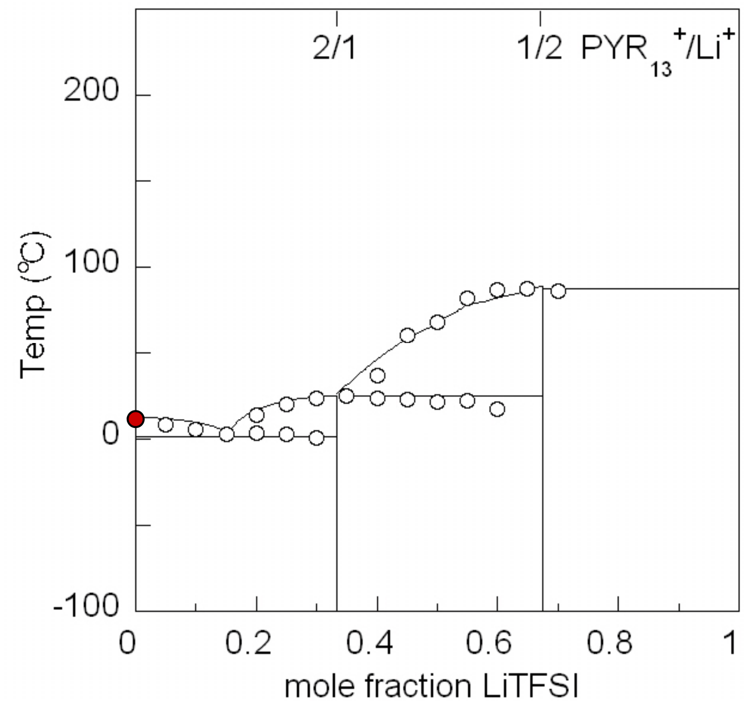
(1-x) PYR_{13}TFSI-(x) LiTFSI

IL-LiX Phase Behavior & Conductivity

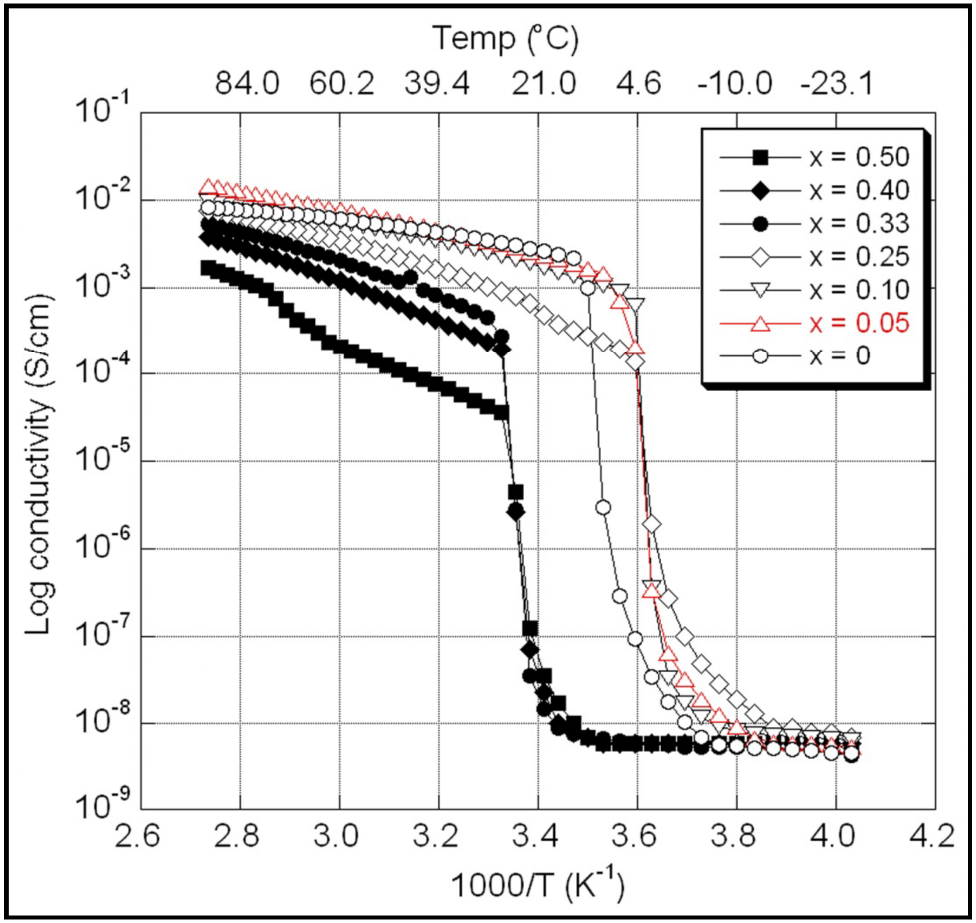


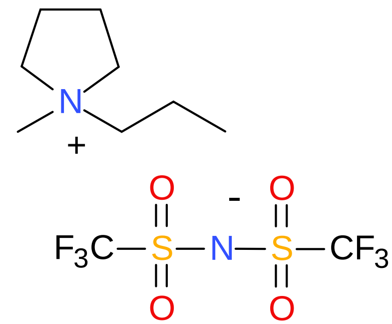


(1-x) PYR_{13}TFSI-(x) LiTFSI (x = 0)

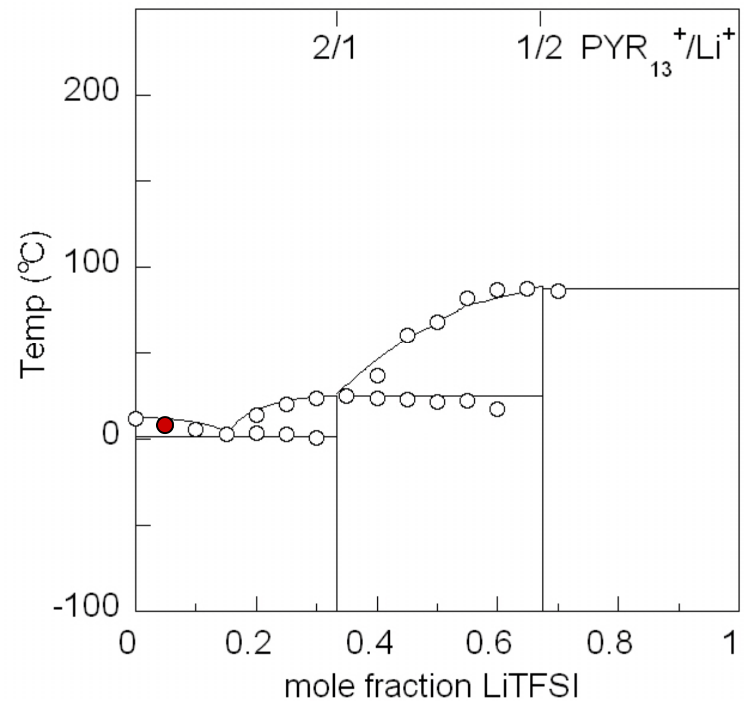


IL-LiX Phase Behavior & Conductivity

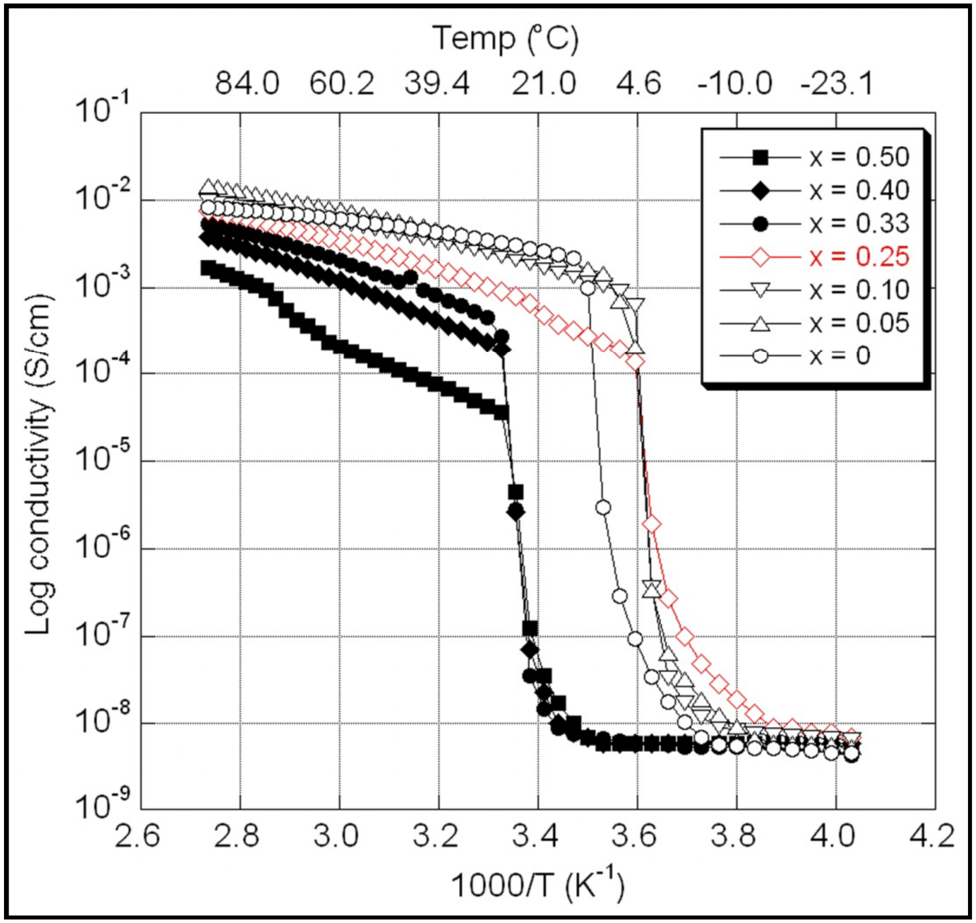


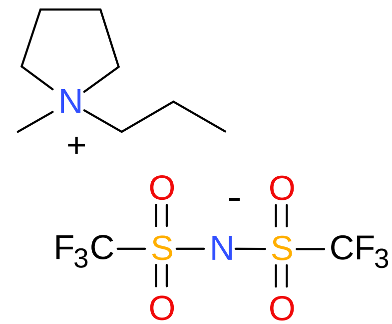


(1-x) PYR_{13}TFSI-(x) LiTFSI (x = 0.05)

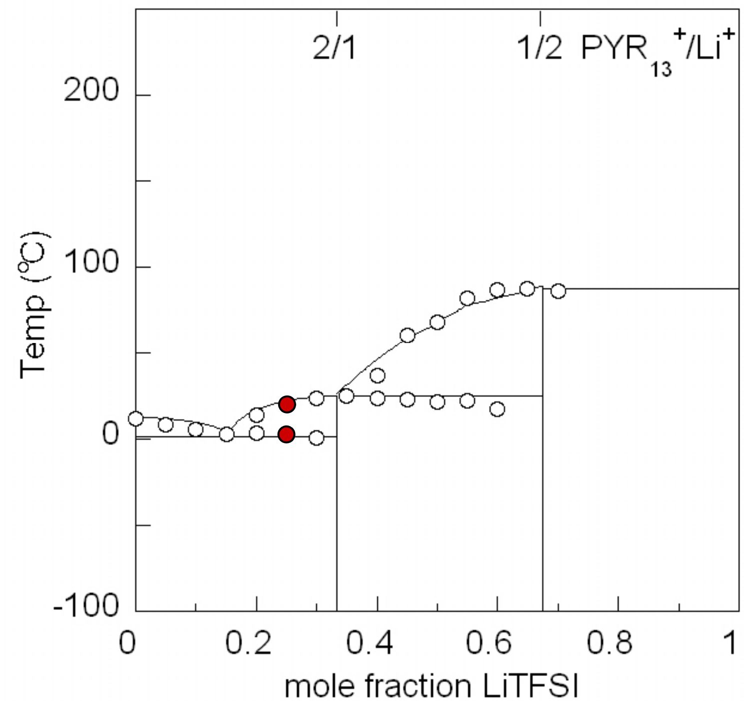


IL-LiX Phase Behavior & Conductivity

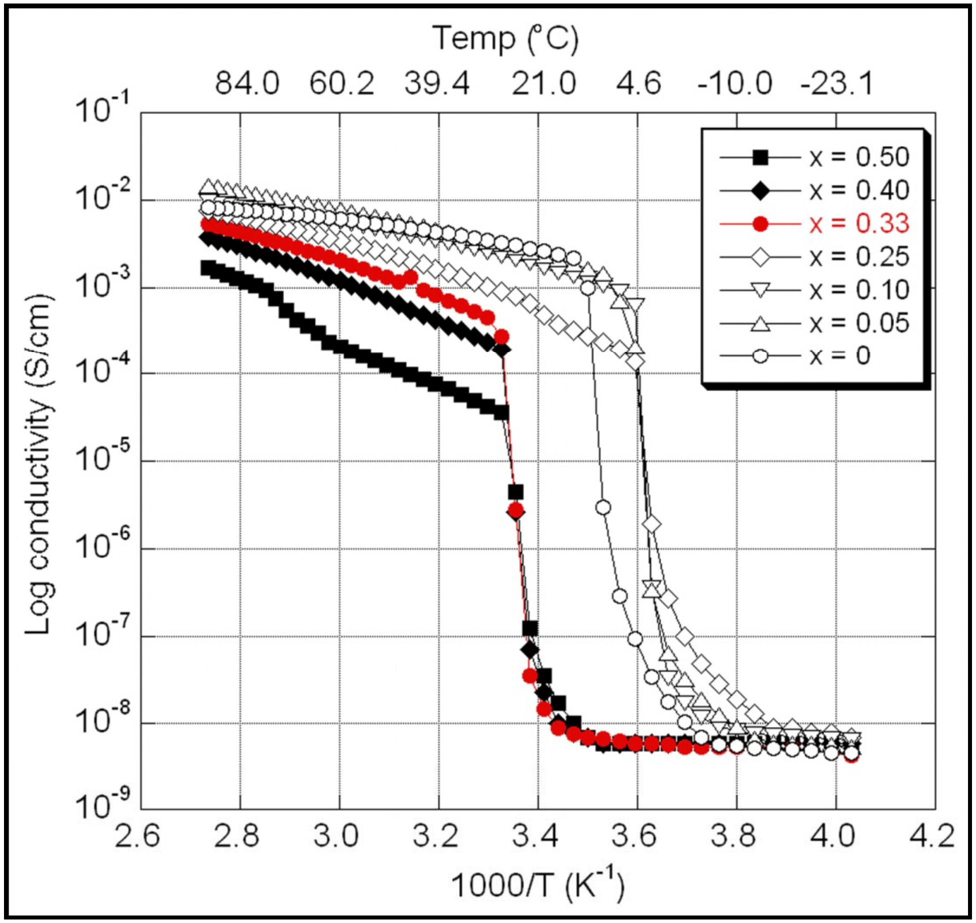


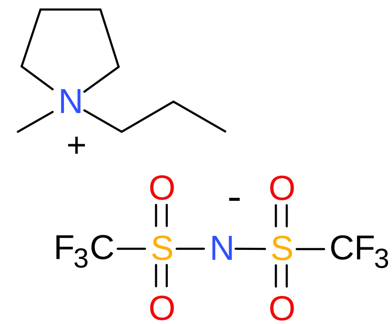


(1-x) PYR_{13}TFSI-(x) LiTFSI (x = 0.25)

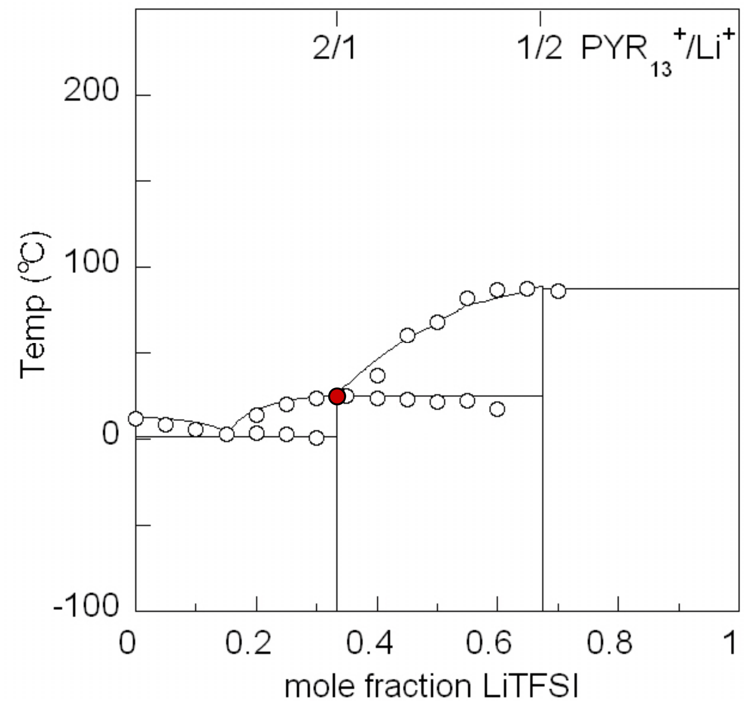


IL-LiX Phase Behavior & Conductivity

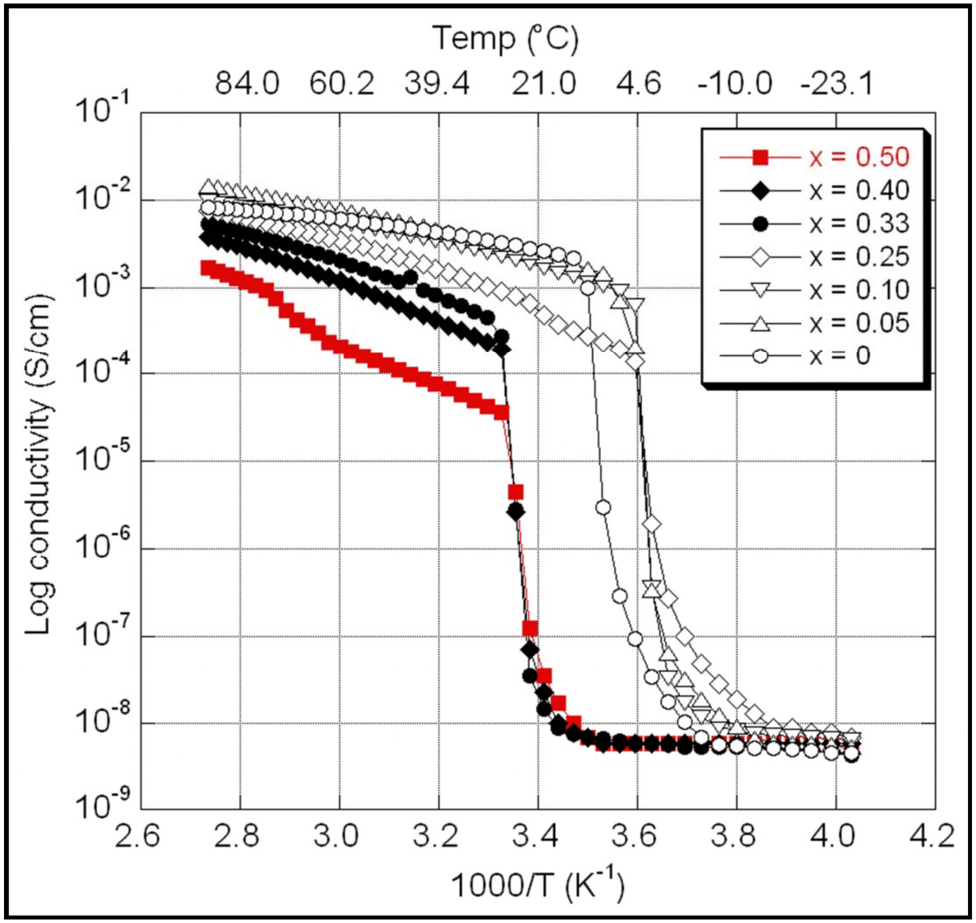


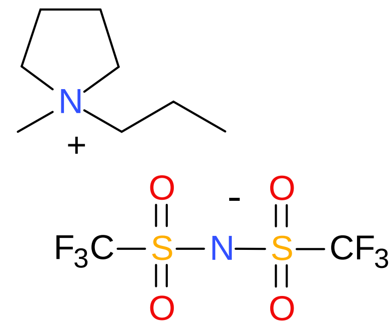


(1-x) PYR_{13}TFSI-(x) LiTFSI (x = 0.33)

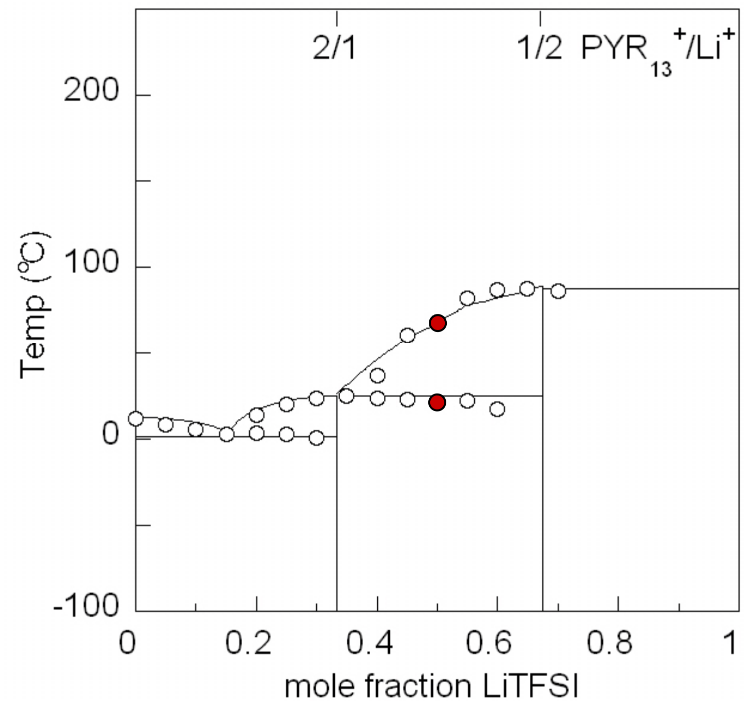


IL-LiX Phase Behavior & Conductivity

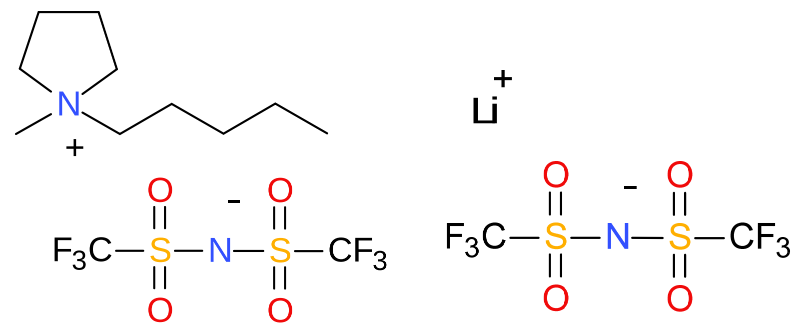


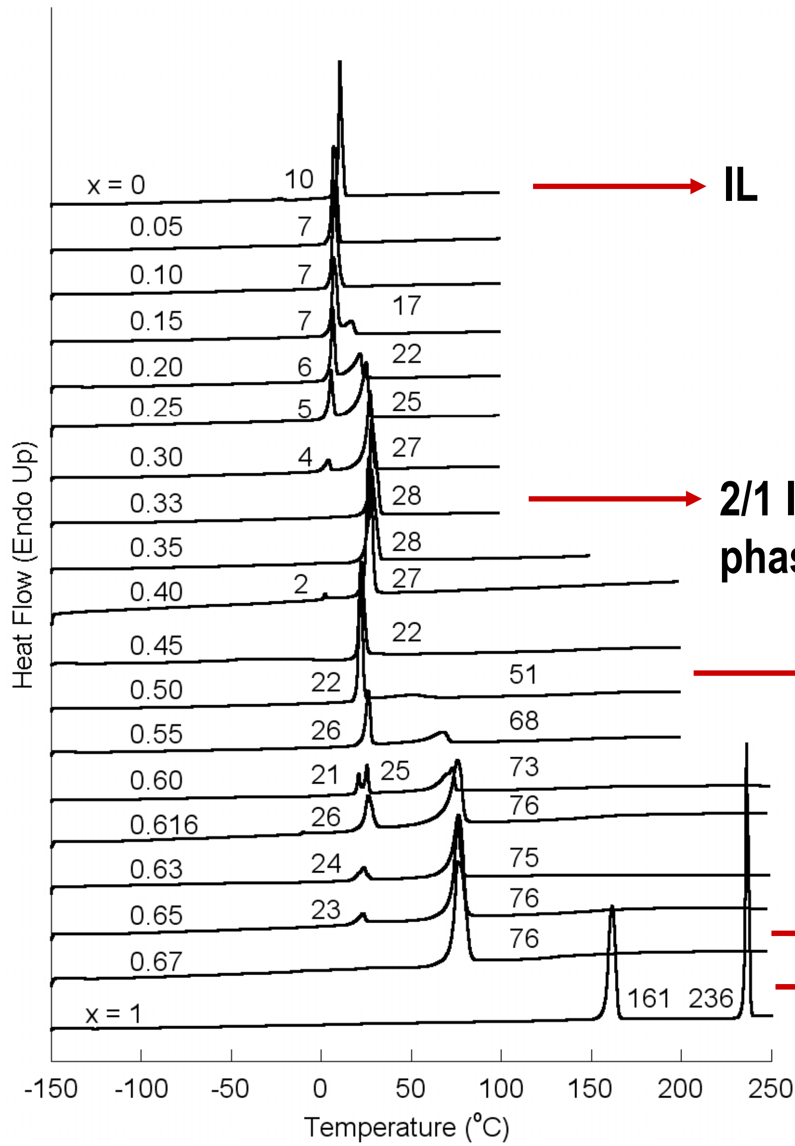


(1-x) PYR_{13}TFSI-(x) LiTFSI (x = 0.50)



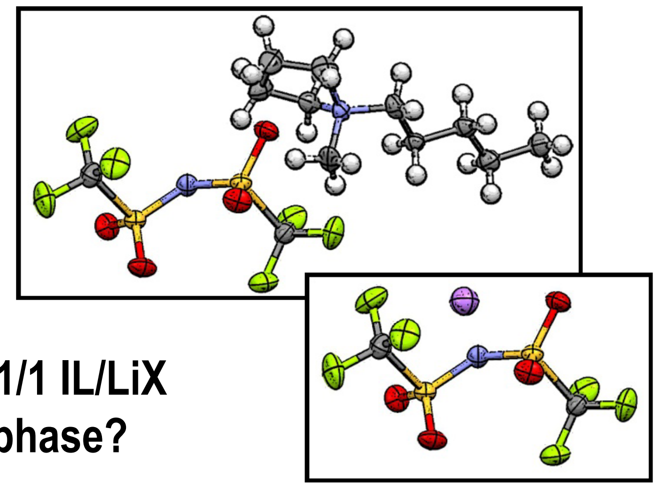
IL-LiX Phase Behavior: (1-x) $PYR_{15}TFSI$ - (x) LiTFSI





IL

2/1 IL/LiX crystalline phase



eutectic or 1/1 IL/LiX crystalline phase?

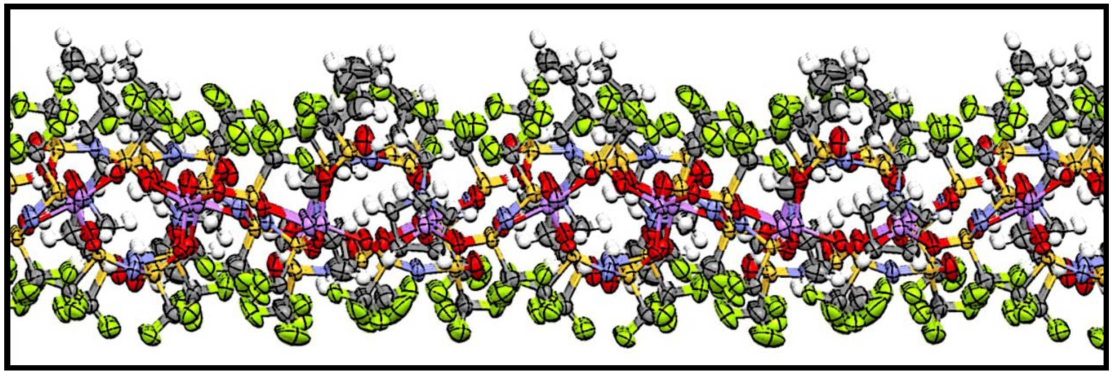
1/2 IL/LiX crystalline phase

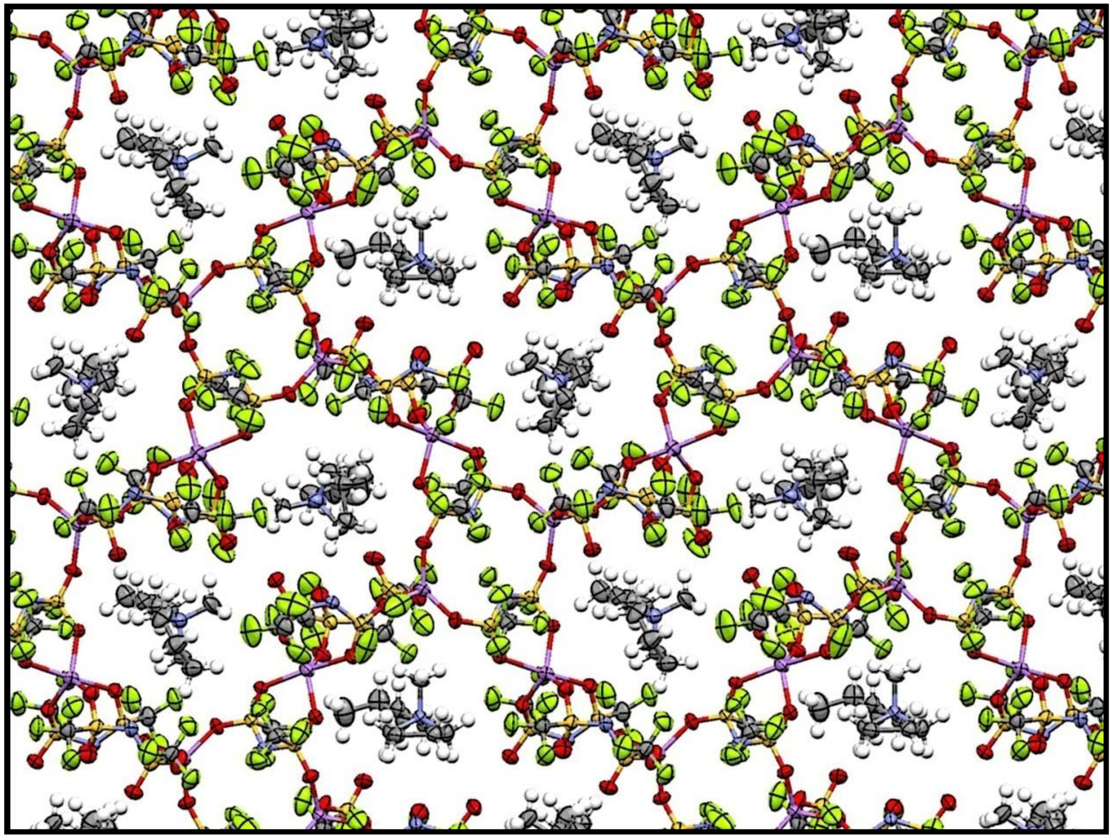
LiTFSI

Phase Behavior of IL-LiX Mixtures: $PYR_{15}TFSI$-LiTFSI

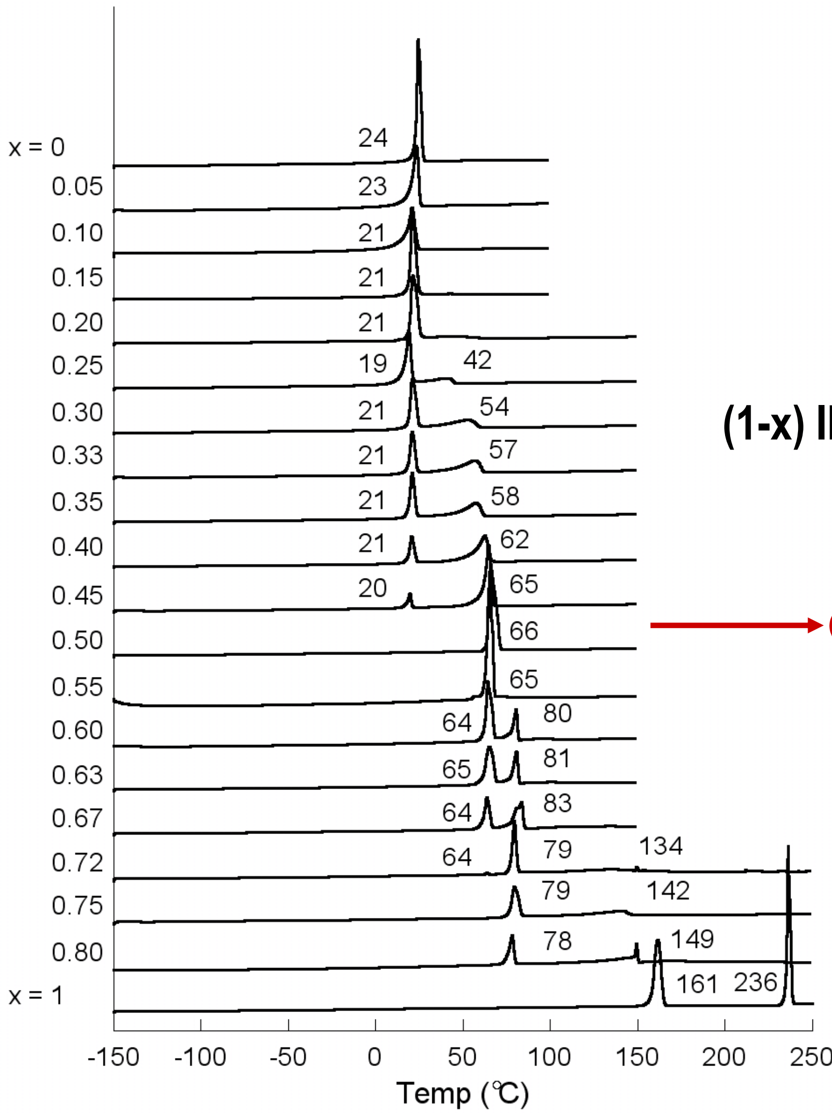
1/2 IL/LiX crystalline phase

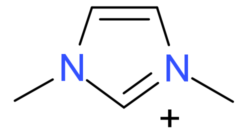
(1-x) $PYR_{15}TFSI$-(x) LiTFSI
(x = 0.67)

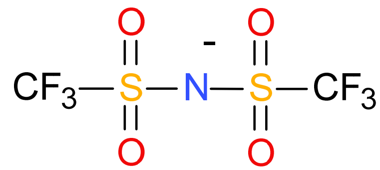




Phase Behavior of IL-LiX Mixtures: $IM_{101}TFSI$-LiTFSI







(1-x) $IM_{101}TFSI$-(x) LiTFSI

1/1 IL/LiX crystalline phase

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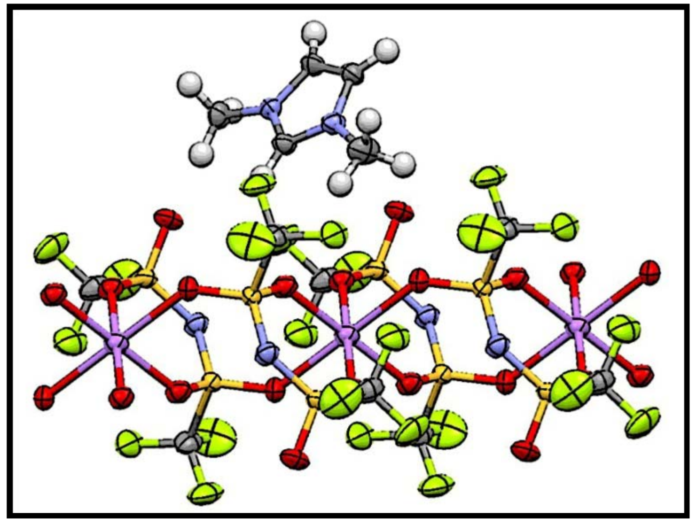
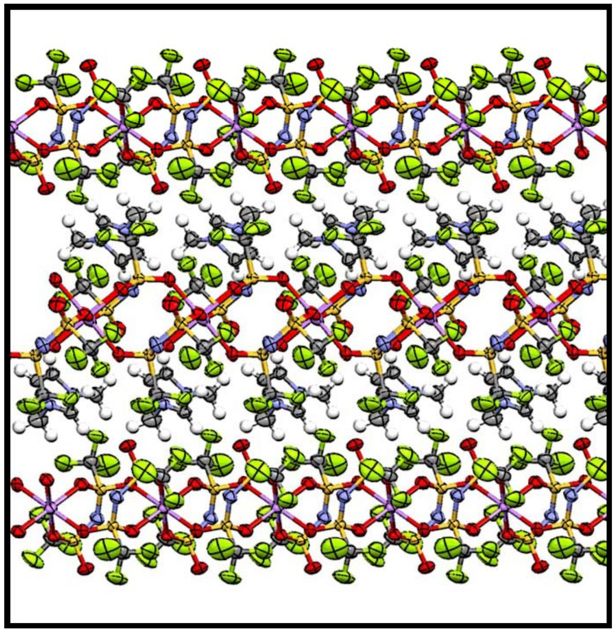
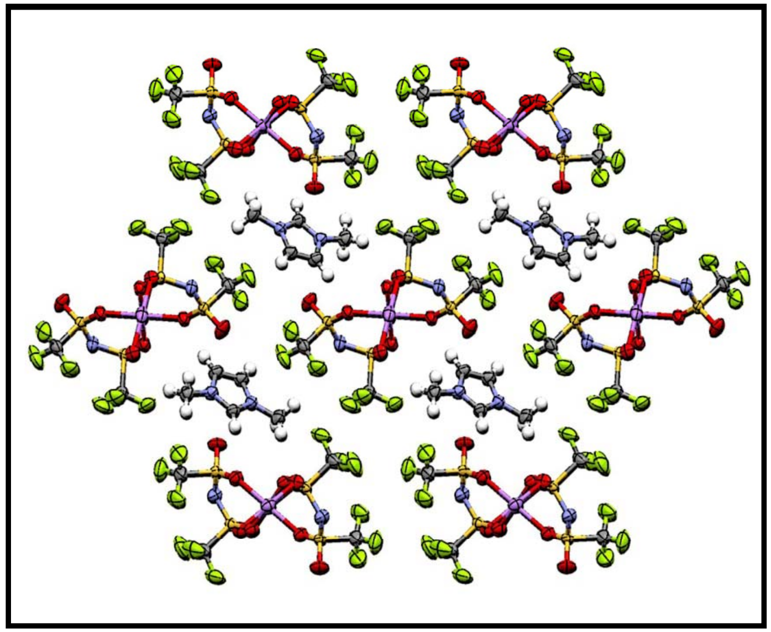
Phase Behavior of IL-LiX Mixtures: IM_{101}TFSI-LiTFSI

1/1 IL/LiX crystalline phase

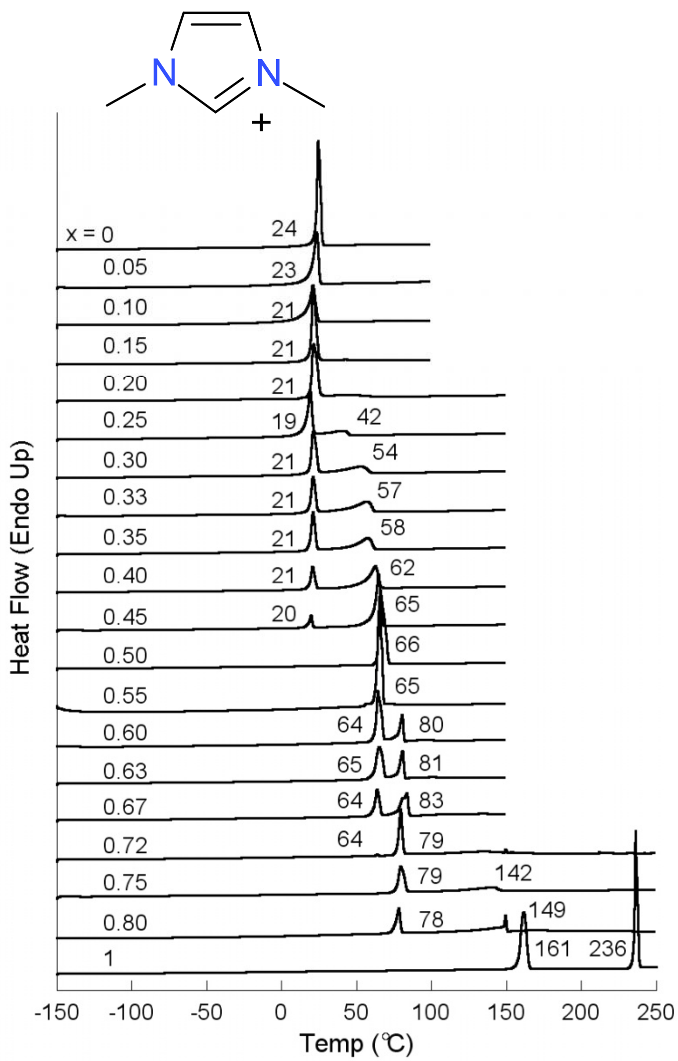
(1-x) IM_{101}TFSI-(x) LiTFSI
(x = 0.50)

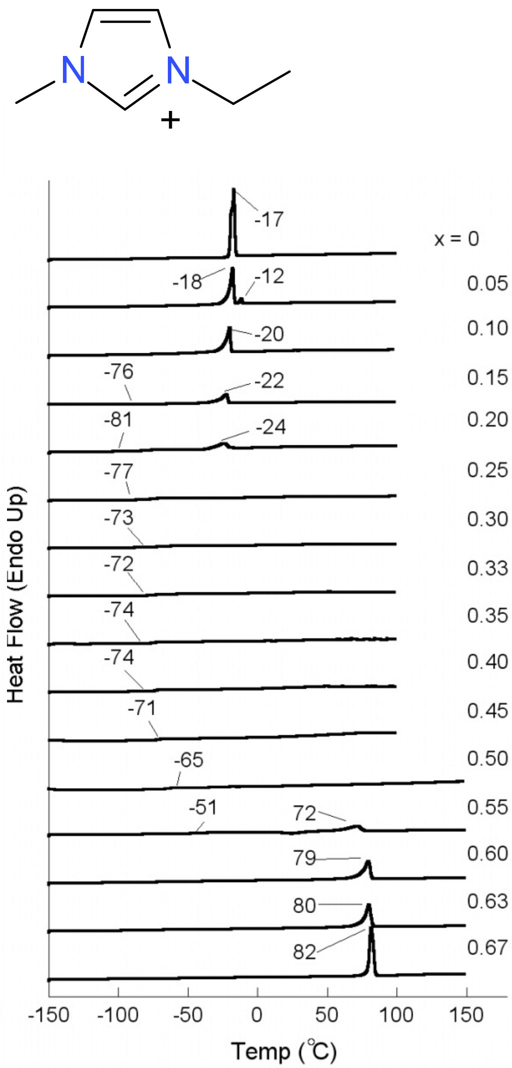


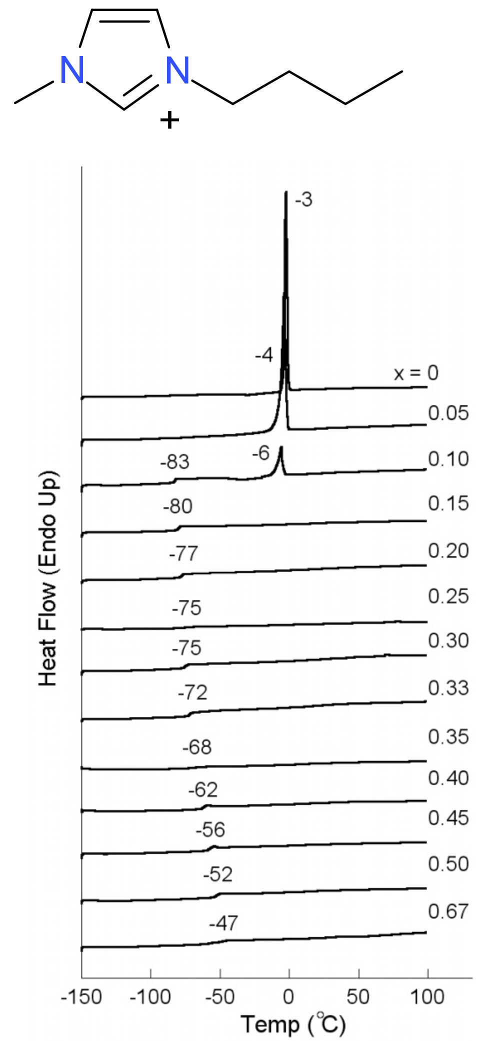




Phase Behavior of IL-LiX Mixtures: IM_{101}TFSI-LiTFSI







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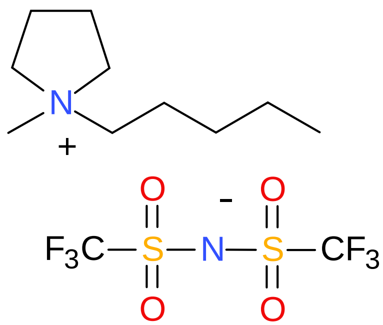
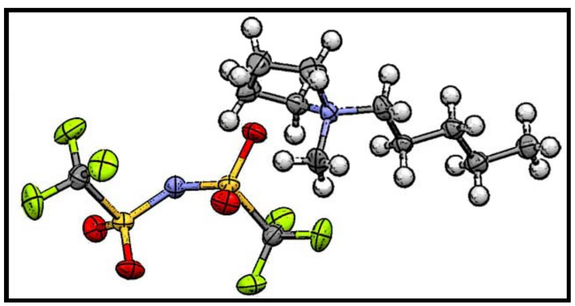
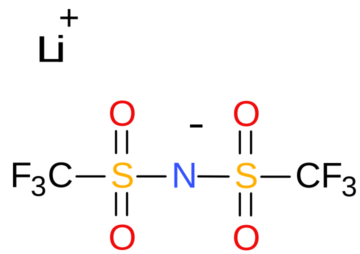
IL-LiX Mixtures - Add Solvent

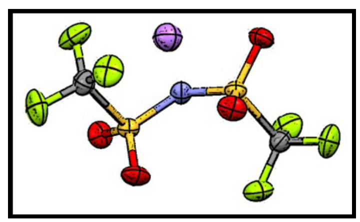


$PYR_{15}TFSI$

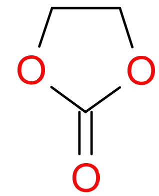




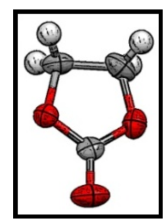
LiTFSI



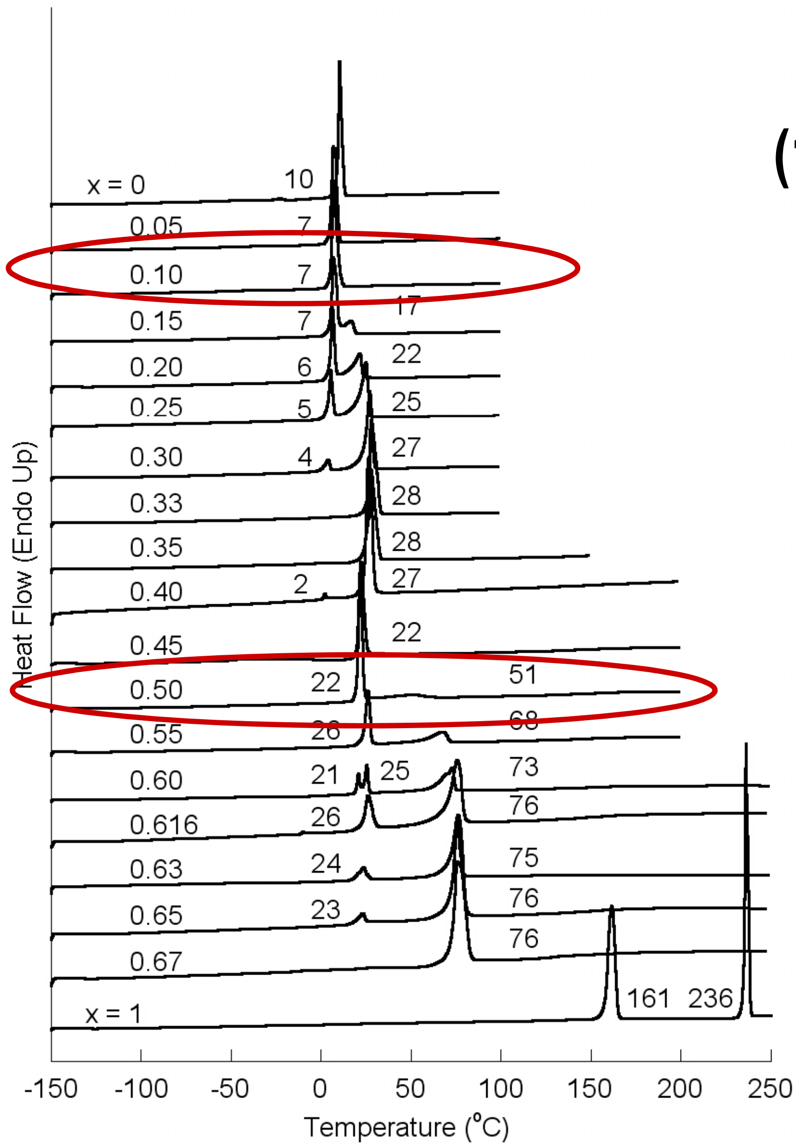
+



ethylene carbonate (EC)



IL-LiX + Solvent



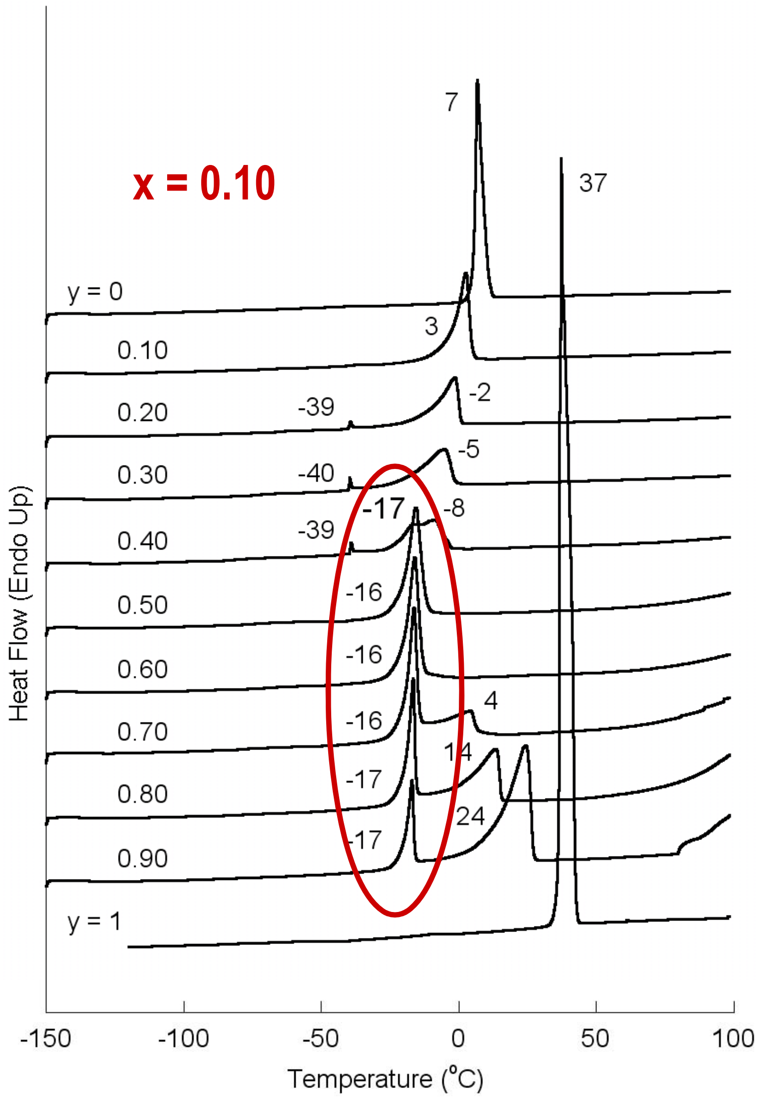
(1-y) [(1-x) PYR_{15}TFSI - (x) LiTFSI]
(y) [EC]

x = 0.10 or 0.50

1 Li^+ / 10 $TFSI^-$

5 Li^+ / 10 $TFSI^-$

(1-y) [(1-x) PYR_{15}TFSI - (x) LiTFSI] - (y) EC



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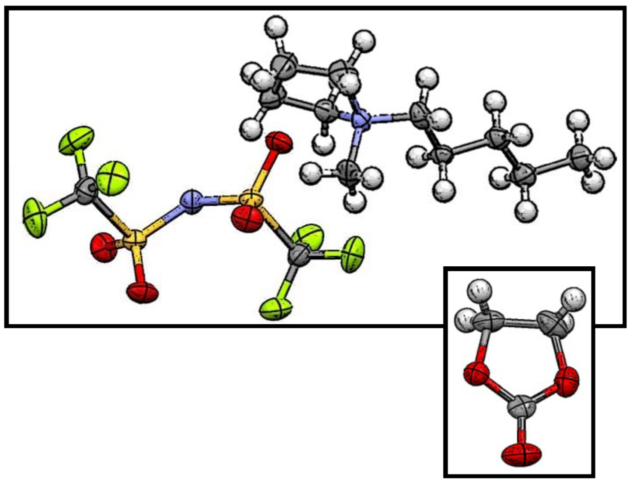
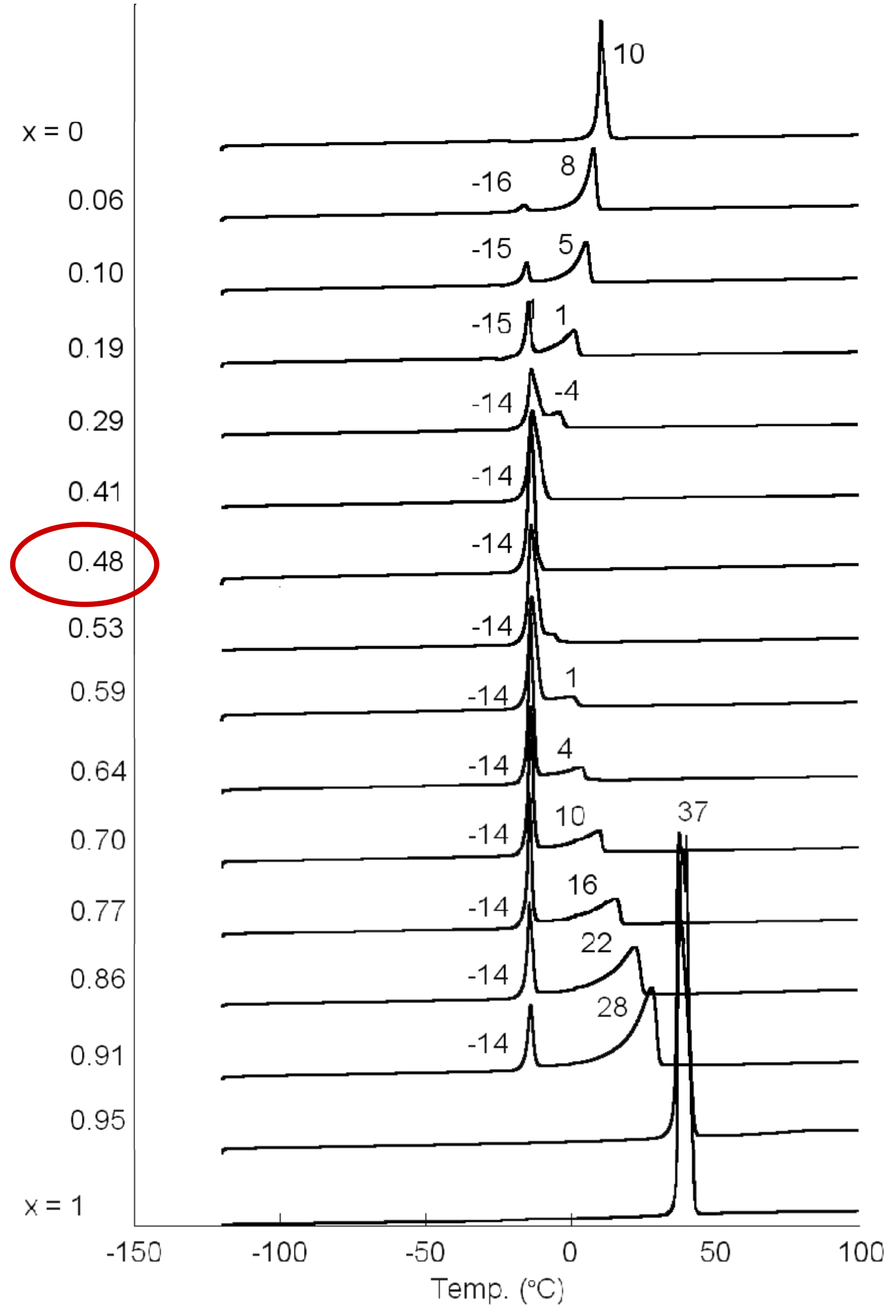
Phase Behavior: $PYR_{15}TFSI$-EC

(1-x) $PYR_{15}TFSI$-(x) EC





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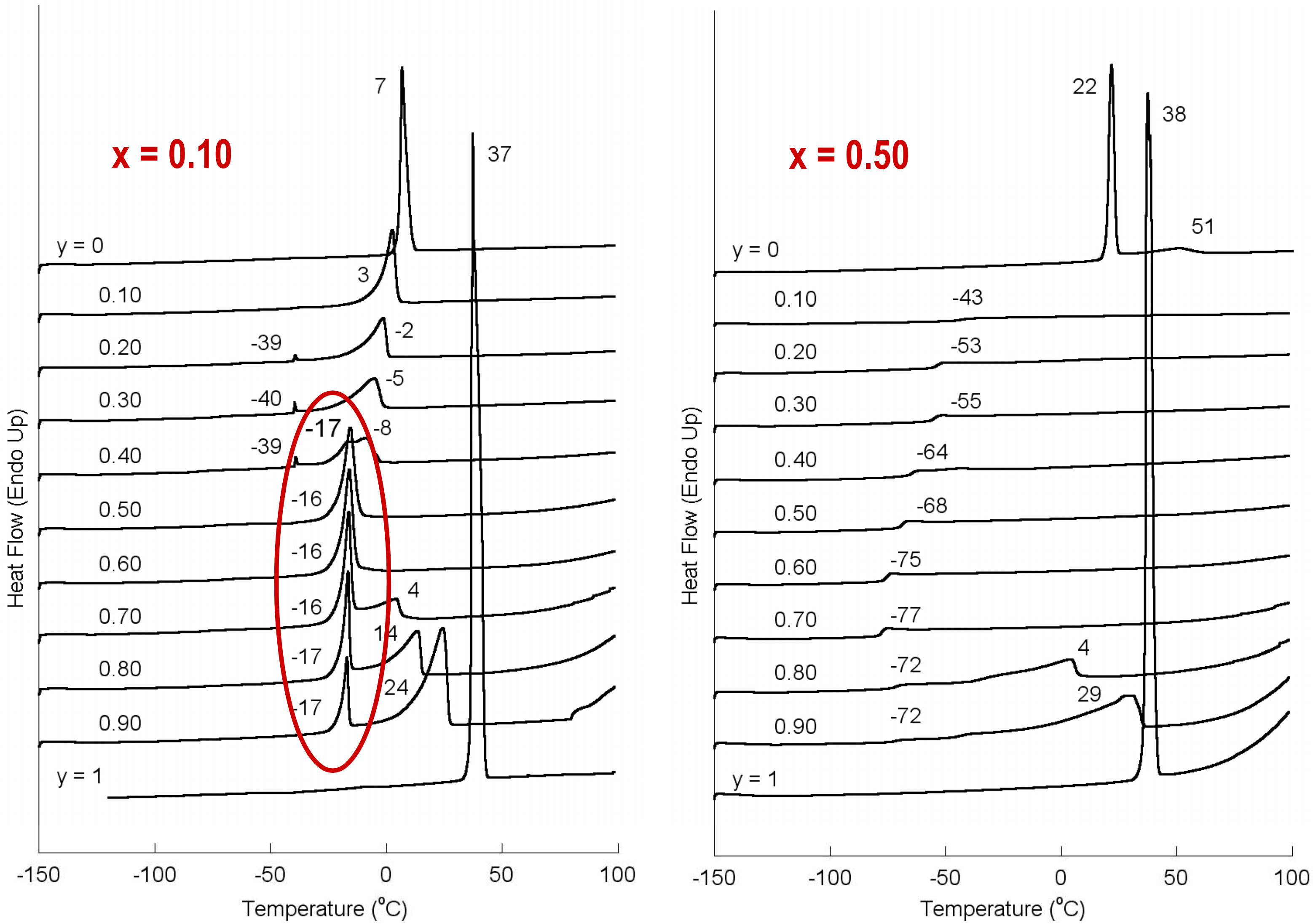
(1-y) [(1-x) PYR_{15}TFSI - (x) LiTFSI] - (y) EC



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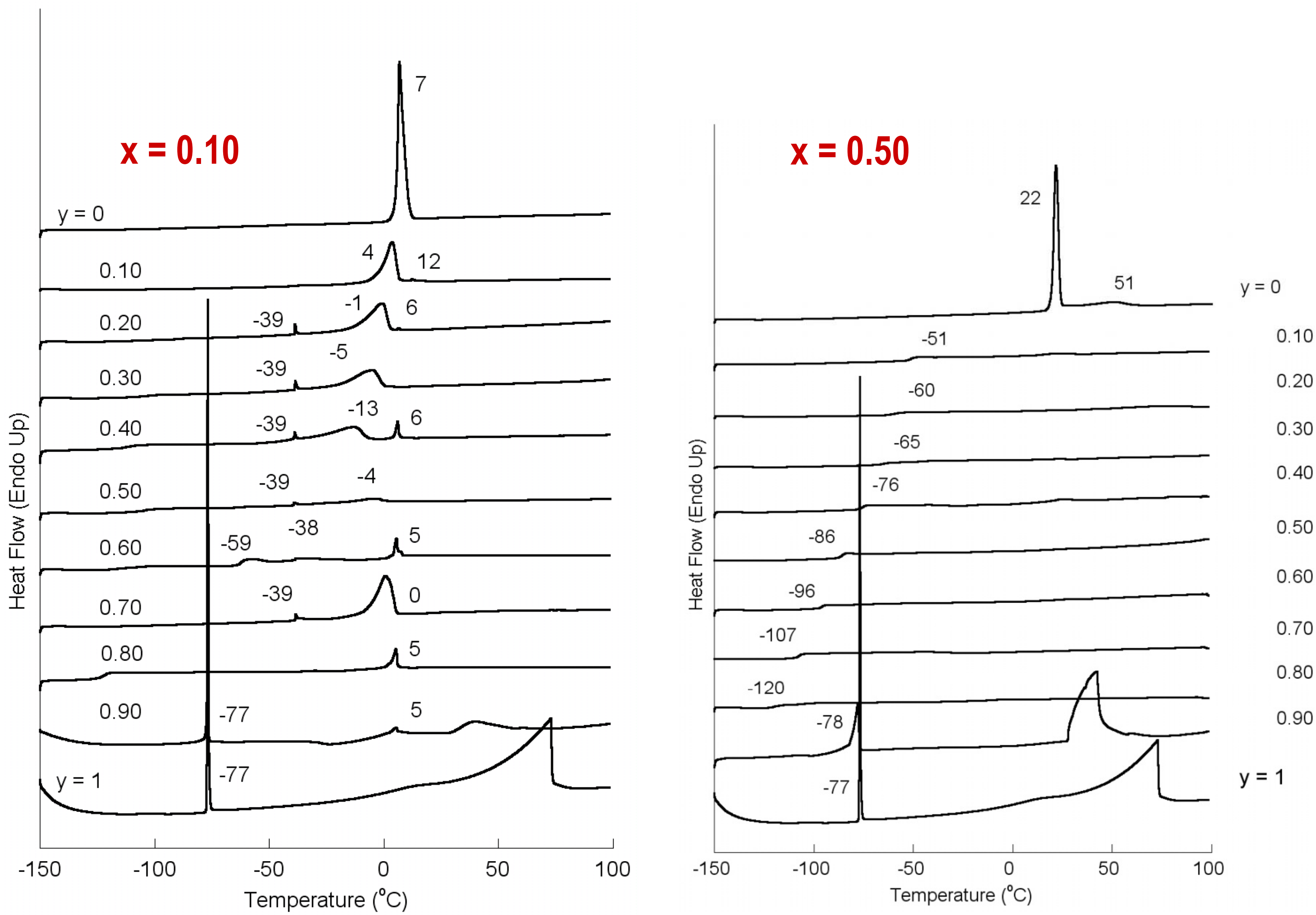
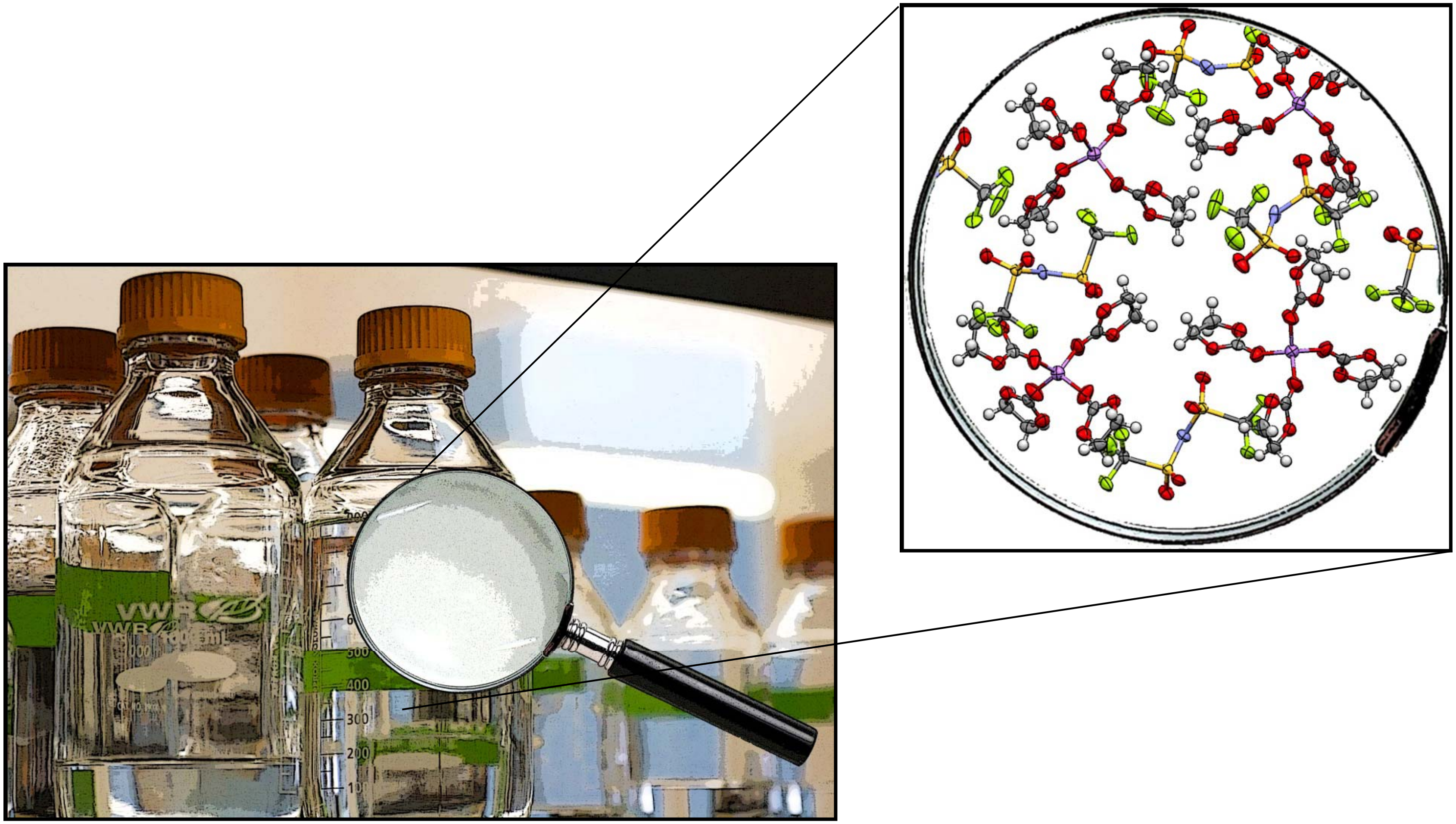
(1-y) [(1-x) PYR_{15}TFSI - (x) LiTFSI] - (y) DEC

ILEET

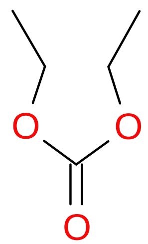


Solvent Volatility?

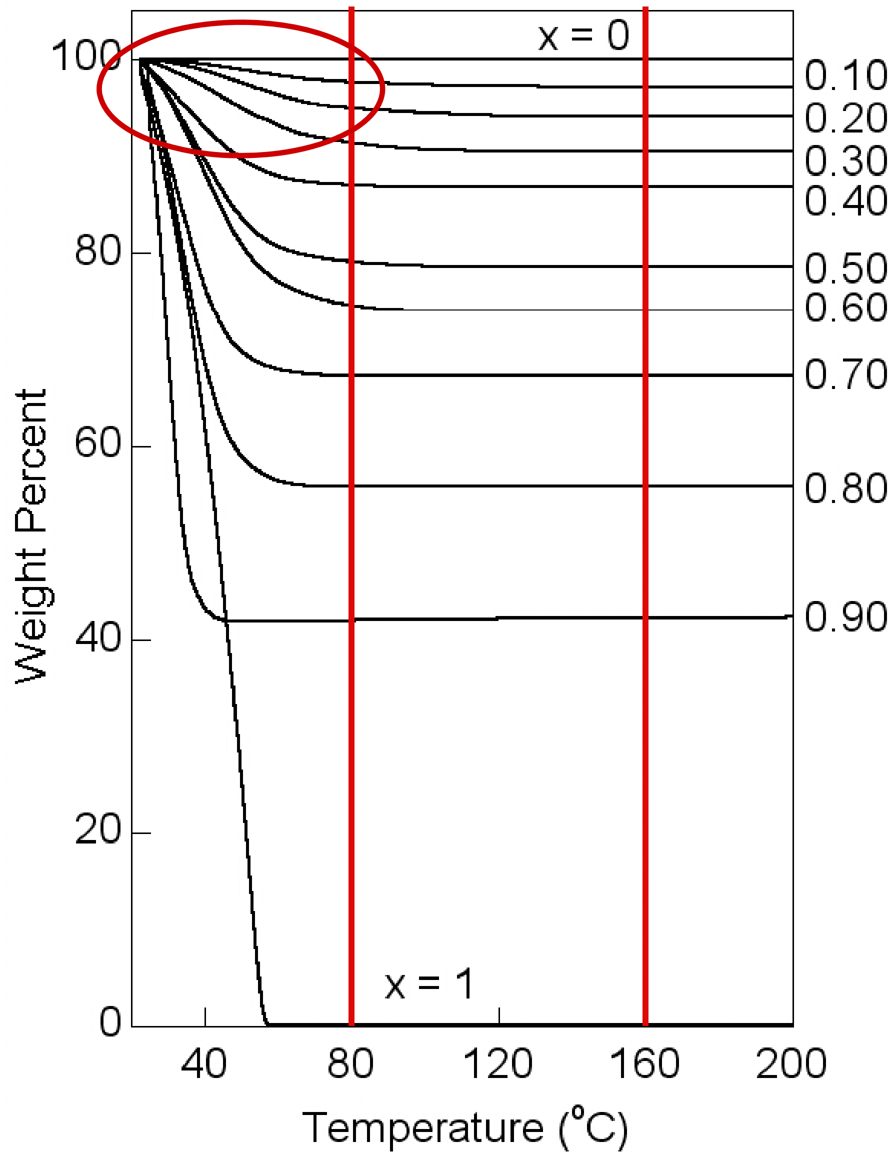


Thermal Loss of Solvent

x = 0.10



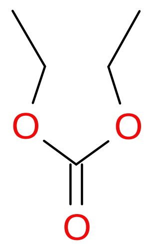
DEC

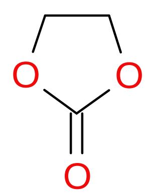


(1-y) [(1-x) PYR_{15}TFSI - (x) LiTFSI] - (y) solvent

Thermal Loss of Solvent

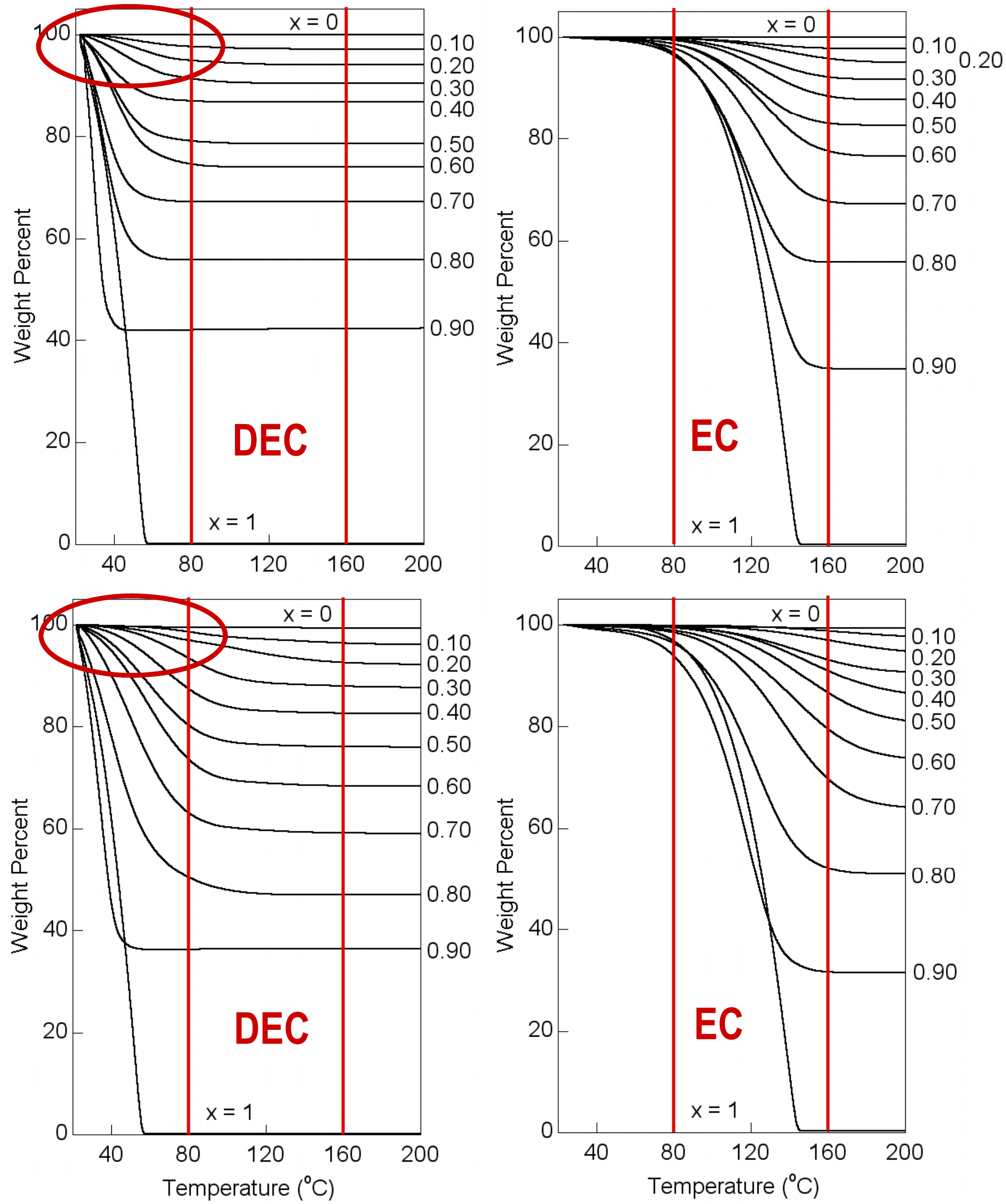
x = 0.10





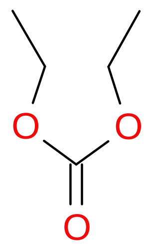
x = 0.50

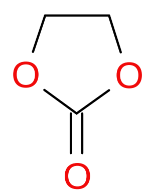
(1-y) [(1-x) PYR_{15}TFSI - (x) LiTFSI] - (y) solvent



Thermal Loss of Solvent

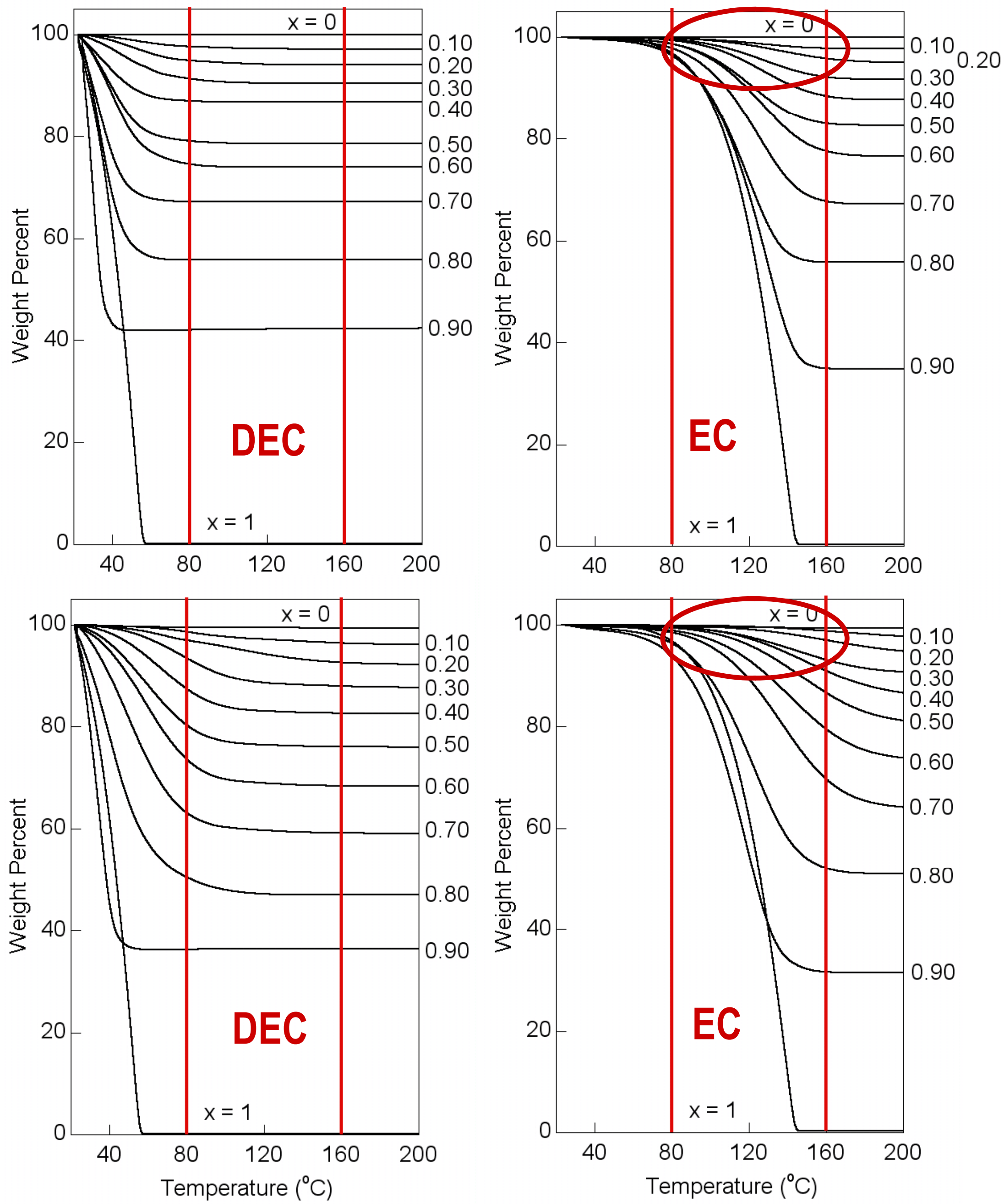
x = 0.10





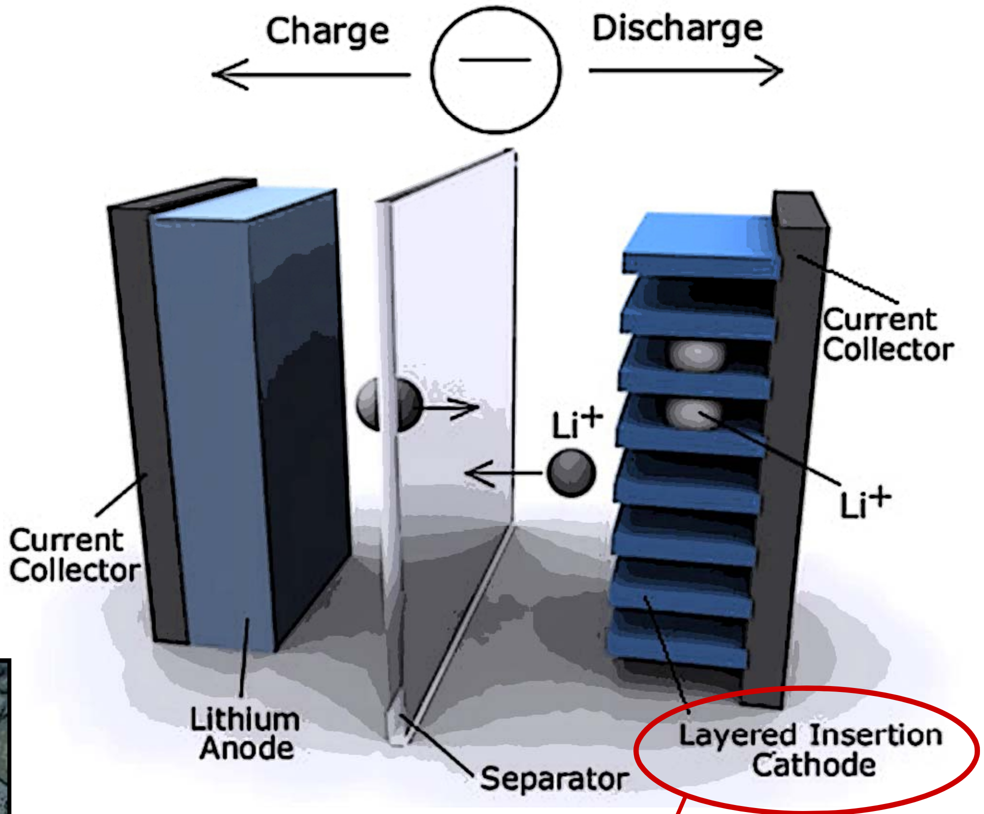
x = 0.50

(1-y) [(1-x) PYR_{15}TFSI - (x) LiTFSI] - (y) solvent



"Hydrophobic" Ionic Liquids – Electrolyte Materials for Lithium/Air Batteries?

Lithium/Air Batteries



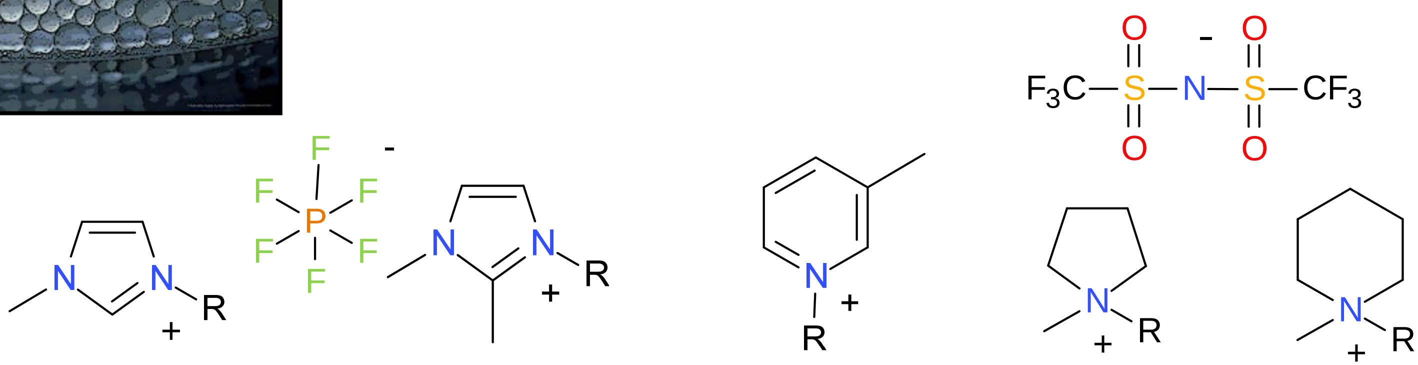
replace with air cathode

parasitic corrosion reaction

$$Li + H_2O \rightarrow LiOH + 1/2\ H_2$$

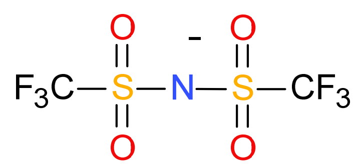
Hydrophobic ILs

Miscibility of soluted in both phases increases with temperature



	IM_{104}^{+}	IM_{106}^{+}	IM_{108}^{+}	IM_{114}^{+}	$3Me\text{-}PY_{3}^{+}$	PYR_{13}^{+}	PYR_{14}^{+}	PIP_{13}^{+}
x_w (in IL)	0.29	0.25	0.22	0.22	0.26	0.25	0.23	0.23
x_{IL} (in water)	0.0013	0.0005	0.0001	0.0009	0.0004			

Freire et al. J. Phys. Chem. B 2007, 111, 13082

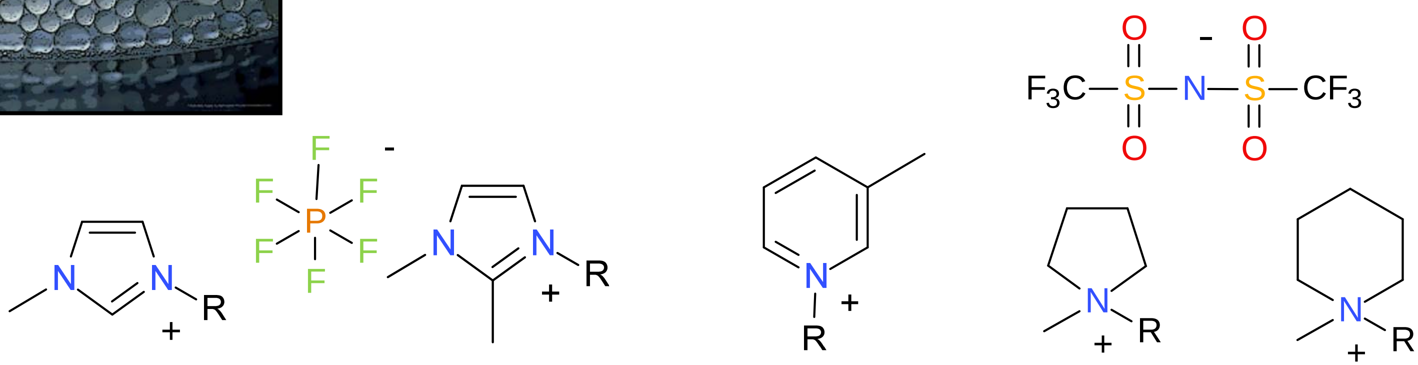


	IM_{102}^{+}	IM_{103}^{+}	IM_{104}^{+}	IM_{105}^{+}	IM_{106}^{+}	IM_{107}^{+}	IM_{108}^{+}
x_{IL} (in water)	0.0009	0.0006	0.0003	0.0002	0.0001	0.00005	0.00004

Freire et al. J. Phys. Chem. B 2008, 112, 1604

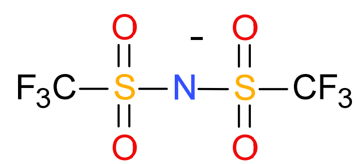
Hydrophobic ILs

All of the ILs are reported to be "hydrophobic", but the water solubility (x_w) indicates that they are, in fact, substantially "hydroscopic"



	IM_{104}^+	IM_{106}^+	IM_{108}^+	IM_{114}^+	$3Me\text{-}PY_3^+$	PYR_{13}^+	PYR_{14}^+	PIP_{13}^+
x_w (in IL)	0.29	0.25	0.22	0.22	0.26	0.25	0.23	0.23
x_{IL} (in water)	0.0013	0.0005	0.0001	0.0009	0.0004			

Freire et al. J. Phys. Chem. B 2007, 111, 13082

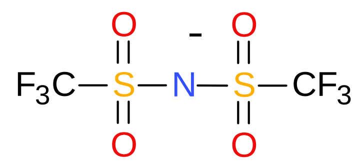


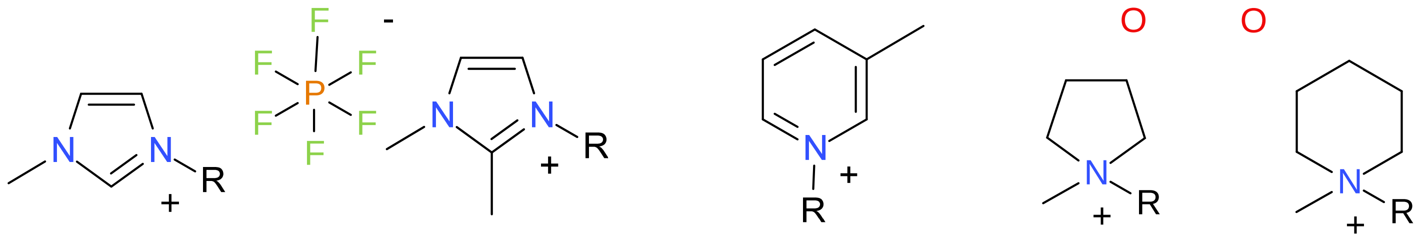
	IM_{102}^+	IM_{103}^+	IM_{104}^+	IM_{105}^+	IM_{106}^+	IM_{107}^+	IM_{108}^+
x_{IL} (in water)	0.0009	0.0006	0.0003	0.0002	0.0001	0.00005	0.00004

Freire et al. J. Phys. Chem. B 2008, 112, 1604

Hydrophobic ILs

Water-rich phase, in contrast, can be considered almost as a "pure" phase (very little dissolved IL)





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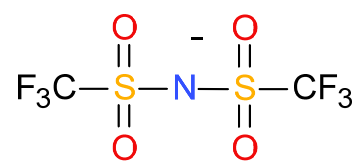
x_{IL} (in water)	0.0013	0.0005	0.0001	0.0009	0.0004			

Freire et al. J. Phys. Chem. B 2007, 111, 13082

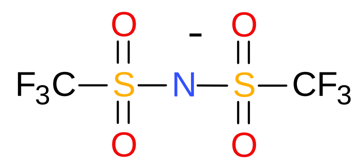


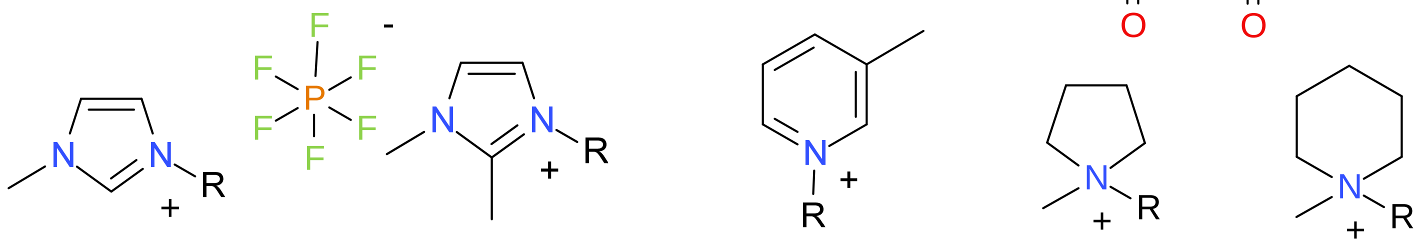
	IM_{102}^+	IM_{103}^+	IM_{104}^+	IM_{105}^+	IM_{106}^+	IM_{107}^+	IM_{108}^+
x_{IL} (in water)	0.0009	0.0006	0.0003	0.0002	0.0001	0.00005	0.00004

Freire et al. J. Phys. Chem. B 2008, 112, 1604

Hydrophobic ILs

The anion plays the dominant role in solubility...followed by the cation alkyl chain length and the cation head group (secondary influence)





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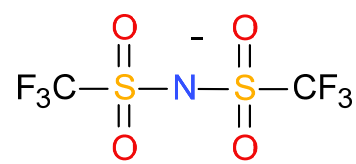
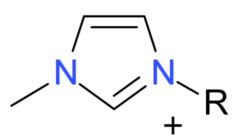
Freire et al. J. Phys. Chem. B 2007, 111, 13082

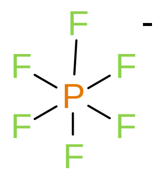


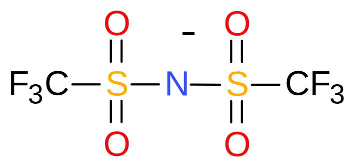
	IM_{102}^{+}	IM_{103}^{+}	IM_{104}^{+}	IM_{105}^{+}	IM_{106}^{+}	IM_{107}^{+}	IM_{108}^{+}
x_{IL} (in water)	0.0009	0.0006	0.0003	0.0002	0.0001	0.00005	0.00004

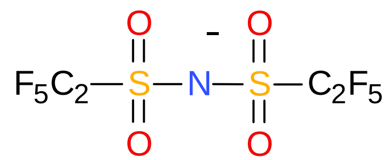
Freire et al. J. Phys. Chem. B 2008, 112, 1604

Water Solubility in Hydrophobic ILs - Further Corroboration









	IM_{106}^{+}	IM_{108}^{+}	IM_{106}^{+}	IM_{108}^{+}	$IM_{10(10)}^{+}$	IM_{106}^{+}	IM_{108}^{+}	$IM_{10(10)}^{+}$
x_w (in IL)$_{amb}$	0.0063	0.0039	0.0179	0.0143	0.110	0.0063	0.0039	0.0027
x_w (in IL)$_{equil}$	0.220	0.212	0.233	0.205	0.204	0.187	0.148	0.140

Fitchett et al. J. Electrochem. Soc. 2004, 15, E219

See also: Kakiuchi Anal. Sci. 2008, 24, 1221
Katase et al. Sci. Tech. Adv. Mater. 2006, 7, 502

Summary

It may be possible to:

- achieve reasonable Li^+ conductivity for practical applications
- improve the electrochemical stability
- reduce the amount of IL required
- increase the Li^+ content
- decrease the volatility/flammability of the electrolyte

using IL-LiX + solvent mixtures

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Ionic Liquids & Electrolytes for Energy Technologies (ILEET) Laboratory

Qian Zhou (grad)
Elie Paillard (postdoc)

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