Electrolytes and separators for high voltage Li ion cells

(an investigation of sulfone-based electrolyte solvents)

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March 11, 2011 **Project ID:** ES100

Overview

Timeline:
Start: May 2010
Finish: Dec./2013

Budget:
$709,977
Funding received in FY 2010 for 2010 and 2011
$249,977
Funding for FY 2012
$230,000

Barriers:

- High viscosities, and melting points, of existing examples.
- Lack of information on additives and mixtures
- Safety issues: flammability
- Sepataor issures: containment impedance and toughness

Partners:

- Oleg Borodin, U. Utah
- Goying Chen, LBL
- Brett Lucht, U. Rhode Island

Jason Zhang, PNNL

Relevance: Once conductivity has been maximized, energy density and power output of VT power train can *only* be increased by increase of cell voltage. REQUIREMENT: high voltage stable electrolyte and **solvent**

Background needed

Aliphatic sulfones, especially those with open-chain alkyls,[10] are recognized by organic chemists as unusual for their combination of polarity with resistance to both oxidation and reduction.[11] [Chemically, aliphatic cyclic sulfones are more easily reduced (ca. 100 times as fast) than open-chain sulfones.] The simplest mem-

DMS

Try destabilization of crystal lattice by making the molecule asymmetrical.

but

		T_m
Dimethyl sulfone	$(CH_3)_2SO_2$	109ºC
Diethyl sulfone	$(Et)_2SO_2$	70ºC
Dipropyl sulfone	etc	

T_m = 35ºC: eutectic with DMS is 25ºC

High Anodic Stability of a New Electrolyte Solvent: Unsymmetric Noncyclic Aliphatic Sulfone

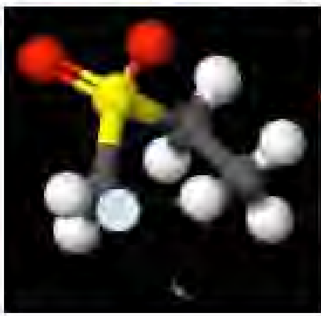
K. Xu** and C. A. Angell**

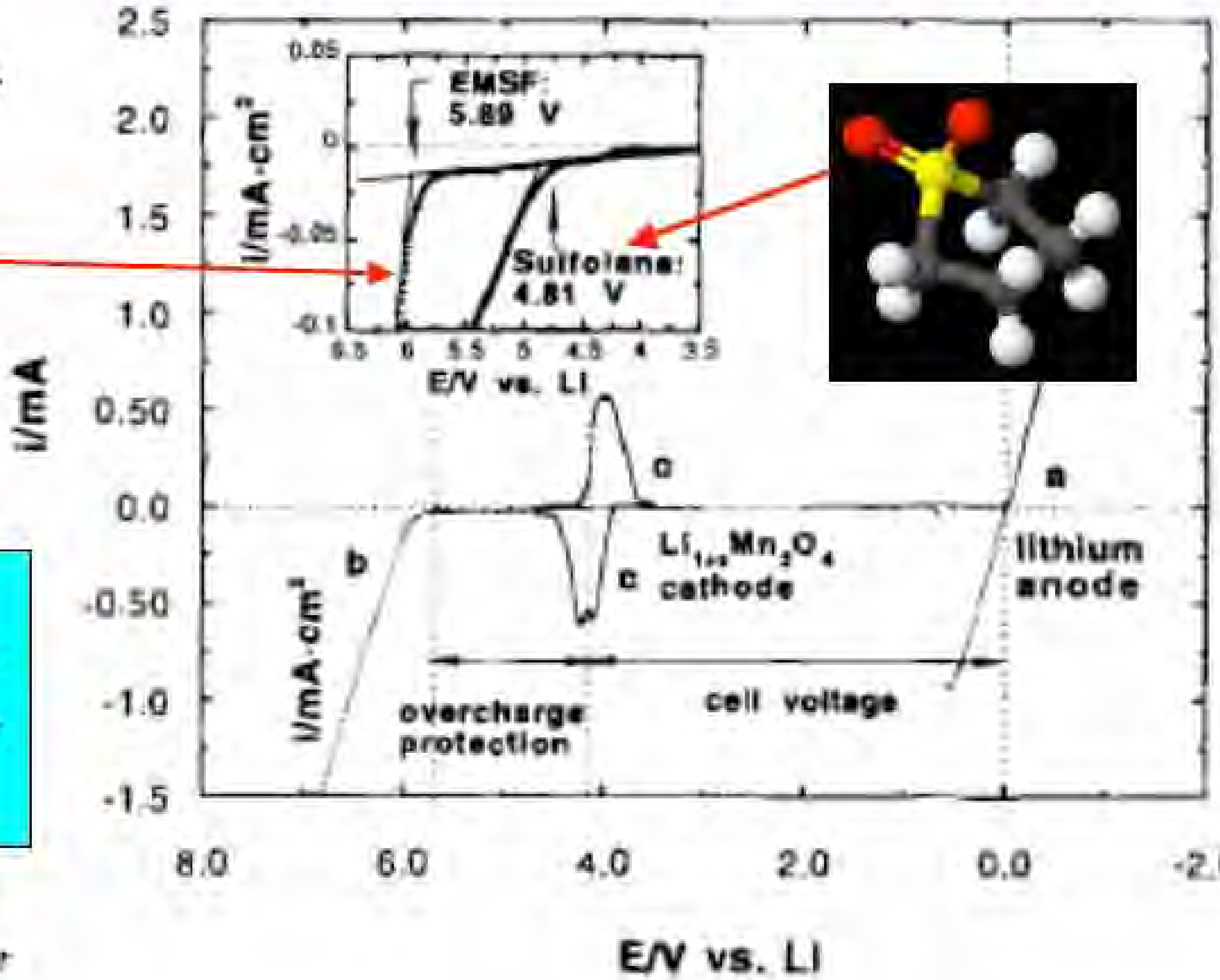
J. Electrochem. Soc., Vol. 145, No. 4, April 1998

5.9 V !!

Background: A 5.9 volt window !

Kang Xu and CAA, *J. Electrochem. Soc.* **145**, L70 (1998).





For capacitative storage, note that the energy of a capacitor is given by:

$$E = \frac{1}{8} c_p V^2 ,$$

Background: The promise of sulfones: conductivity of FEMS vs EC:DMC

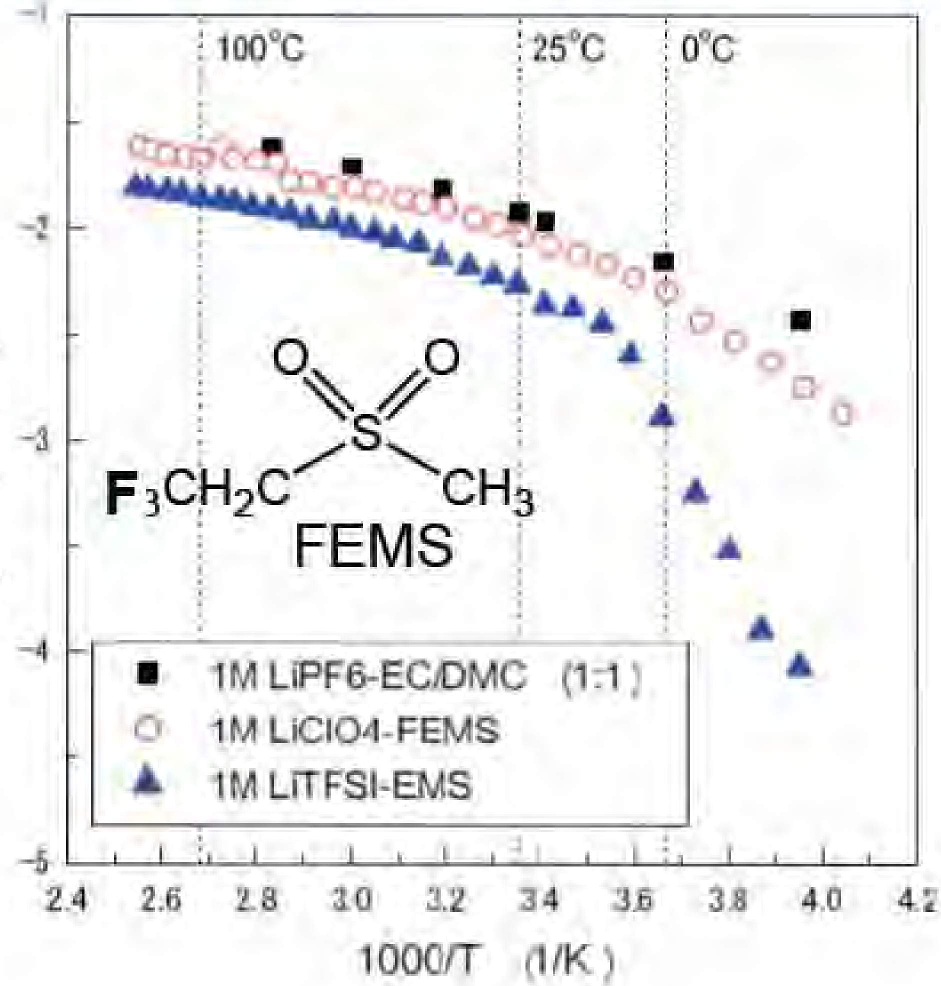
US Patent No. 6,245,465
Angell et al., 2001

Visit by Toyota
Delegation 2005

Methylethoxymethylsulfone (MEMS)

Melting point 7^{o}C

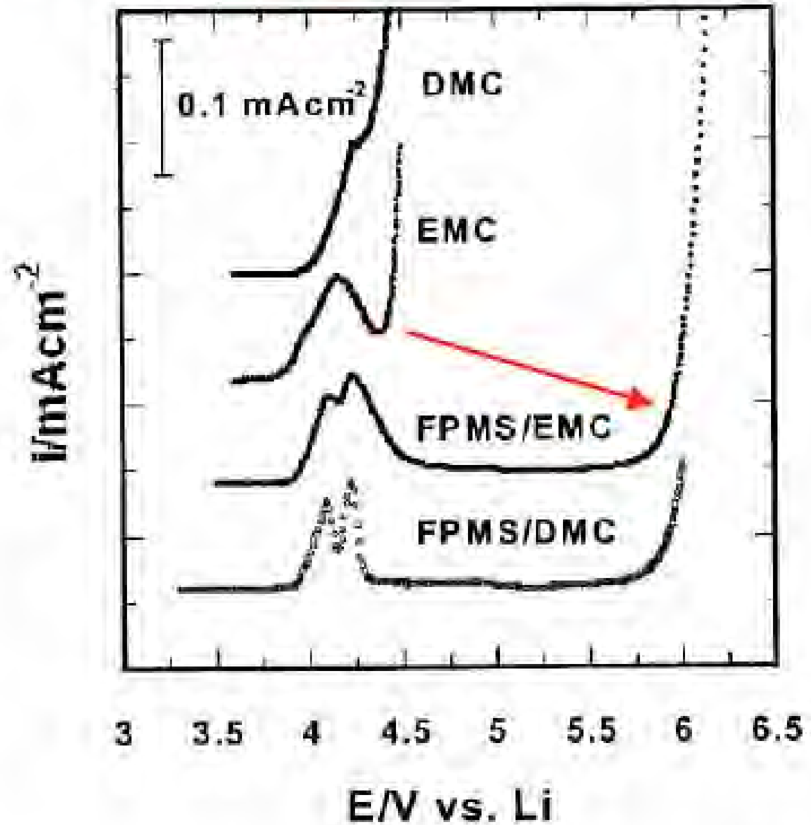
US Patent No. 6,245,465
Angell & Sun., 2010
(DOW inc option)



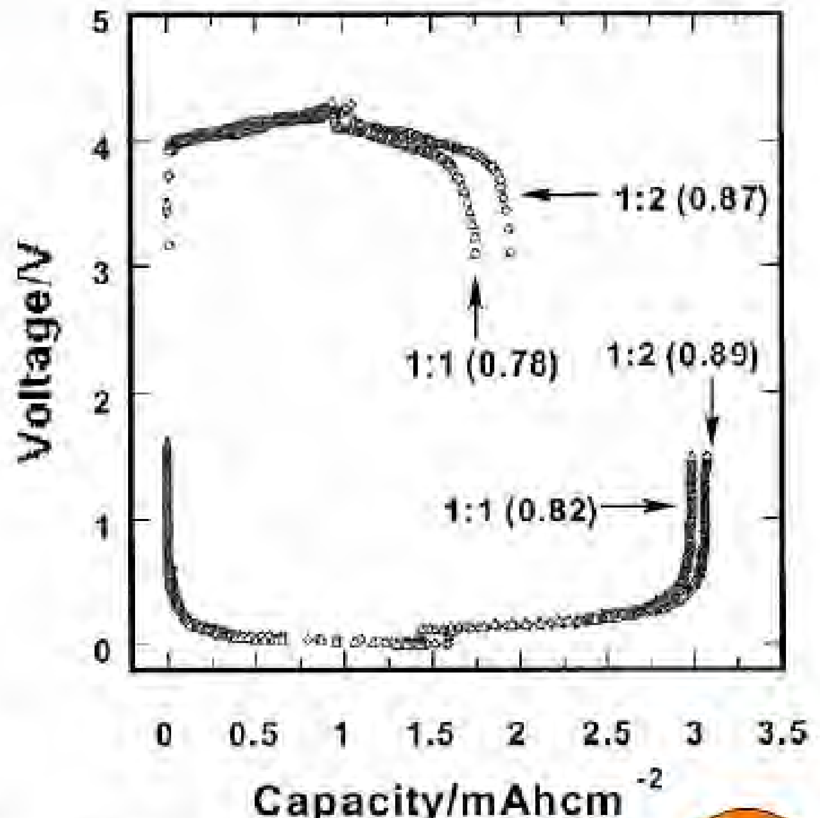
Background: And sulfones seem to protect lower EC "window"(but higher fluidity) co-solvents

Work of Kang Xu (JECS,2002)

FPMS is $CF_3CH_2CH_2[SO_2]CH_3$



Forms good SEI



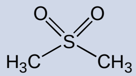
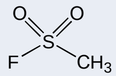
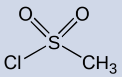
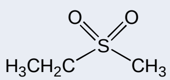
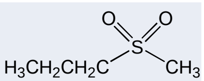
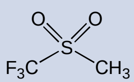
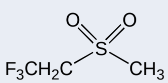
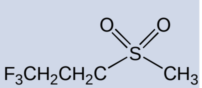
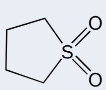
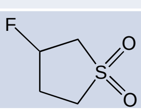
But T_m of FPMS is 56°C

OBJECTIVES and milestones

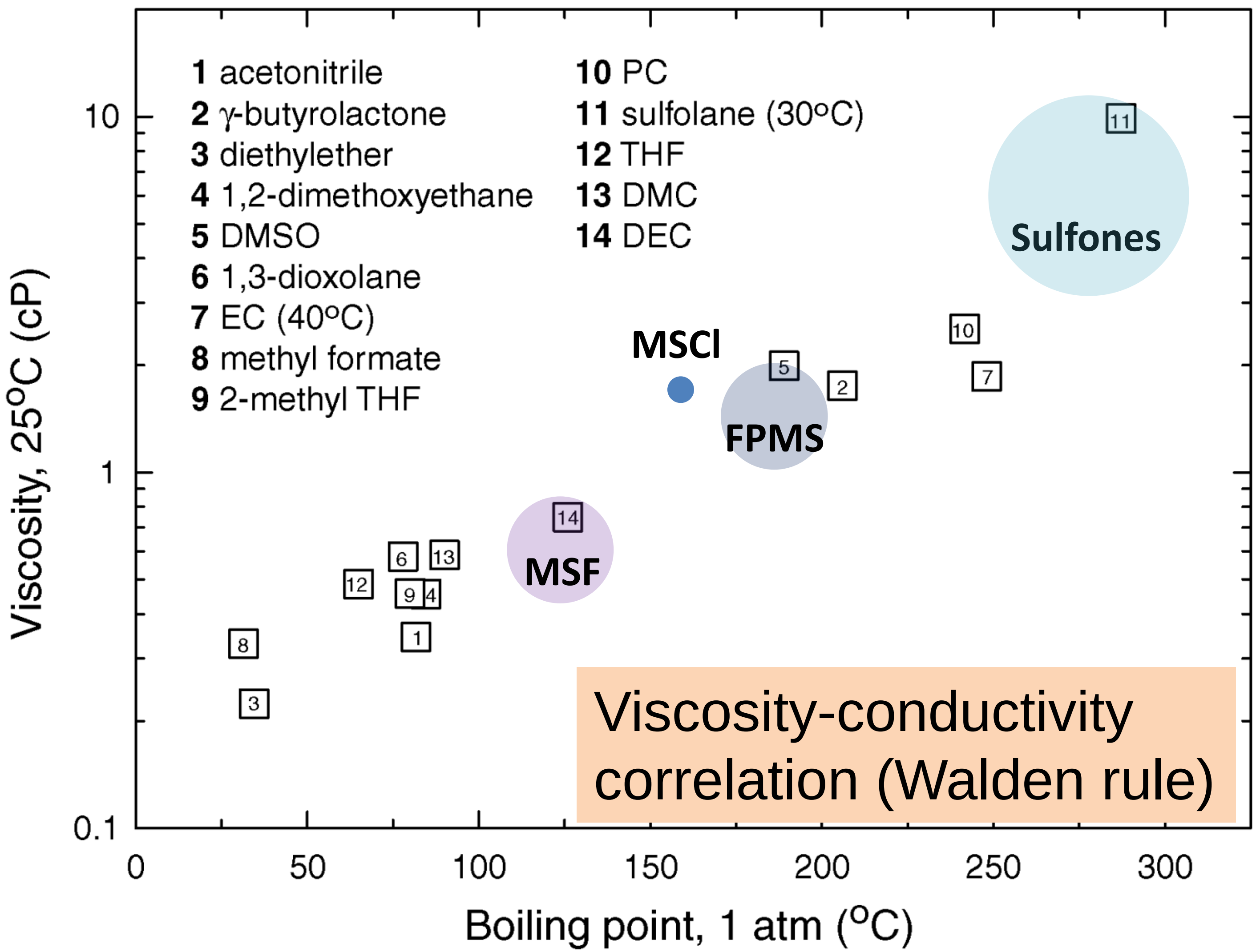
1. Identify unstudied sulfones for evaluation
2. Determine key properties, conductivity and "windows", taking any commercially available cases first.
   (a) pure sulfones (**Dec. 10, 2010**)
   (b) mixed sulfones
   (c) mixed sulfones and carbonates(**Dec. 10, 2010**)
3. Synthesize new sulfones
   (a) fluorinated (**March 11, 2011**)
   (b) fluorinated oxygenated (**March 11, 2011**)
4. Test sulfolane-based cases by synthesis, following predictions of collaborator (Oleg Borodin) (**March 11, 2011**)
5. Conceive new strategies (second year… achieved already)

6. Commence investigation of novel separator concept (**March 2011**)

SETTING UP: SELECTED SULFONES & THEIR PROPERTIES

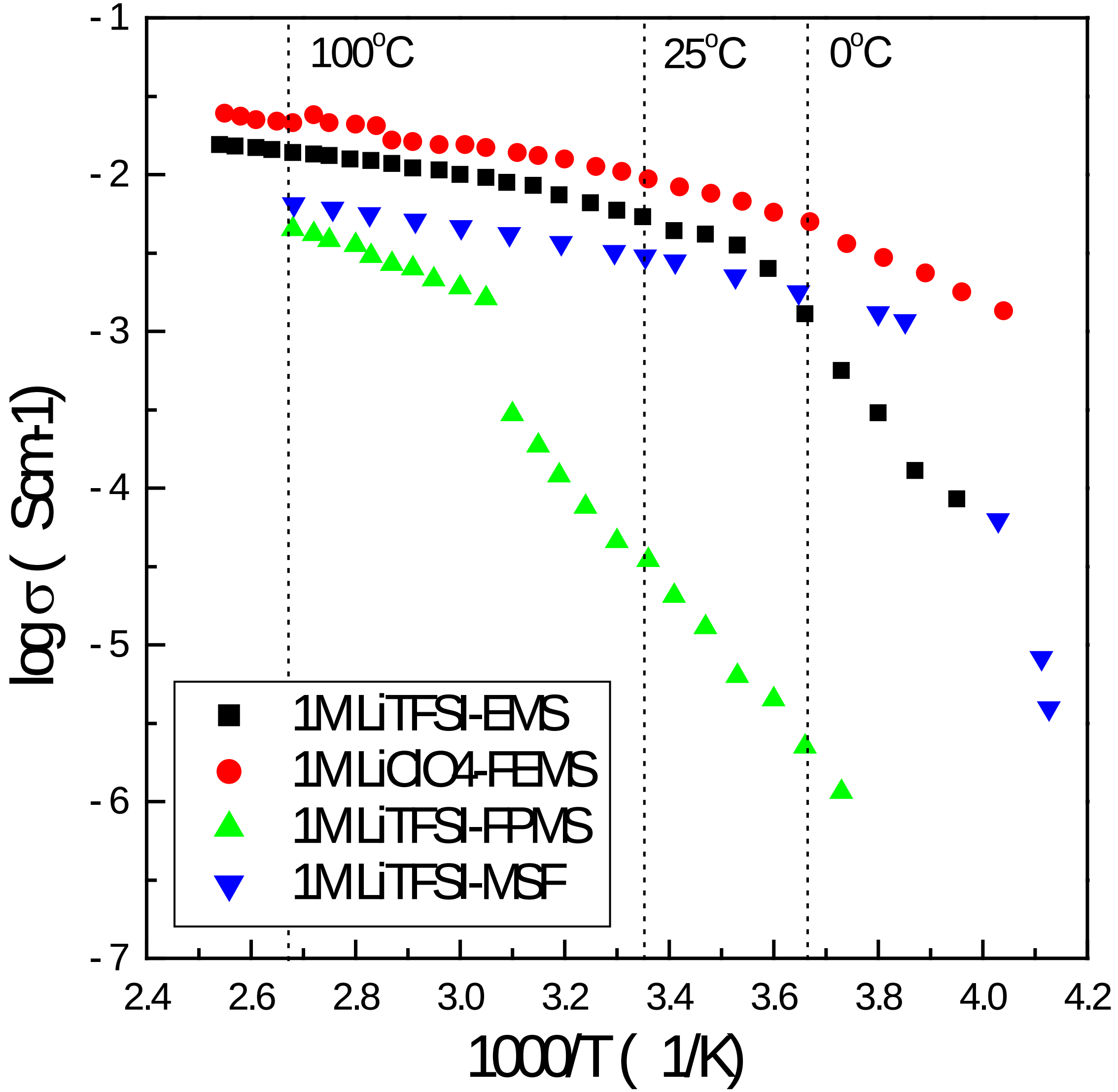
	Name	T_m (ºC)	T_b (ºC)	η (cP)	ε	σ_{25} (mS/cm)	Window (V vs Li/Li+)
	Dimethylsulfone (DMS)	110	(238)	-	-	-	-
	Methanesulfoneyl fluoride (MSF)	-	123	-	-	3.0 (1M LiTFSI)	5.3 /LiTFSI
	Methanesulfoneyl chloride (MSCl)	-33	160	1.97@25	-	-	3.7 /LiPF6
	Ethylmethylsulfone (EMS)	36.5	(240)	-	95	6.3 (1M LiTFSI) 3.2 (1M LiPF6)	5.9 /LiTFSI
	EMS-DMS eutectic (85:15 mol/mol)	25 (T_e)	-	-	-	2.2 (0.5 M LiTFSI)	-
	Methylpropylsulfone (PMS)	28	(245)	-	-	-	-
	Trifluoromethylmethylsulfone (FMMS)	-	130	-	-	-	-
	Trifluoroethylmethylsulfone (FEMS)	-	-	-	-	8.9 (1M LiClO4)	-
	Trifluoropropylmethylsulfone (FPMS)	56	180	-	-	0.035 (1M LiTFSI)	5.8 /LiPF6+DMC
	Sulfolane	27	285	10.1@30 31.2@30 (1M LiPF6)	60	3.1(1M LiTFSI) 2.5 (1M LiPF6)	5.8 /LiPF6
	3-fluorosulfolane	0.7	(303)	29.1@30 (1M LiPF6)	-	0.74 (1M LiPF6)	5.6 /LiPF6

Selection **strategies**: When no viscosity data? boiling point correlation



NEW DATA: Specific conductivities of various Li salts in sulfone solvents. The puzzle of low-boiling FPMS cf. MSF

ACCOMPLISHMENTS



The need for mixtures (see Xu review)

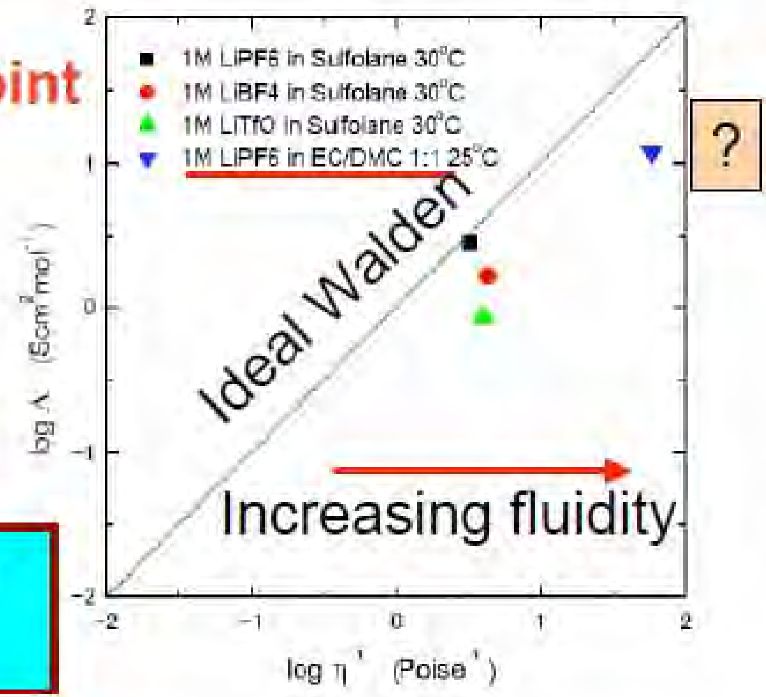
No single solvent can satisfy simultaneously all solvent needs

e.g Large dipole moment needed for overcoming crystal lattice energy (dissolving) causes high melting point and high viscosity, so low conductivity.

Resolution: mix with co-solvent of low dielectric constant and low boiling point. Thus EC-DMC

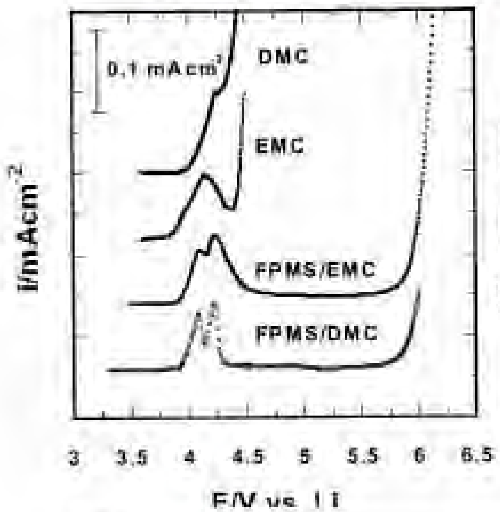
Mixing also reduces freezing point

Ionicity. How free are the ions from one another? Are we optimizing the decrease of viscosity, or losing some of the ions to associated pairs?

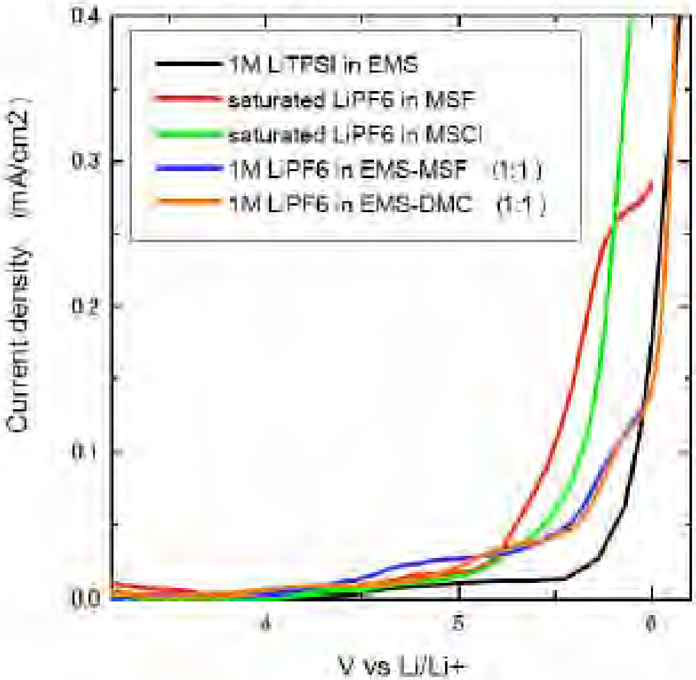


The first Walden plot for Li battery electrolytes

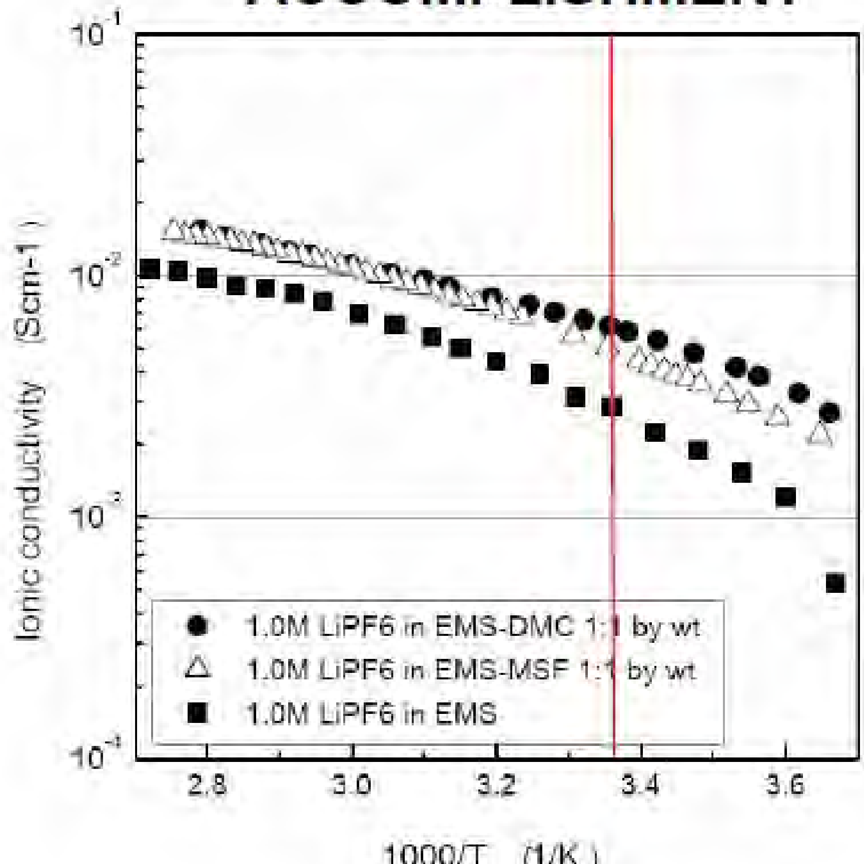
The mixture strategy: EMS vs new mixtures.



Earlier work from Kang Xu & CAA (JECS 2002) suggested mixture synergism



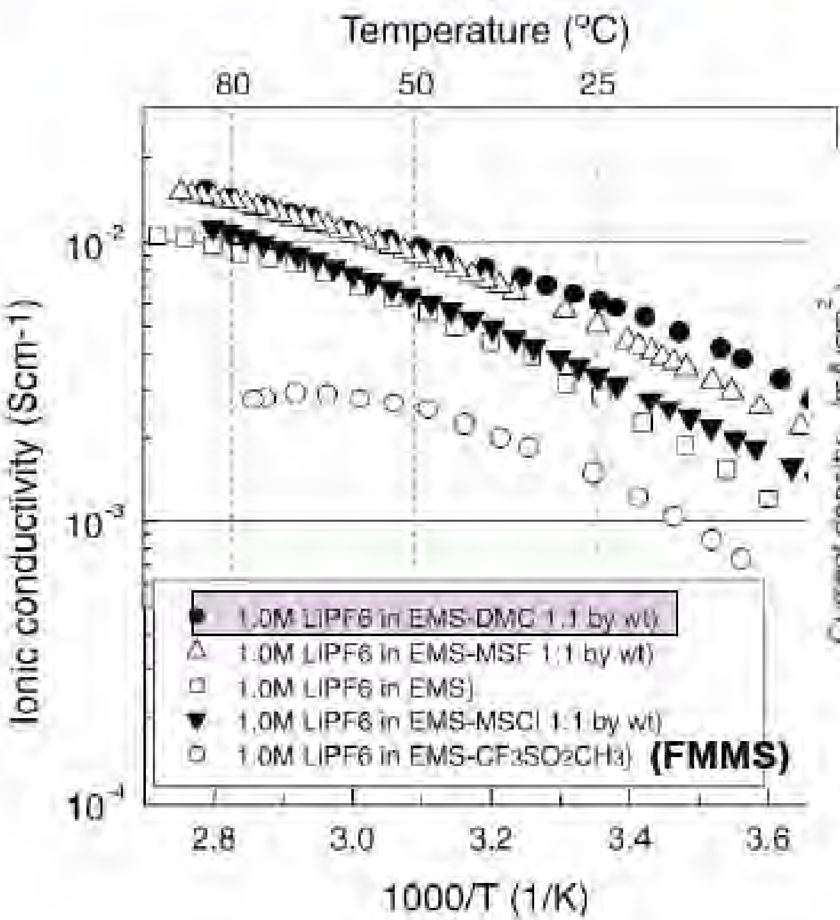
ACCOMPLISHMENT

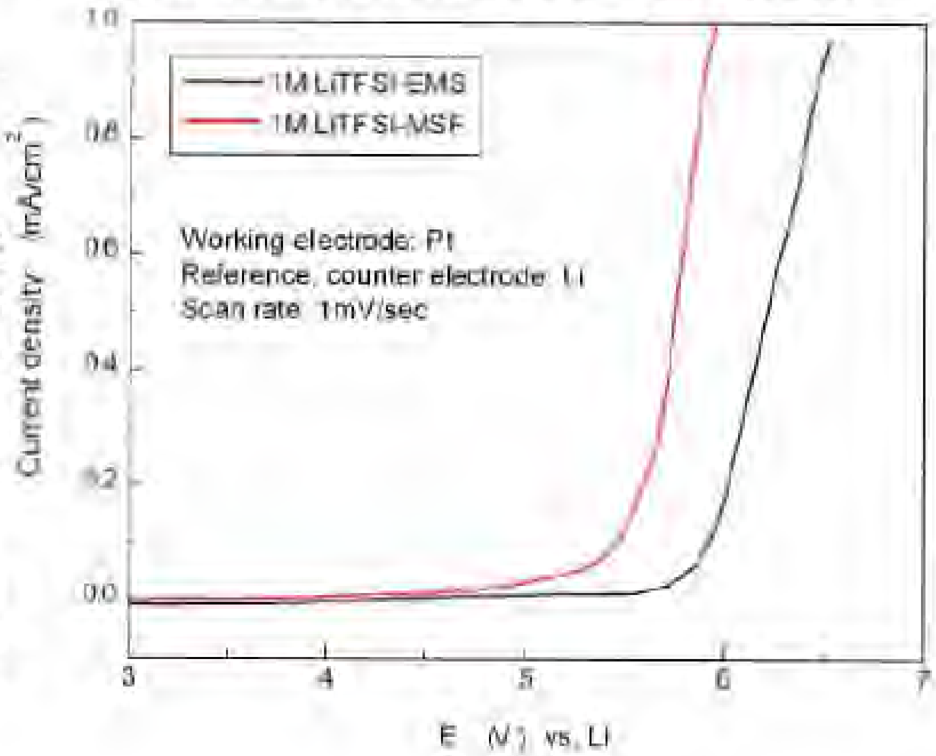


Other interesting mixtures
(with high fluidity MSF)

Accomplishment slide

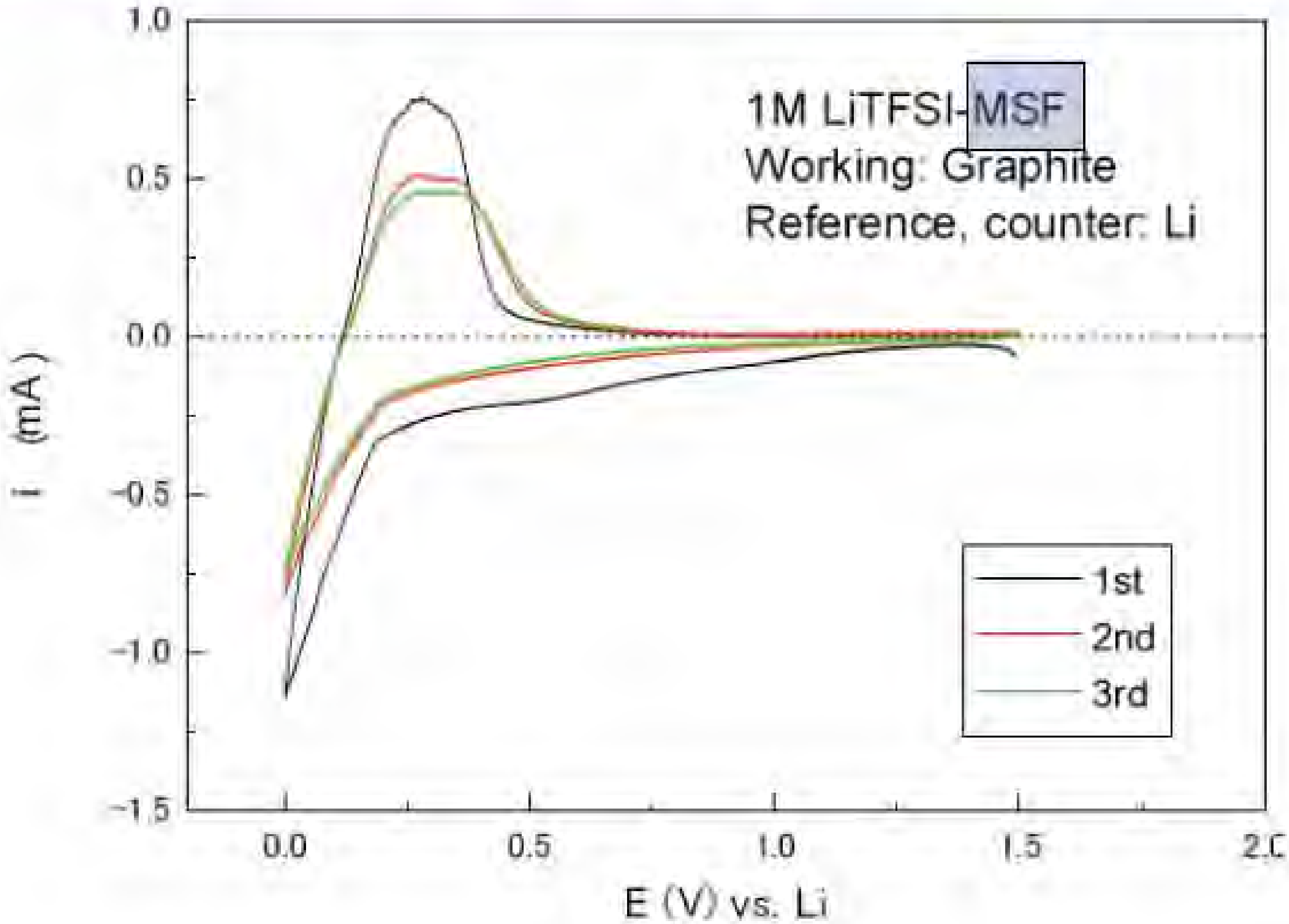
EMS-MSF not only has good conductivity and window, but also good Li deposition and stripping, i.e. good SEI (next)





ACCOMPLISHMENT SLIDE

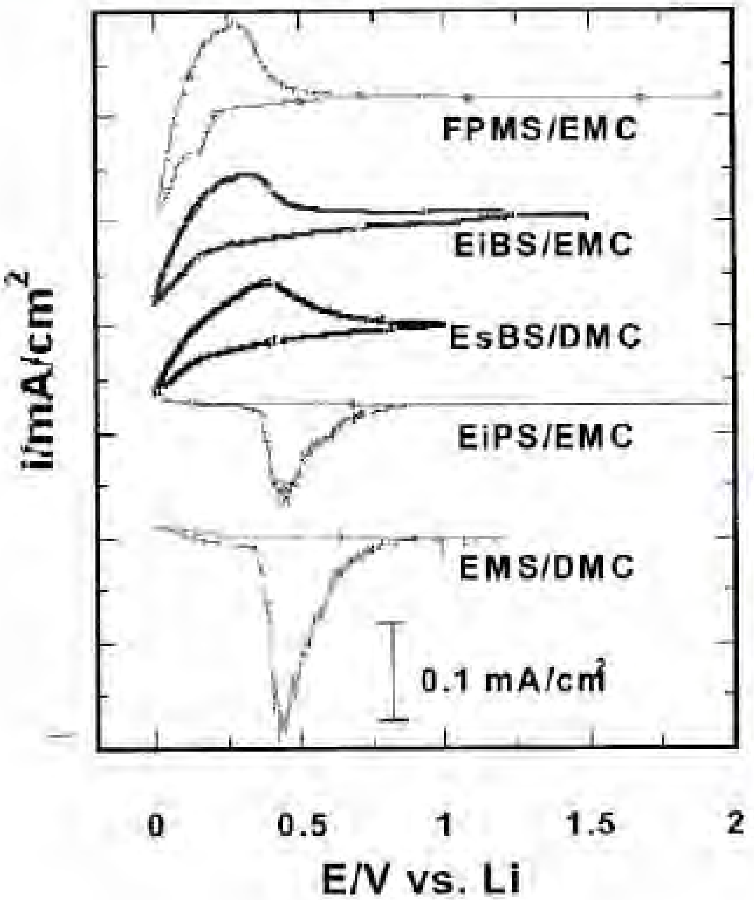
Lithium deposition and stripping in **MSF** & EMS-MSF solutions

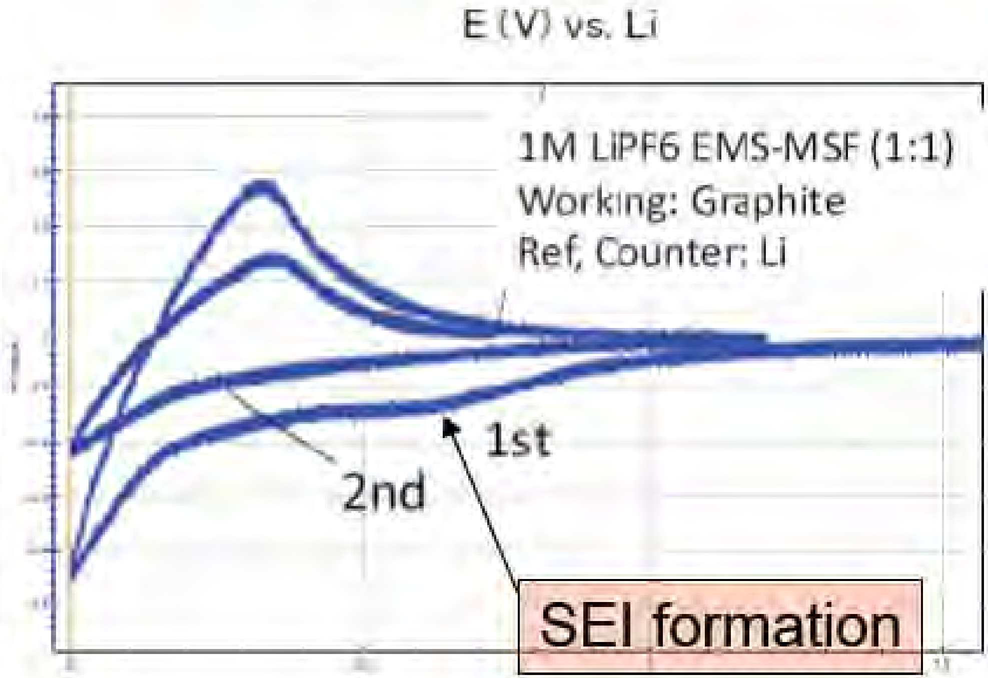


Lithium deposition and stripping in MSF & EMS-MSF solutions

From Xu and Angell JECS (2001)

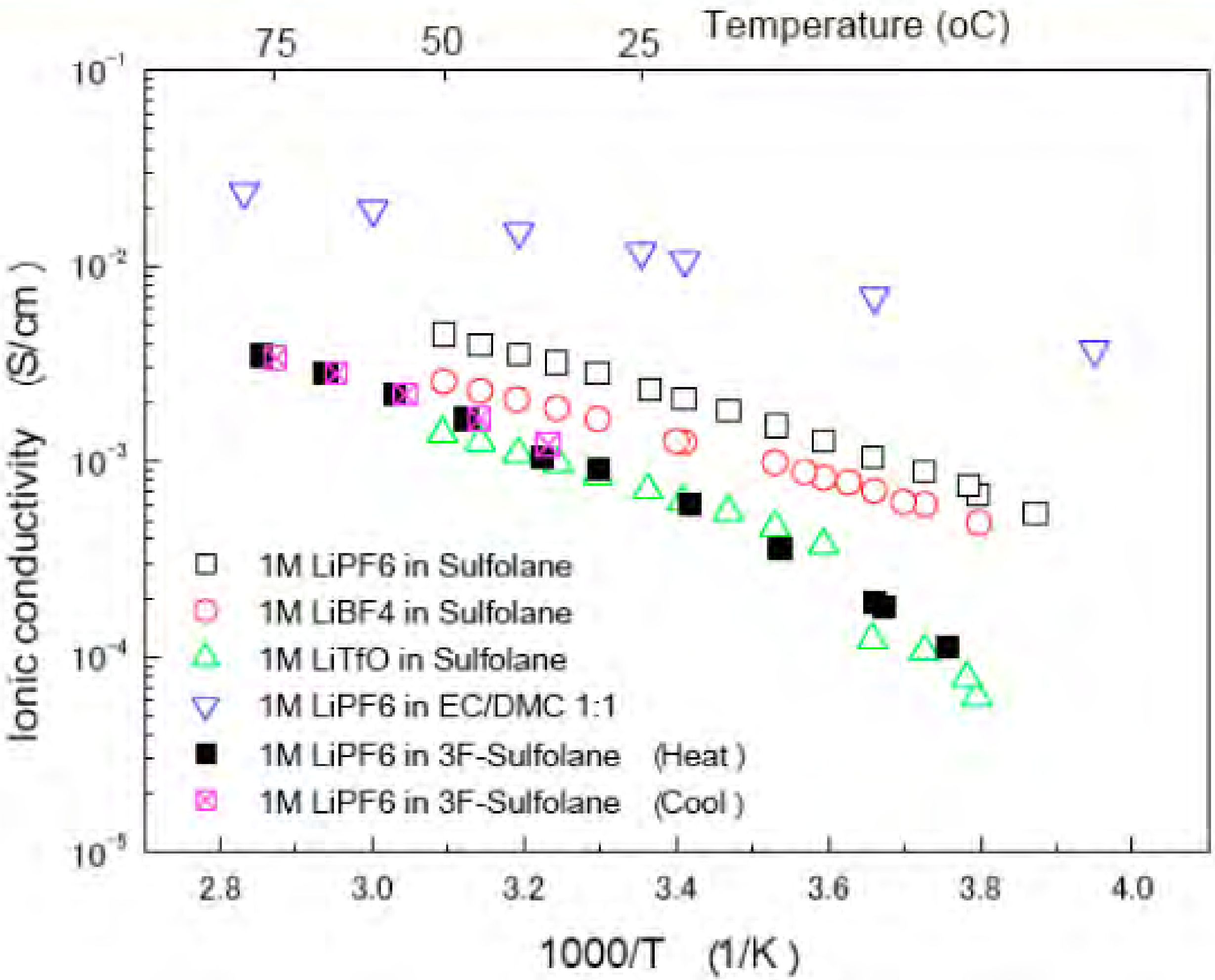
Accomplishment slide: formation of effective SEI in EMS-MSF solution





ACCOMPLISHMENT SLIDE

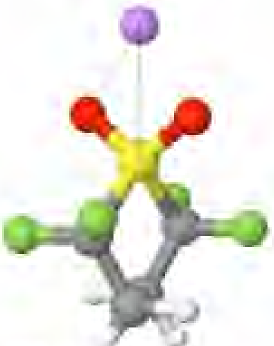
Conductivity Arrhenius plots for sulfolanes and fluorinated sulfolane, relative to EC:DMC. Can we improve on things with fluorination?



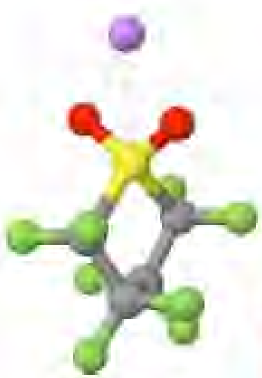
Fluorination can improve fire resistance

Contribution from Collaborating laboratory- **Oleg Borodin**

SL



SL(F_4)



SL(F_8)

Fluorinated Solvents

- ★ **Influence of sulfolane fluorination on the solvent oxidative stability, transport properties and its ability to coordinate Li^+ has been investigated complementing experimental studies that are currently performed by Austen Angell group (ASU)**

The Li^+/solvent binding energy (in kcal/mol) from QC					
	Li^+/SL	Li^+/SL(F_4)	Li^+/SL(F_8)	Li^+/EC	Li^+/DMC
MP2/cc-pvTz or ***MP2/aug-cc-pvTz***	-52.7	-40.8	-29.5	***-47.5***	***-40.9***
Solvent self-diffusion coefficient					
T (K)	303	303	303	313	298
D (10^{-10} m^2/s)	1.1	2.5	4.7	8	25.4

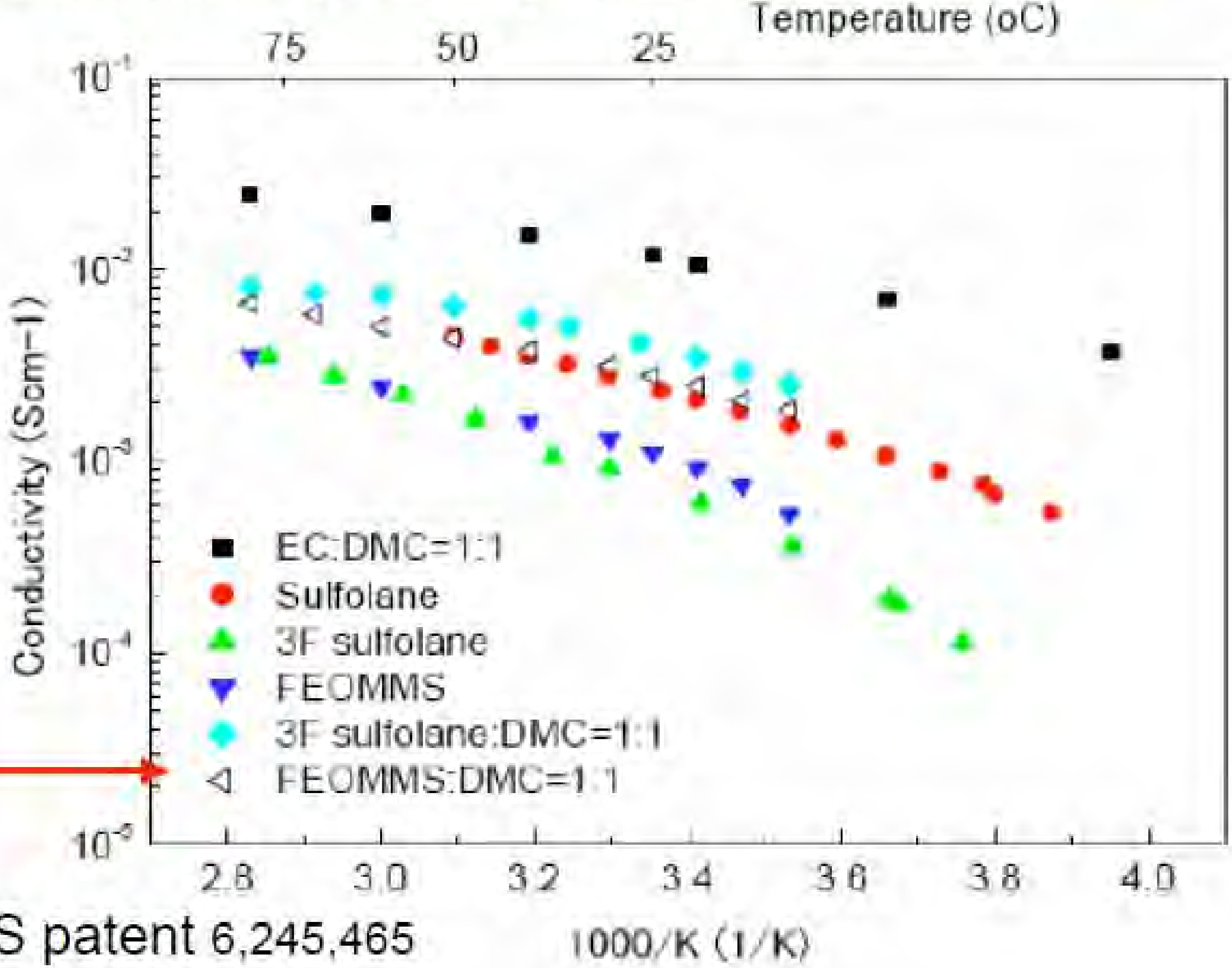
- ★ **Completely fluorinated SL(F_8) is not expected to be good solvent for typical Li salts such as $LiPF_6$ or LiTFSI.**
- ★ **Semifluorinated sulfolane SL(F_4) is expected to have lithium salt dissociation similar to DMC, while SL(F_4) dynamics is predicted to be a factor of 2.5 faster than SL but a factor of five slower than DMC.**

OTHER COLLABORATIONS: The order-disorder transition in $LiNi_xMn_{2-x}O_4$ (with **Guoying Chen**, LBL)

ACCOMPLISHMENT/COLLABORATION SLIDE

Sulfolane-based systems

With **collaboration of Oleg Borodin** (U. Utah)



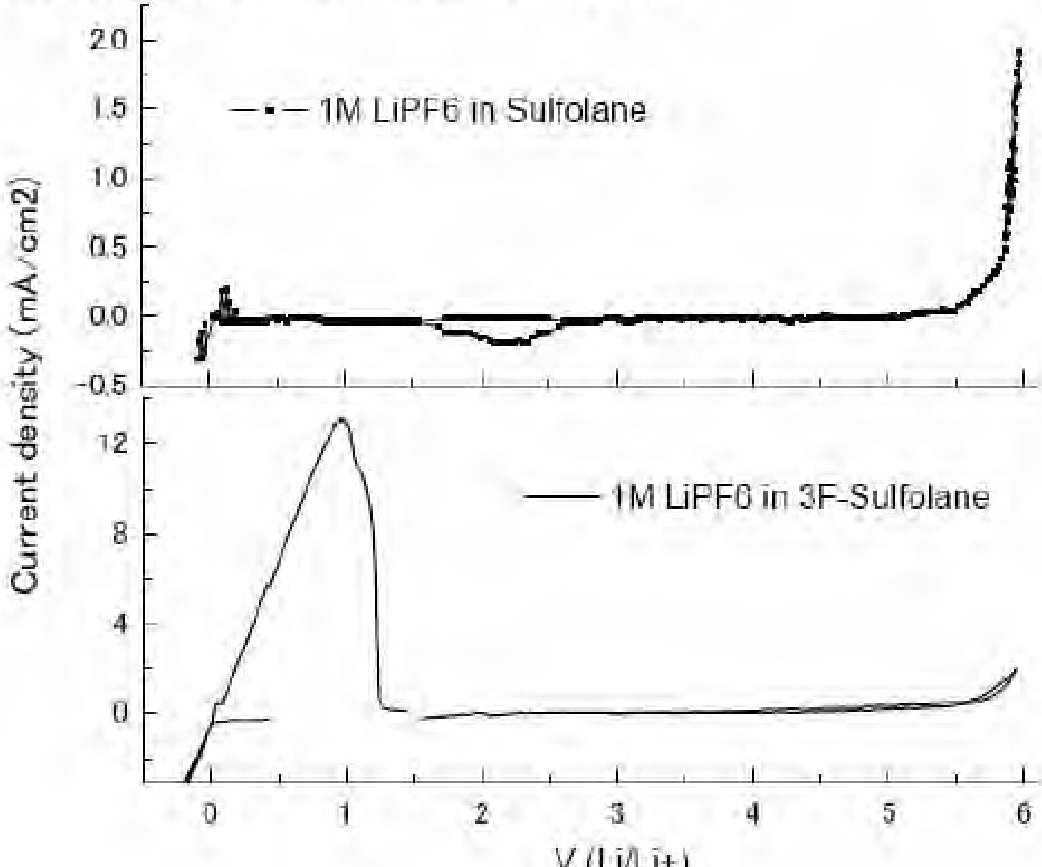
And a fluorinated ethersulfone

Follow-up of US patent 6,245,465

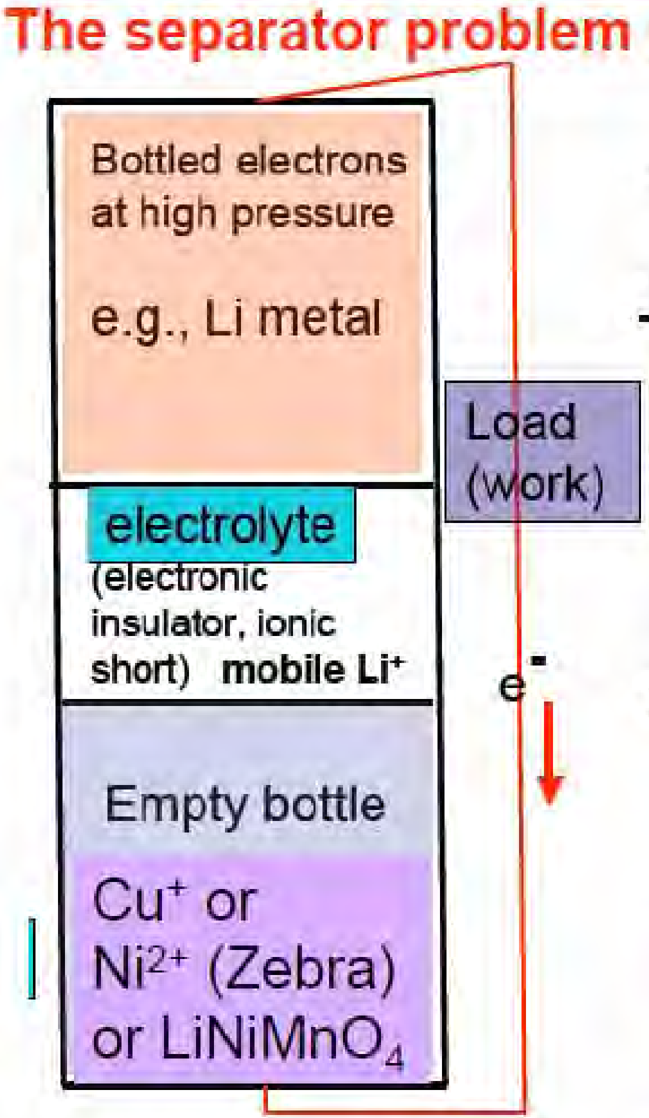
ACCOMPLISHMENT SLIDE

Good electrochemical aspects of fluorinated sulfolane

- Complete deposition and subsequent stripping of Li in fluorinated sulfone. No extraneous processes.
- Excellent wide electrochemical window



NEXT: Keeping the electrolyte in place



Electrolyte is mobile liquid: It can be kept in the right place by

1. soaking it up in some sort of sponge:porous medium with wettable surfaces,
2. or creating a solid around it by using a polymerizing component which is then reacted.

EXAMPLES

1. Celgard is a microporous polypropylene membrane surface-derivatized to soak up carbonate solvents.
2. **methacrylate** can be added to the electrolyte and then thermally, or by light, polymerized to create a gel (costs conductivity)

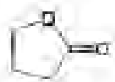
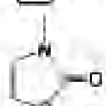
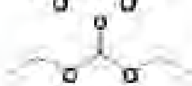
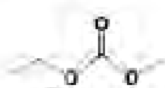
NOW: a novel solution - nanoporous membrane strategy: the Maxwell slat net by rigidity percolation.

TECHNICAL BACKUP SLIDES

From K. Xu, Chem. Reviews

Chem. Rev. **2004**, *104*, 4303–4417

Organic Carbonates and Esters as Electrolyte Solvents

Solvent	Structure	M. Wt	T_m/ °C	T_b/ °C	η/cP 25 °C	ε 25 °C	Dipole Moment/debye	T_f/ °C	d/gcm^{-3}, 25 °C
EC		88	36.4	248	1.90 (40 °C)	89.78	4.61	160	1.321
PC		102	-48.8	242	2.53	64.92	4.81	132	1.200
BC		116	-53	240	3.2	53			
γBL		86	-43.5	204	1.73	39	4.23	97	1.199
γVL		100	-31	208	2.0	34	4.29	81	1.057
NMO		101	15	270	2.5	78	4.52	110	1.17
DMC		90	4.6	91	0.59 (20 °C)	3.107	0.76	18	1.063
DEC		118	-74.3[a]	126	0.75	2.805	0.96	31	0.969
EMC		104	-53	110	0.65	2.958	0.89		1.006
EA		88	-84	77	0.45	6.02		-3	0.902
MB		102	-84	102	0.6			11	0.898
EB		116	-93	120	0.71			19	0.878

Issues with liquid electrolytes

1. Ionic shorts…. Wot to do?

2. With in situ polymerization to yield gel, the conductivity decrease always seems to be larger than tortuosity constants would e expected to account for.

3. Conductivity reduction: with celgard the reduction in conductivity should just decrease by a tortuosity factor

4. A new idea, the variable nanoporous net the Maxwell rigidity, and the Phillips-Thorpe rigidity percolation model