New lithium-based ionic liquid electrolytes that resist salt concentration polarization

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Purpose of the Work

- ***<u>Synthesize</u>* lithiated ionic melt (IM) electrolytes with low-lattice-energy anions attached to a suitable solvating matrix (e.g. a polyether);**
- ***<u>Characterize</u>* electrolytes with respect to structure, transport properties, reactivity, and charge-discharge behavior in graphite / electrolyte / cathode cells.**

- ***<u>Starting in Nov 2007</u>; <u>Synthesize</u> fluorosulfonimide ionomers in lithiated form (LiFSI) as dispersions in solvent;**
- ***<u>Fabricate</u> high-voltage cathodes using LiFSI ionomers as binders and/or integral electrolytes;**
- ***<u>Characterize</u> the resulting cathodes with respect to initial capacity, high-rate charging / discharging capability, and capacity fade.**

Barriers

- ***Poor electrolyte transport properties (conductivity, salt diffusion)***
- ***Low capacity***
- ***Capacity fade***
- ***Low power***
- ***Short life***
- ***Abuse tolerance***

Approach

- ***Electrolytes are synthesized using variants of methods develop at Clemson over the past 20 years. Specific approaches include;***
  - ***Coupling reactions between trifluorovinyl ether lithium salts and (i) aliphatic alcohols (ii) aryl halides; and (iii) imidazole.***
  - ***Emulsion co-polymerization reactions of trifluorovinyl ether lithium salt monomers with tetrafluoroethylene***
- ***Characterization with respect to structure and electrochemical properties is accomplished using NMR (^{1}H, ^{19}F), IR, thermal analysis, LC / ESI-MS, impedance spectroscopy, voltammetry, and DC polarization.***
- ***Cell testing utilized Li / graphite / $Li_4Ti_5O_{12}$ anodes and $LiCoO_2$ cathodes in small-scale Swage-style cells, following conventional protocols.***

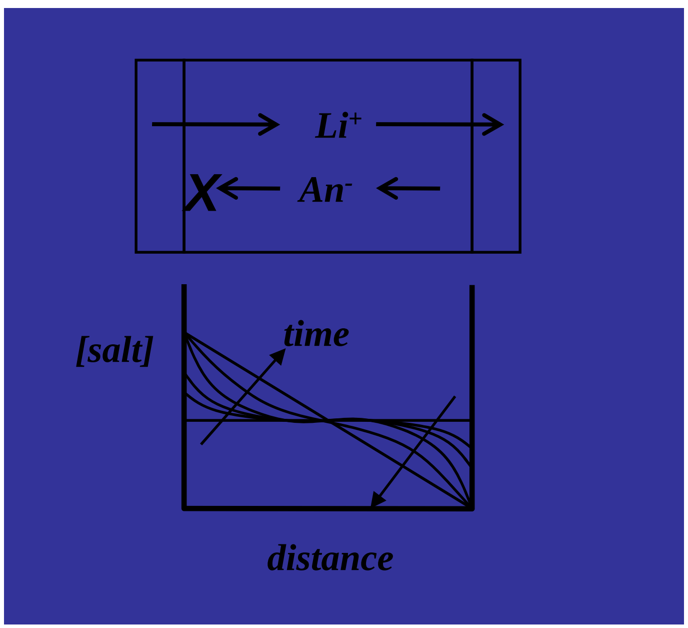
Technical Accomplishments

Part 1. Polyether-based ionic liquids with lithium as the only mobile cation

Salt concentration polarization in battery electrolytes

***Ideally*, $t_{Li+} = 1.0$** → ***Really*, t_{Li+} usually < 1.0**

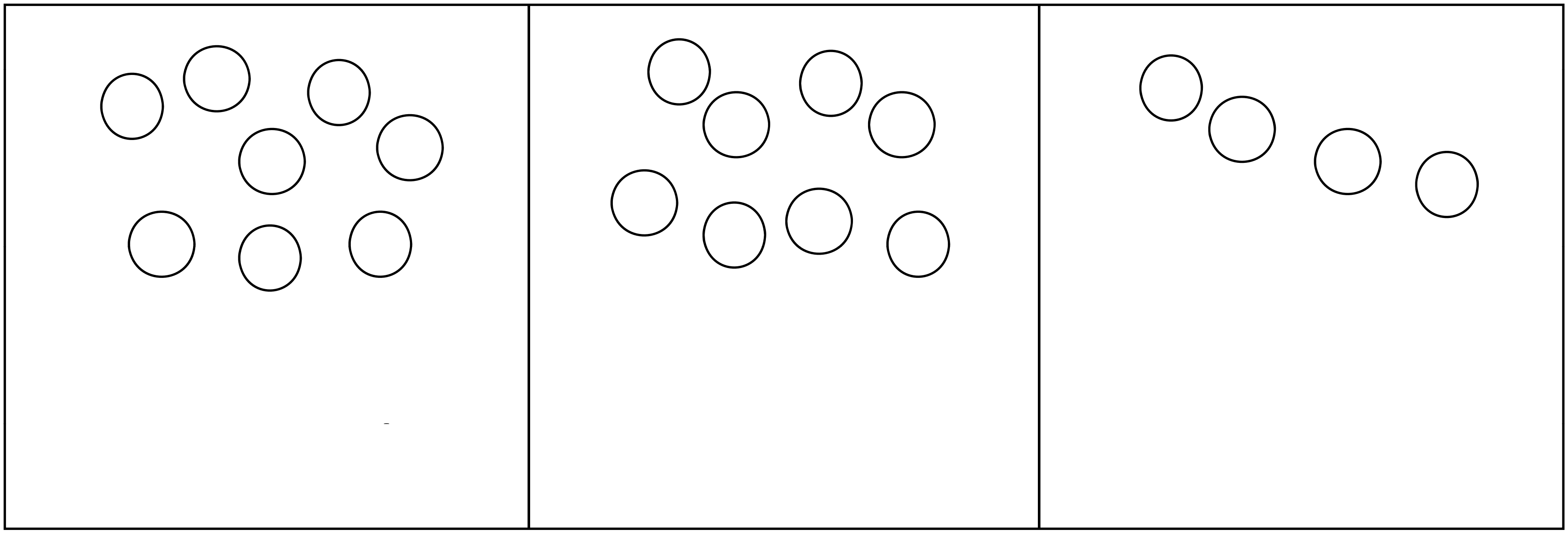
Low Li transference causes salt concentration polarization which is associated with anion motion in the electrolyte, coupled with electrodes that are blocking toward the anions.



Problems with salt concentration for battery operation include they following:

- ***Diminished overall electrolyte conductance***
- ***Nernstian voltage losses at electrodes***
- ***Salt precipitation***
- ***Lithium deposition on current reversal***
- ***Limiting current behavior***

Electrolyte architecture and salt concentration polarization

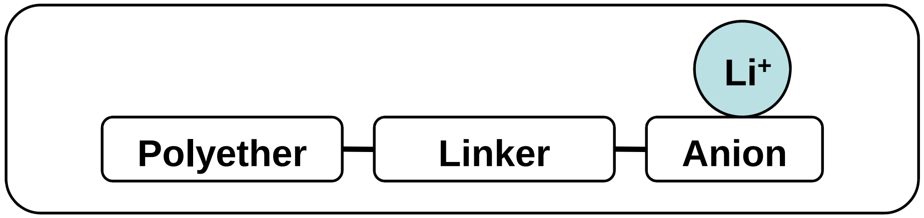


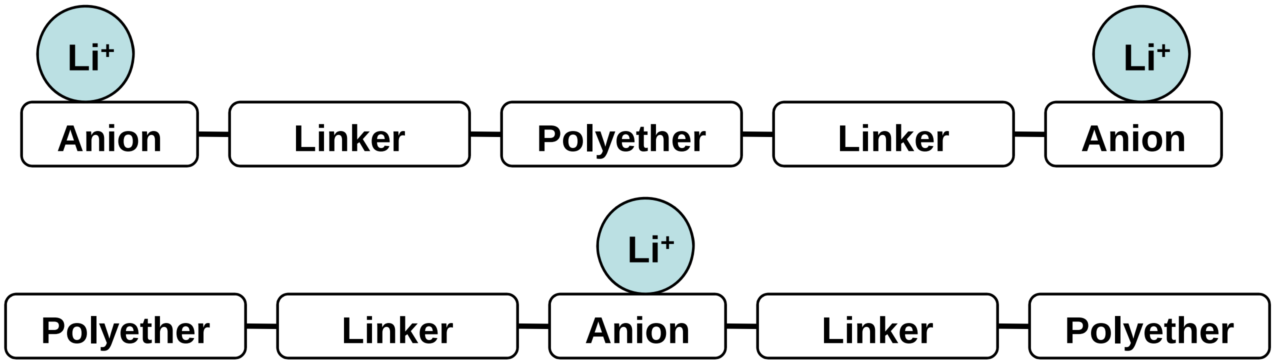
Anions and cations can both move. High conductivity but subject to salt concentration polarization.

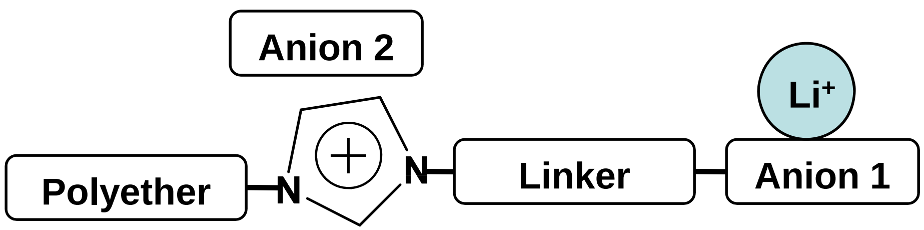
Only Li ions can move. High Li transference but conductivity is often low.

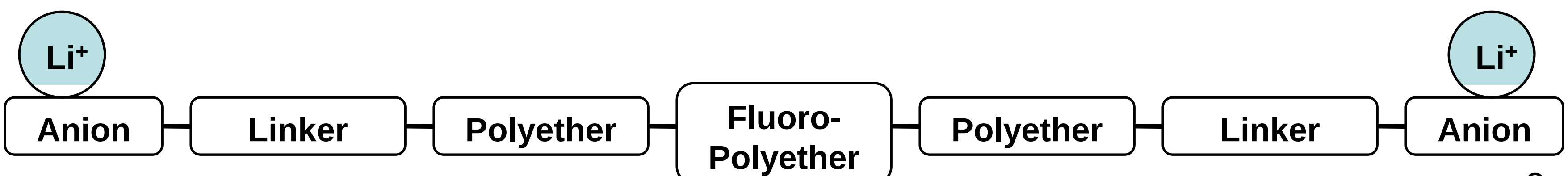
Anions and cations can both move…but salt concentration polarization cannot occur! Salt concentration is fixed by melt density.

Representative Ionic Liquid Structures





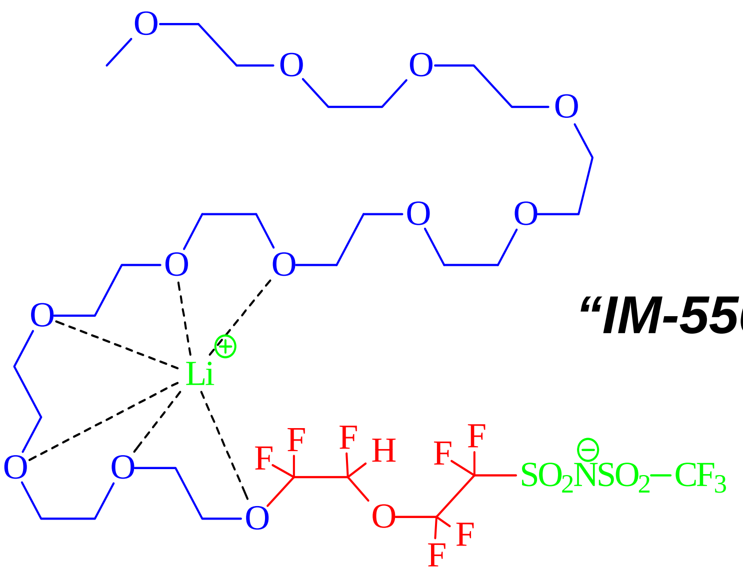




Lithium-based ionic liquid / melt electrolytes

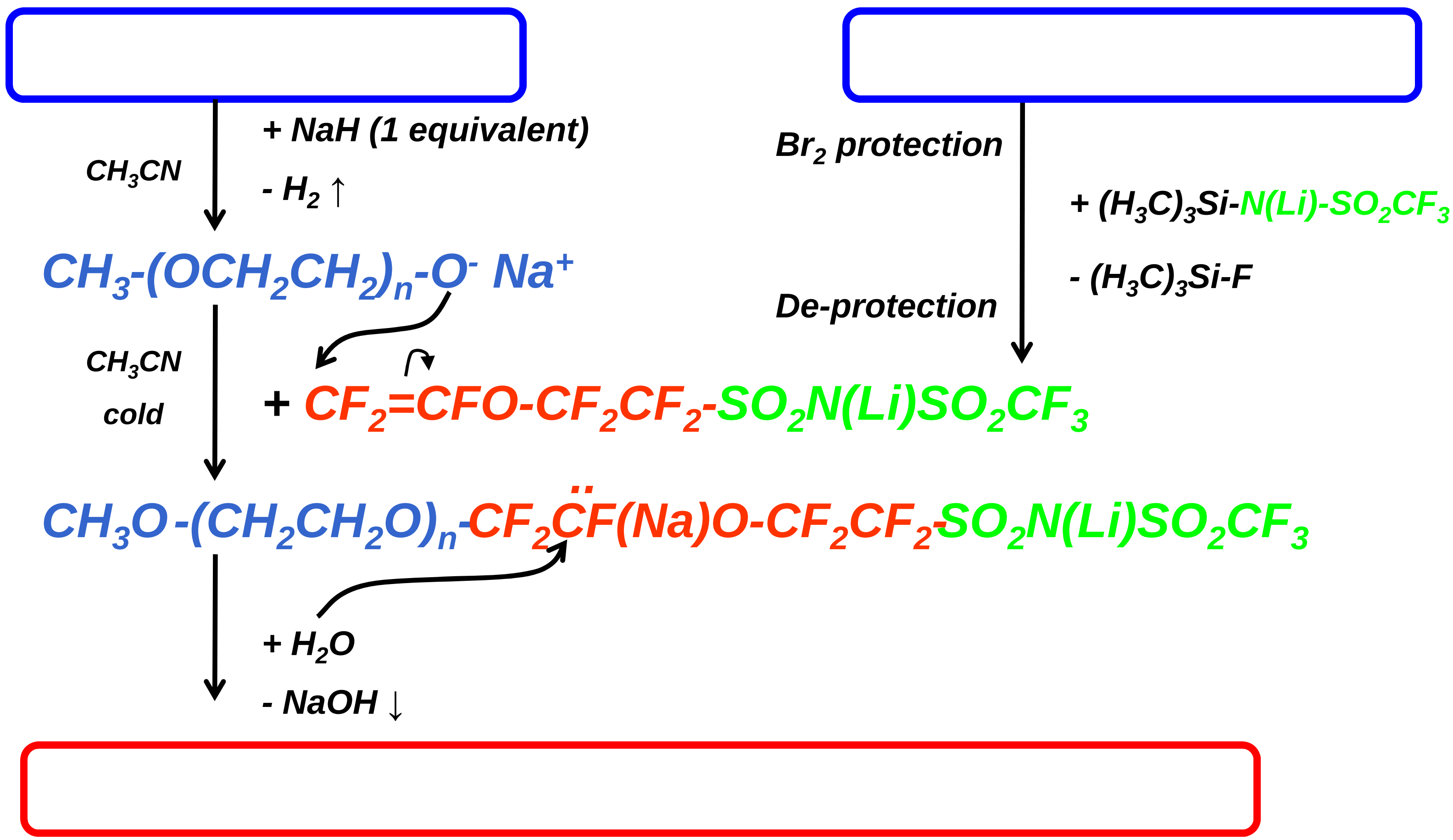
<u>Key features;</u>

- ***A low-lattice-energy anion coupled to a lithium-solvating polyether chain***
- ***Ionic liquids for which <u>lithium is the only mobile cation</u>***
- ***These are high-viscosity liquids relative to conventional solvents, but they are liquids none-the-less***



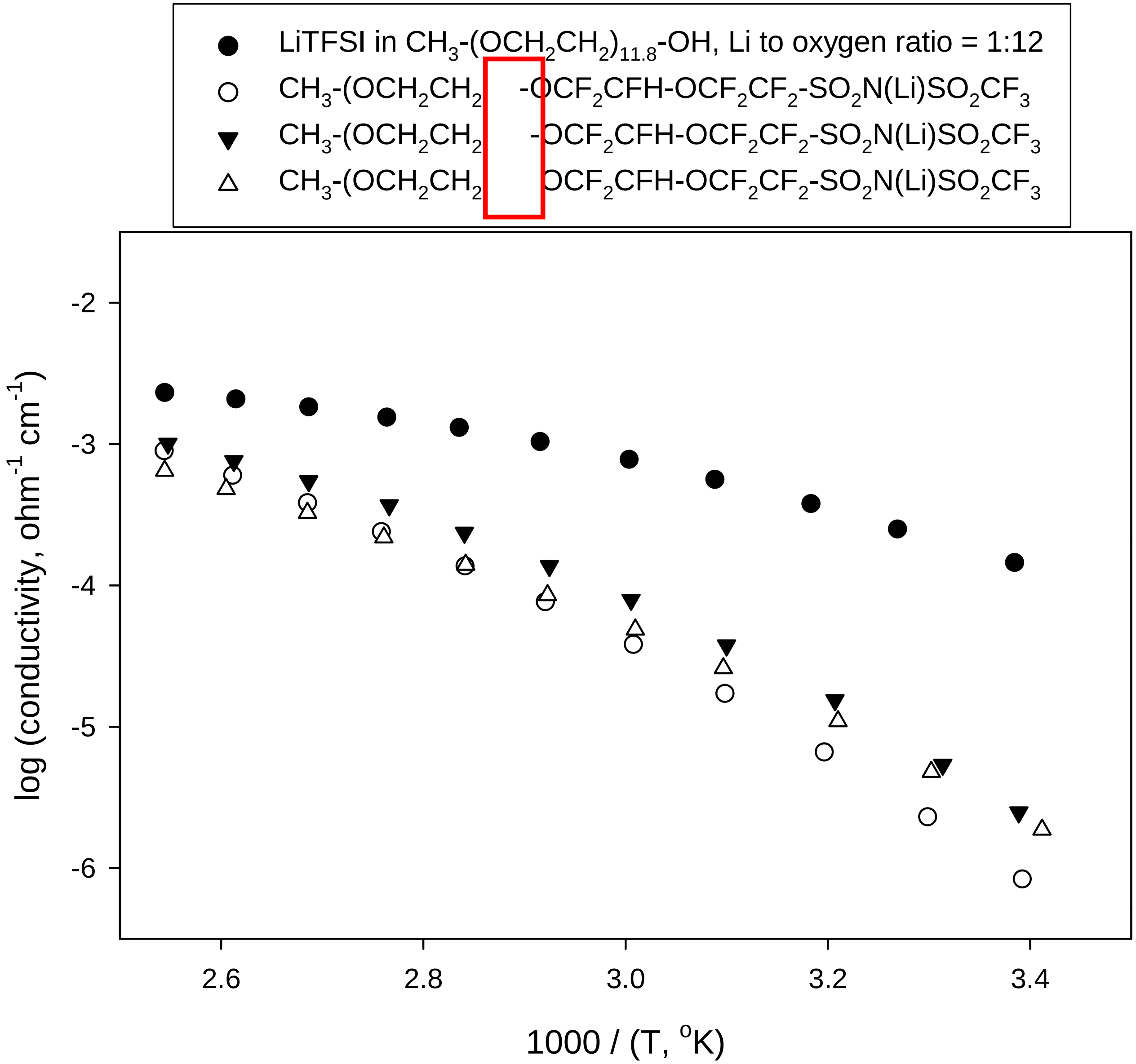
"IM-550"

Synthesis from polyethylene glycol and trifluorovinyl ether sulfonyl fluoride

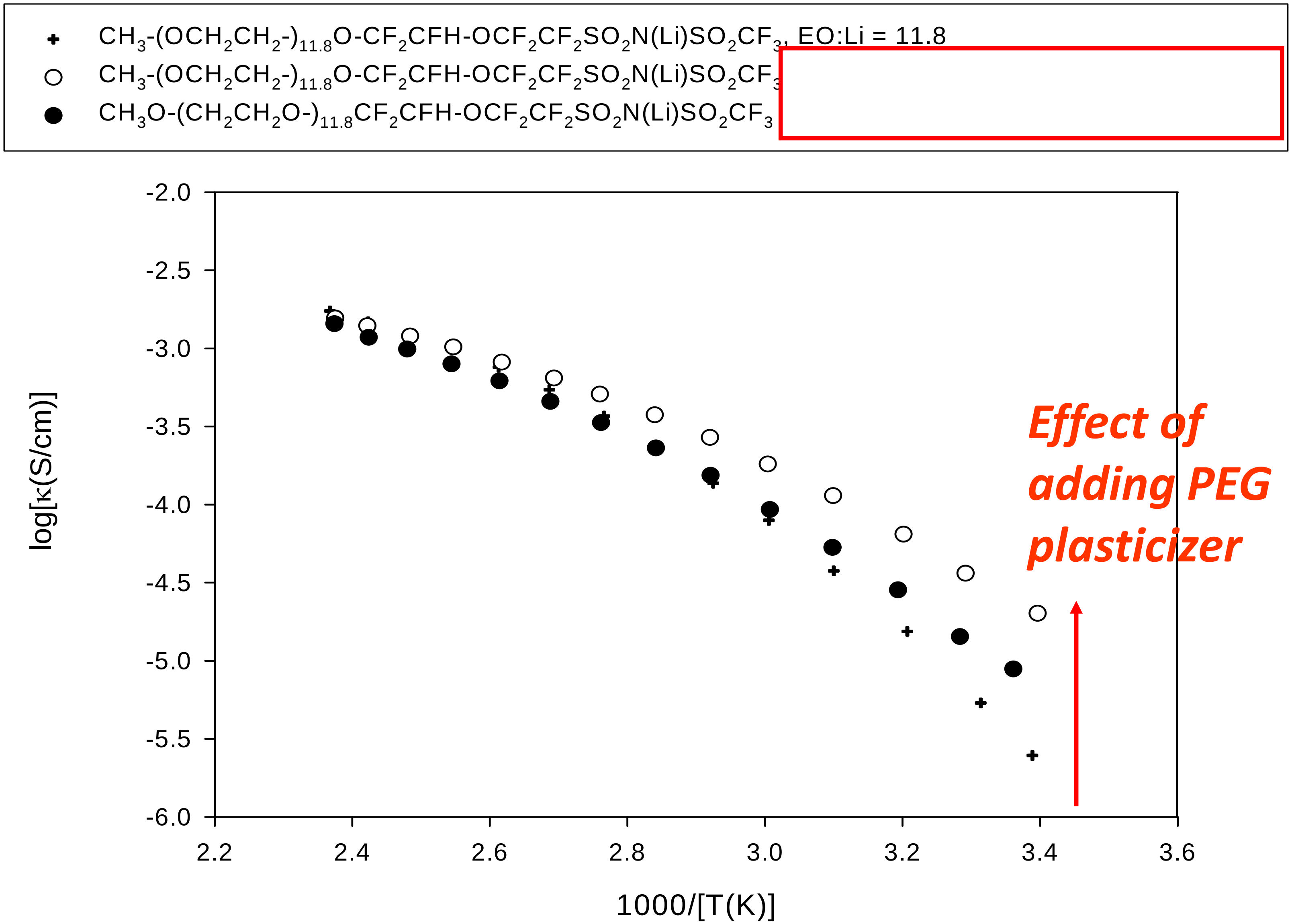


For IM550, n = 11.8

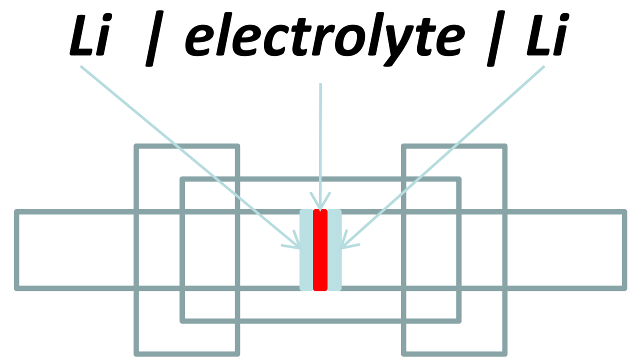
Ionic conductivity

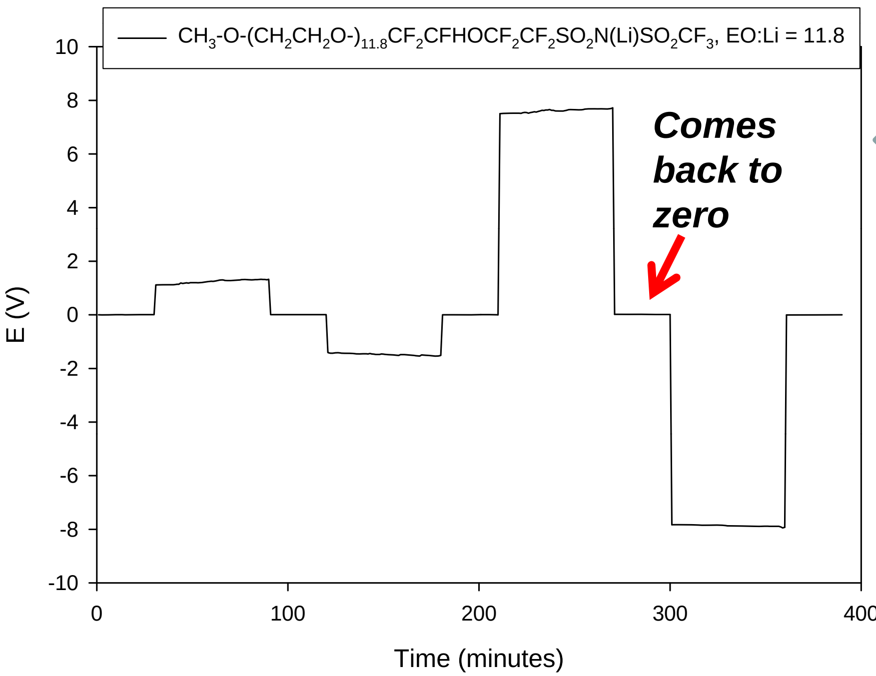


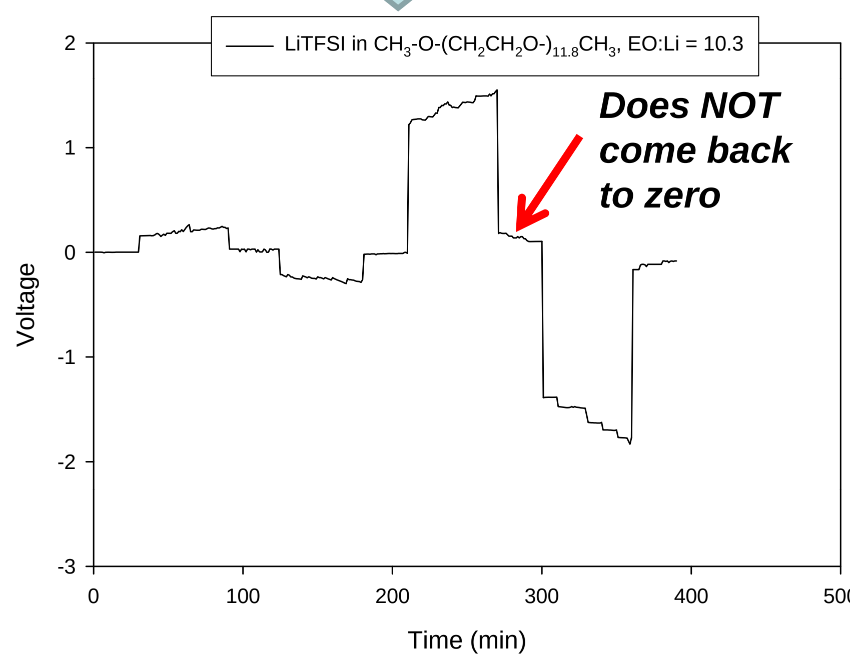
Ionic conductivity



DC polarization studies







Currents = 10 μA and 50 μA
Data recorded every 5 sec but points are shown only every 1 min.

Cell Charging - Discharging

$Li_4Ti_5O_{12}$ | IM550 electrolyte | $LiCoO_2$

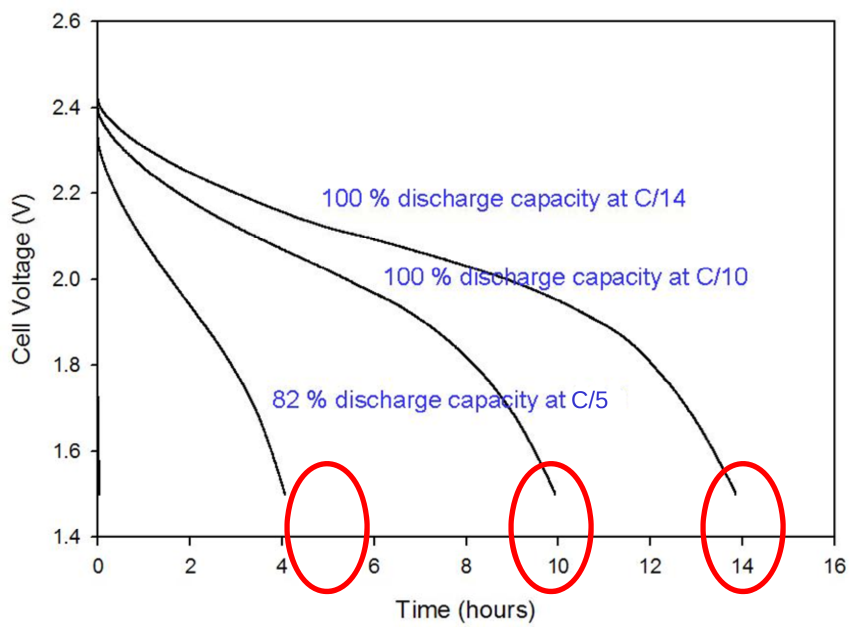
Cell capacity approx. 0.3 mAh
CC charging at C/100, room temperature

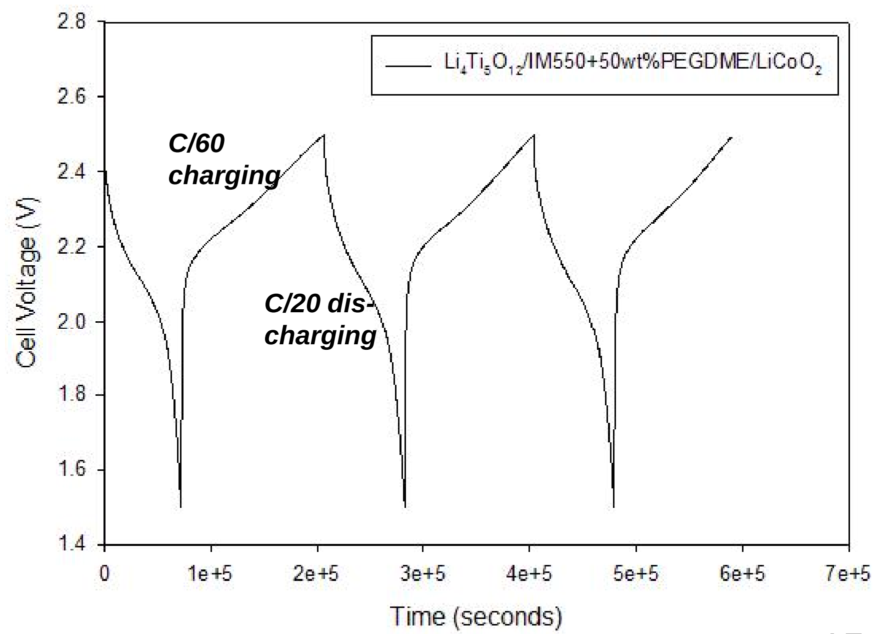
- ***Full charge capacity was never achieved even after very long charging times at low current.***
- ***Attempts at discharging gave low capacity even at very low rates.***
- ***These facts are thought to reflect a combination of ohmic losses in the bulk electrolyte, and poor wetting of the electrode(s) by the IM550 electrolyte.***

Cell Charging - Discharging

$Li_4Ti_5O_{12}$ | IM550 electrolyte + PEGDME plasticizer | $LiCoO_2$ + Fluorolink electrolyte

- ***Cell capacity approx. 0.3 mAh***
- ***CC charging @ C/100 - 100% capacity achieved;***
- ***Discharging @ C/20, C/14 and C/10, full capacity achieved***
- ***Discharging @ C/5 and 1C achieved 82 and 4%, respectively;***
- ***100% reversible capacity was achieved upon 3 cycles.***





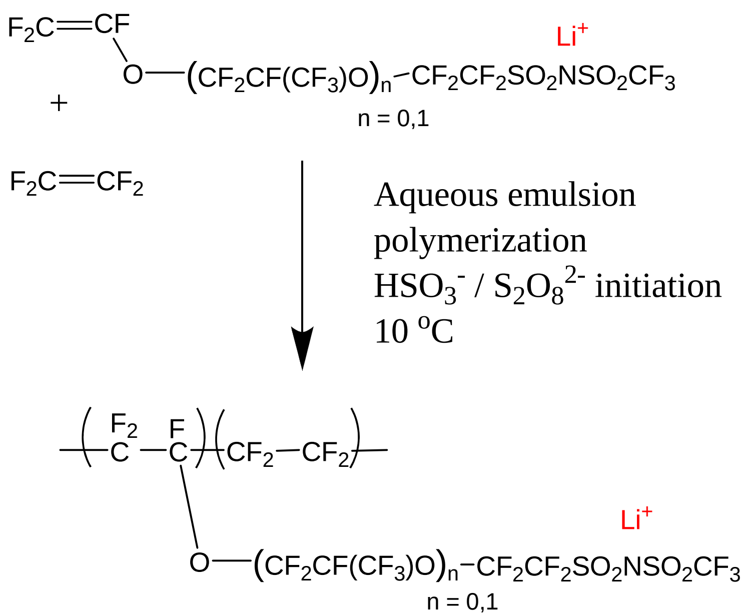
Summary of Part 1

- ***Many ionic liquids with lithium as the only mobile cation were synthesized and characterized.***
- ***Salt concentration polarization was prevented as DC current passed through these electrolytes via non-blocking electrodes for lithium (i.e. Li^0)***
- ***Cell charging / discharging was achieved in cells with these electroltyes but only at relatively low rates.***
- ***Electrolytes with added plasticizers and electrodes containing electrol yte in the binder performed best***
- ***Use of polymer electrolytes in the electrodes may offer a route forward to achieving high power, high capacity utilization, and low capacity fade***

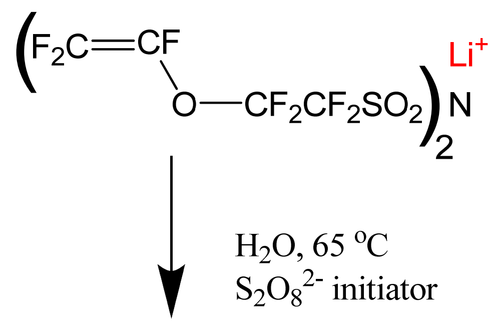
Technical Accomplishment

Part 2. Lithiated fluoropolymer electrolytes as battery cathode binders

Lithiated fluoropolymer ionomers for use as cathode binders

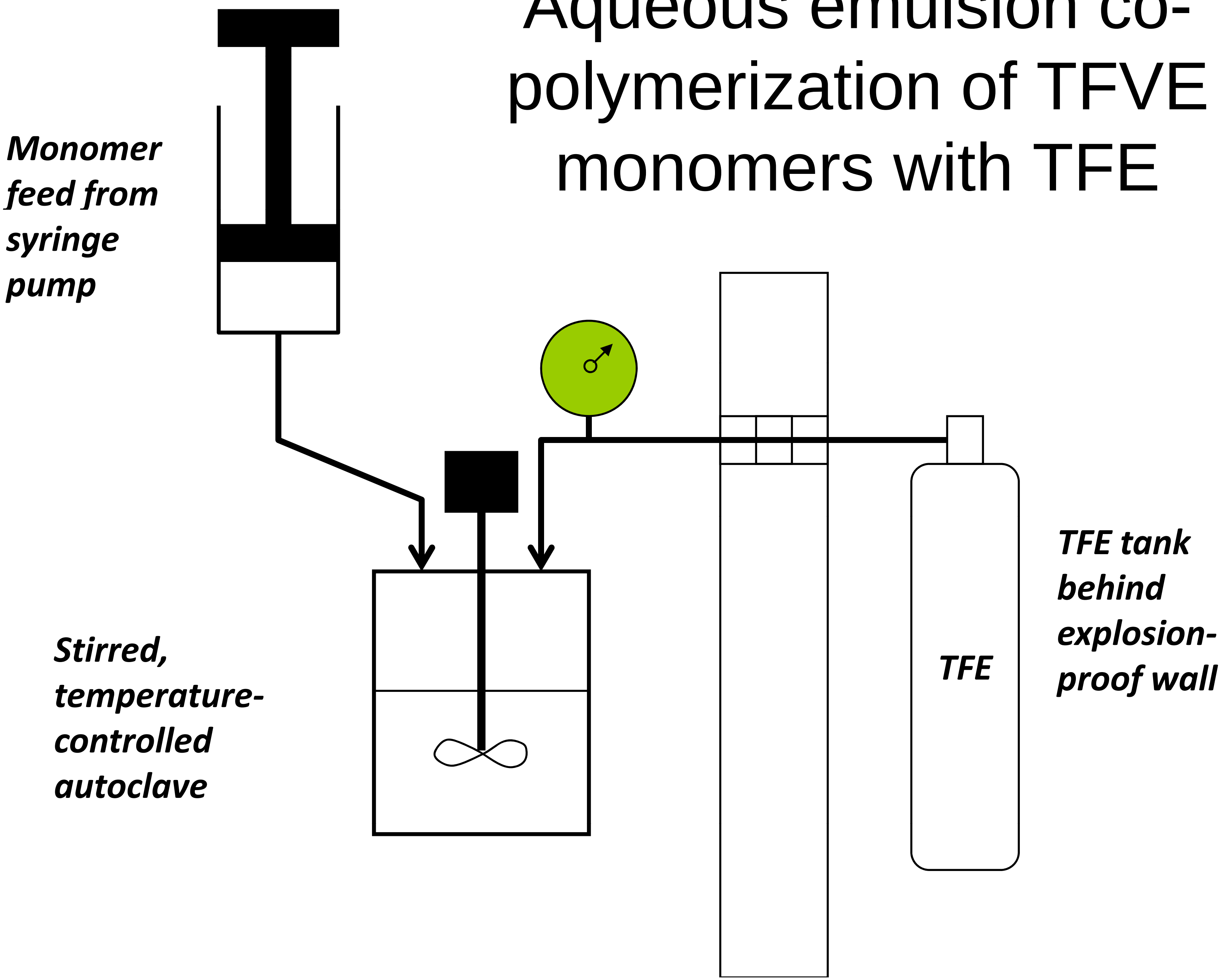


TFE co-polymer ionomer



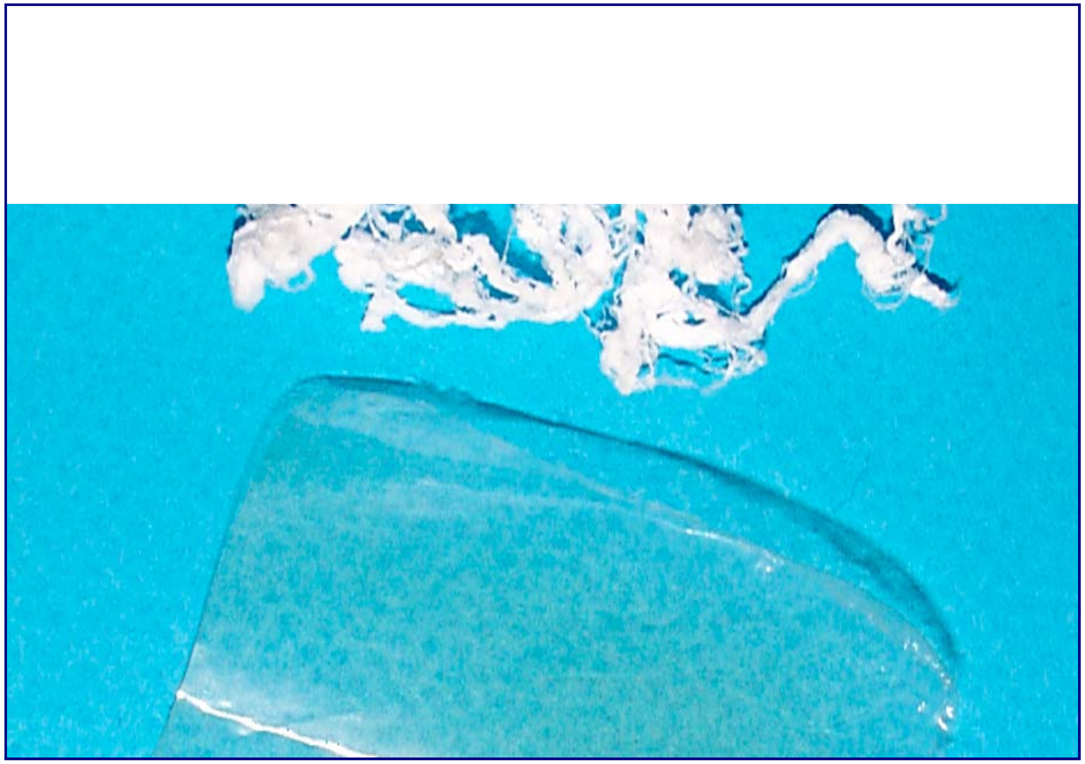
Homopolymer Ionomer

Aqueous emulsion co-polymerization of TFVE monomers with TFE



Fluoropolymer Ionomers

- ***The bulk polymer is typically a fibrous white solid which can be solution-cast into clear membranes.***
- ***Dissolution into polar organic solvents is readily accomplished using high temperature / pressure in an autoclave***



Summary of Part 2

- ***Lithiated electrolytes comprised of low-lattice-energy anions on a fluoropolymer backbone have been synthesized and are available for use in formulating high-voltage cathodes.***
- ***Improved performance is expected in terms of high-rate charge/discharge, capacity utilization, and capacity fade.***

Response to BATT review from June 2006

Comment: ***Poor conductivity, not relevant to low-T requirements***

Response: ***Conductivity is high relative to most polyether and polymer electrolytes but low relative to conventional liquid electrolytes. Based on findings from cell testing, project work is being re-directed to focus on lithiated fluoropolymer electrolytes as binder constituents in cathodes, to improve performance of cells with conventional electrolytes***

Current / Future work

- ***Preparation / characterization*** ***of lithiated fluoropolymer electrolytes suitable for use as high-voltage cathode binders***
- ***Formulation*** ***of high-voltage cathodes using the target electrolytes***
- ***Characterization*** ***of the resulting electrodes via charge-discharge cycling***
- ***Adjustment*** ***of electrolyte structures / electrode formulations for optimal performance***

Publications / Conferences

- *“Ionic Melt Electrolytes Based on Oligomeric PEG Functionalized with Lithium Fluorosulfonates or Fluorosulfonimide Pendants”, B.H. Hallac, O.E. Geiculescu, R.V. Rajagopal, C. Topping, S.E. Creager, D.D. DesMarteau, Chimica Oggi / Chemistry Today 25 (3/2007): 36-40*

- *“Lithium-conducting Ionic Melt Electrolytes from Polyether-functionalized Fluorosulfonimide Anions”, B.H. Hallac, O.E. Geiculescu, R.V. Rajagopal, S.E. Creager, D.D. DesMarteau, accepted for publication in Electrochimica Acta*

- *“The Effect of Low Molecular Weight Polyethers as Plasticizers on the Transport Properties and Rheology of Fluorosulfonimide Ionic Melts”, O.E. Geiculescu, B.H. Hallac, R.V. Rajagopal, S.E. Creager, D.D. DesMarteau, O. Borodin, G.D. Smith, submitted for publication to Journal of Physical Chemistry B*

- *“Oligomeric PEG-Based Lithium Fluorosulfonate/Fluorosulfonimide Ionic Melts Used as Electrolytes for Rechargeable Lithium Batteries”, O. Geiculescu, R. Rajagopal, B. Hallac, S. Creager, D.D. DesMarteau, Abstract 533, 59th Southeast Regional Meeting of the American Chemical Society, Greenville, SC, United States, October 24-27 (2007)*

- *“Li Ionic Melt Mixtures Based on PEG and Fluorolinks as Electrolytes for Rechargeable Lithium Batteries”, O.E. Geiculescu, R.V. Rajagopal, P.B. Hallac, S.E. Creager, D.D. DesMarteau, Abstract 692, The 212th Meeting of the Electrochemical Society, Abstract No.2017, Washington, DC, USA, October 7-12, 2007*

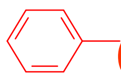
- *“Recent Progress in Fluorinated Ionic Liquids Based on Fluoroalkylsulfonimides”, D.D. DesMarteau, S.E. Creager, O.E. Geiculescu, R. Rajagopal, P. Hallac, T. Hickman, The 15th European Symposium on Fluorine Chemistry, Prague, Czech Republic, July 15-20, 2007*

- *“New Ionic Melts for Secondary Lithium Batteries Using Fluorolink Polymer Modifiers”, O. Geiculescu, R. Rajagopal, P. Hallac, C. Topping, J. Kim, S. Creager, D.D. DesMarteau, The 18th Winter Fluorine Conference, St. Pete Beach, FL, January 14-19, 2007*

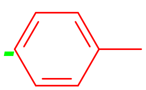
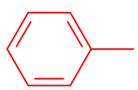
Additional Slides

PEG-Based Ionic Melt Structures

One anion per polyether chain

Structure	Salt	Parameters
CH_3O-$(CH_2CH_2O)_n$- CF_2CFHO-CF_2CF_2- Salt	Salt = SO_3Li $SO_2N(Li)SO_2CF_3$ $SO_2N(Li)SO_2C_4F_9$	n = 7, 12, 17
CH_3O-$(CH_2CH_2O)_n$- CF_2CFHO-$CF(CF_3)CF_2O$-CF_2CF_2- Salt	Salt = SO_3Li $SO_2N(Li)SO_2CF_3$	n = 7, 12, 17
CH_3O-$(CH_2CH_2O)_n$-  $(CF_2CF_2O$-$CF_2CF_2)_m$- Salt	Salt = $SO_2N(Li)SO_2CF_3$	n = 7, 12, 17 m = 0, 1

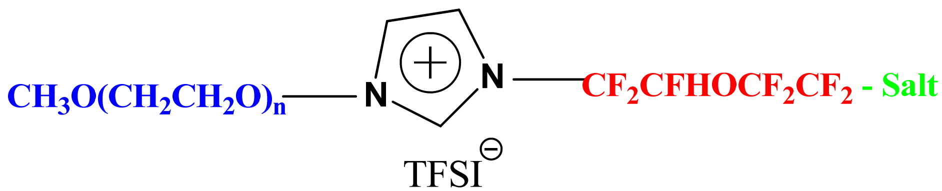
Two anions per polyether chain

Structure	Salt	Parameters
Salt -CF_2CF_2O-$CFHCF_2O$-$(CH_2CH_2O)_n$-CF_2CFHO-CF_2CF_2- Salt	Salt = SO_3Li $SO_2N(Li)SO_2CF_3$	n = 13, 22, 45
Salt -  $(CH_2CH_2O)_n$-  Salt	Salt = $SO_2N(Li)SO_2CF_3$	n = 13, 22, 45

Two polyether chains per anion

CH_3O-$(CH_2CH_2O)_n$- CF_2CFHO-CF_2CF_2-$SO_2N(Li)SO_2$-CF_2CF_2O-$CFHCF_2$-O-$(CH_2CH_2O)_n$-CH_3

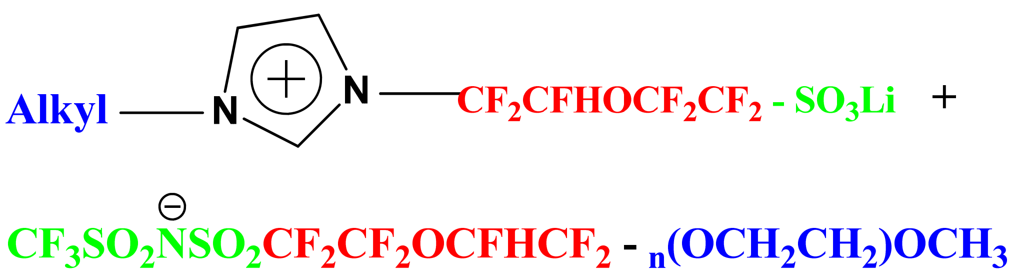
PEGME-Based Imidazole-PFVE-Derived Ionic Melts



Salt = *SO_3Li*

$SO_2N(Li)SO_2CF_3$

n = 7, 12, 17



Alkyl = *n - Butyl*

n - Octyl

n = 12

Fluorolink E-Based PFVE-Derived Ionic Melts

$$X - CF_2O\text{-}(CF_2CF_2O)_p\text{-}(CF_2O)_q\text{-}CF_2 - X$$

$X = CH_2(OCH_2CH_2)_nO$ - $CF_2CFHOCF_2CF_2$ - Salt

for M_w = 500 Da (E10): p = 2.387, q = 0.597, n = 0.066

for M_w = 1000 Da (E): p = 5.897, q = 1.474, n = 0.467

$X = CH_2(OCH_2CH_2)_pO$ - $CF_2CFHOCF_2CF_2$ - Salt

for M_w = 2100 Da (Z-DOL TX): p = q = 7.12

Salt = SO_3Li or $SO_2N(Li)SO_2CF_3$

Viscosity

Solvent	Salt	Plasticizer	Temp (°C)	Viscosity (Pa.s)	Conductivity (S cm^{-1})
EC:DEC	--	--	ambient	0.0013	--
EC:DEC	1 M $LiPF_6$	--	ambient	0.0035	1.0×10^{-2}
PEGME 550	--	--	ambient	0.01	--
PEGME 550	LiTFSI	--	ambient	0.46	1.5×10^{-4}
IM 550	n/a	--	ambient		
IM 550	n/a	PEGME 20%	ambient		
IM 550	n/a	PEGME 50%	ambient	.	.
IM 550	n/a	--	60	1.8	7.9×10^{-5}
IM 550	n/a	--	120	0.07	1.0×10^{-3}

Lithium "Transference" in ionic melts

$$t_+ = \frac{i_{ss}\left(\Delta V - i_0 R_0\right)}{i_0\left(\Delta V - i_{ss} R_{ss}\right)}$$

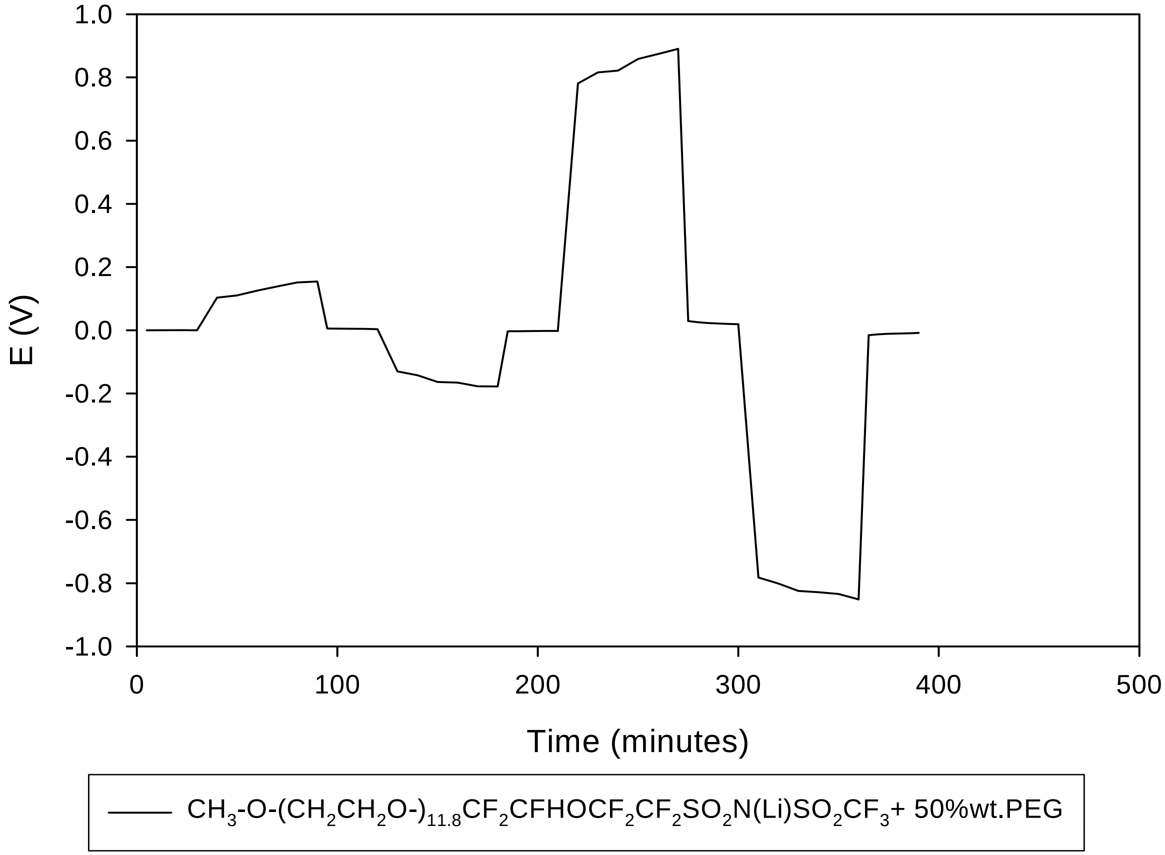
i_0, R_0: ***Initial current and resistance***

i_{ss}, R_{ss}: ***Steady-state current and resistance***

Bruce & Vincent, J. Electroanal. Chem. 225, 1 (1977)

	Ionic Melt	Ionic Melt + 50% by weight PEGME (MW=550 Da)	LiTFSI + PEGME (MW=550 Da)
i_0 i_{ss}	0.000682 A 0.000633 A	0.000264 A 0.000238 A	0.000237 A 0.000138 A
R_o R_{ss}	190 Ω 218 Ω	944 Ω 993 Ω	729 Ω 1250 Ω
t_+	**0.98**	**0.72**	**0.58**

DC polarization with plasticizers



Currents = 10 and 50 μA

Battery Testing for Ionic Melt IM550

Electrolye : ***$CH_3O\text{-}(CH_2CH_2O)_{12}$- $CF_2CFHO\text{-}CF_2CF_2$- $SO_2N(Li)SO_2CF_3$ (IM550)***

Anode : ***$Li_4Ti_5O_{12}$ (provided by HQ)***

Cathode : ***$LiCoO_2$ (88 wt% $LiCoO_2$, 5 wt% C black, 7 wt% hydrophilic binder)***

Separator : ***Celgard – 3400 grade***

Testing : CC charging @ C/100 achieved only 50% capacity (poor Li transport within pores).

Anode : ***Li4Ti5O12 (provided by HQ)***

Composite ***$LiCoO_2$ (86 wt% $LiCoO_2$, 5 wt% C black, 4 wt% hydrophilic binder***

Cathode : ***and 5 wt% DiLi fluorosulfonimide salt of diol Fluorolink E)***

(– $CF_2O\text{-}(CF_2CF_2O)_6\text{-}(CF_2O)_{1.5}\text{-}CF_2$ –)($CH_2(OCH_2CH_2)_{0.5}O$-$CF_2CFHOCF_2CF_2$ - $SO_2N(Li)SO_2CF_3)_2$

Separator : ***Celgard – 3400 grade***

Testing : CC charging @ C/100 - 100% capacity;
Discharging @ C/100 - only 7% capacity (high viscosity, large ohmic polarization).

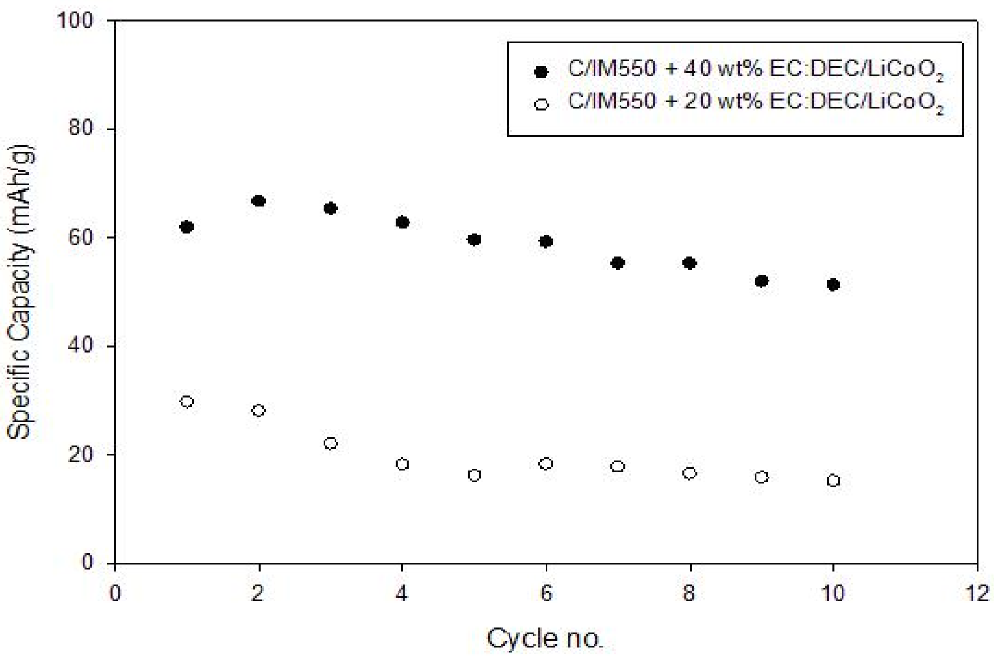
Battery Testing for IM550 + Plasticizers (EC:DEC)

Electrolye : ***IM550 + 20 or 40 wt% EC:DEC (1:1 vol:vol)***

Anode: ***Graphite (90 wt% potato graphite, 10 wt% hydrophilic binder)***
Cathode: ***$LiCoO_2$ (88 wt% LiCoO2, 5 wt% C black , 7 wt% hydrophilic binder)***
Separator : ***Celgard – 3400 grade***

Testing : CC charging @ C/100 achieved full capacity;

Discharging @ C/5 - only 42% capacity.



Specific capacity vs. cycle number obtained at C/5 rate for two electrolyte formulations of IM550 and carbonate solvents

Battery Testing for IM550 + Plasticizers (PEGDME)

Electrolye : ***IM550 + 50 wt% PEGDME (M=500 Da)***

Anode: ***Li metal***
Cathode: ***$Li_4Ti_5O_{12}$ (HQ) (C_{HQ}=0.842 mAh/cm^2 vs. C_{exp}=0.8 mAh/cm^2)***
Separator : ***Celgard – 3400 grade***
Testing : ***CC charging @ C/100 achieved full capacity;***
Discharging @ C/100, C/80 full capacity while @ C/60, C/50 and C/10 only 91, 33 and 1.4%, respectively (possibly slow Li diffusion or intercalation).

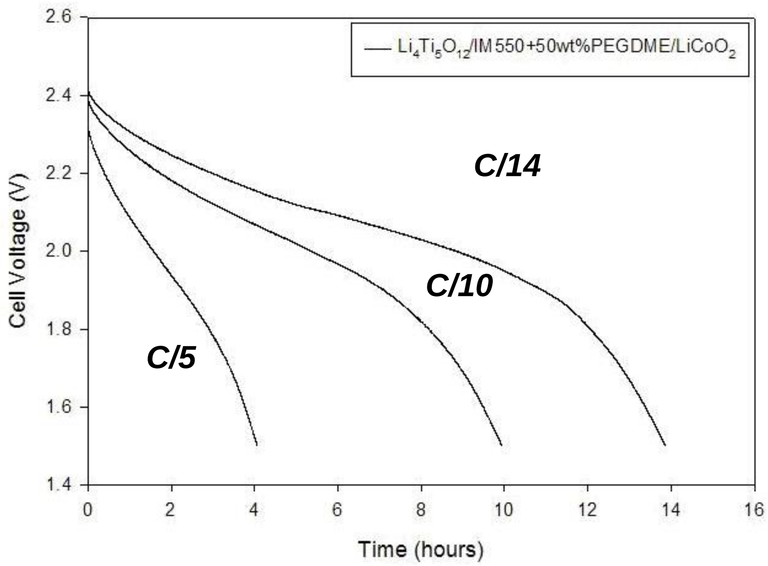
Anode: ***Li metal***
Cathode: ***Graphite (90 wt% potato graphite, 10 wt% hydrophilic binder)***
Separator : ***Celgard – 3400 grade***
Testing : ***CC charging @ C/100 achieved only 42% capacity on the 1st intercalation;***
CC charging @ C/100 achieved only 16% capacity on the 2nd intercalation (likely due to the formation of an SEI layer that contributes to the large irreversible capacity).

Anode: ***Li metal***
Composite Cathode : ***$LiCoO_2$ (86 wt% $LiCoO_2$, 5 wt% C black, 4 wt% hydrophilic binder and 5 wt% DiLi fluorosulfonimide salt of diol Fluorolink E)***
Separator : ***Celgard – 3400 grade***
Testing : ***CC charging @ C/100 achieved full capacity;***
Fading in capacity immediately after the 1st discharge (due to SEI layer formation).

Battery Testing for IM550 + Plasticizers (PEGDME)

$Li_4Ti_5O_{12}$ / IM550 + 50 wt% PEGDME (M=500 Da) / $LiCoO_2$ composite

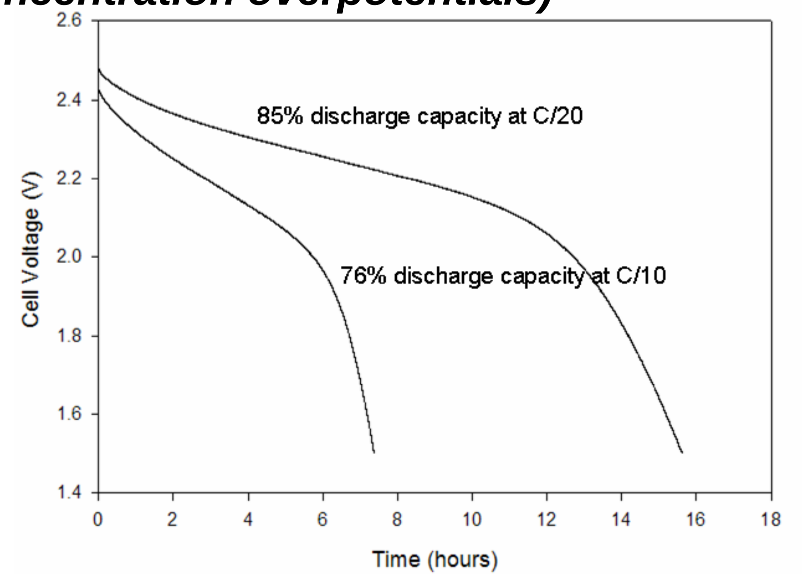
Testing : CC charging @ C/100 - 100% capacity;
Discharging @ C/20, C/14 and C/10 at full capacity (100%);
Discharging @ C/5 and 1C achieved 82 and 4%, respectively;
100% reversible capacity was achieved upon 3 cycles.



$Li_4Ti_5O_{12}$ / LiTFSI in PEGDME / $LiCoO_2$ composite

Decrease in capacity @ high discharge rates due to:

- ***Larger initial ohmic drops***
- ***Low Li transference number (higher concentration overpotentials)***



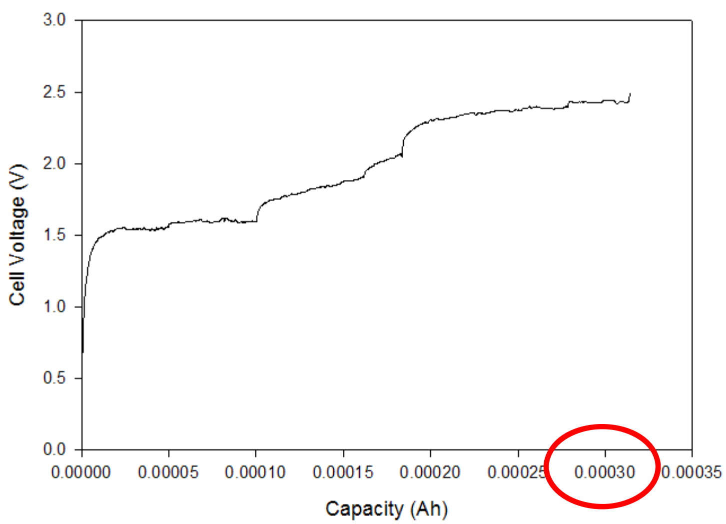
Conclusions

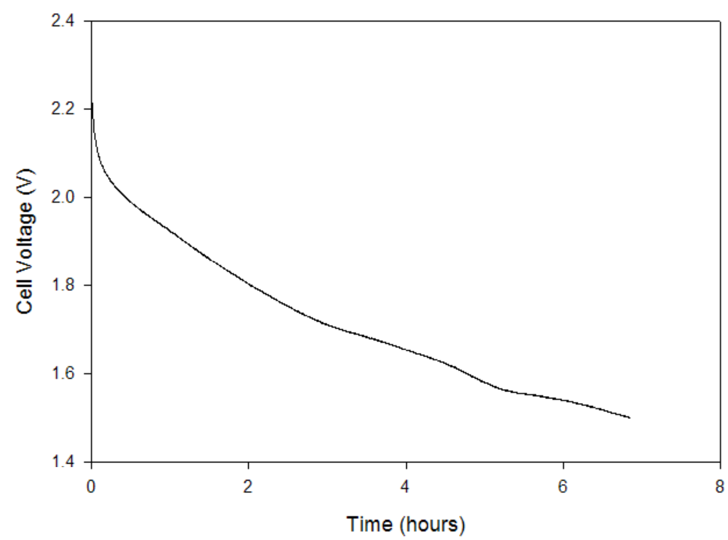
- The use of $Li_4Ti_5O_{12}$ electrode provided :
  - zero-strain intercalation / deintercalation of Li^+
  - does not form SEI
- Adding PEGDME to the electroltye;
  - increased transport by decreasing viscosity
    decreased Li^+ transference number
- Adding dilithium salt of fluorosulfonimide Fluorolink E electrolyte to the cathode formulation:
  - increased transport properties within the bulk of the cathode

Cell Charging - Discharging

$Li_4Ti_5O_{12}$ | IM550 electrolyte | $LiCoO_2$ + Fluorolink electrolyte

Cell capacity approx. 0.3 mAh
Charging at C/200 then C/100, room temperature



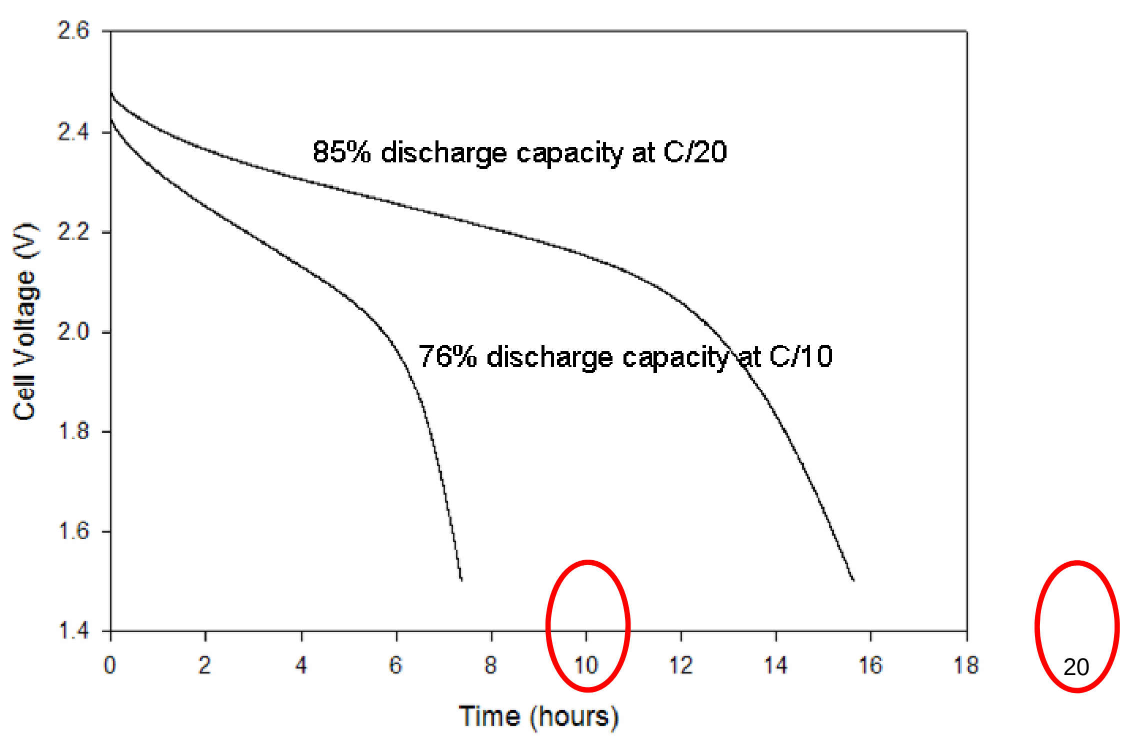


- ***Full capacity was achieved with slow charging***
- ***Discharging at C/100 yielded only 7 percent of full capacity***
- ***This fact is also thought to reflect poor ion transport in the electrodes and in the bulk electrolyte.***

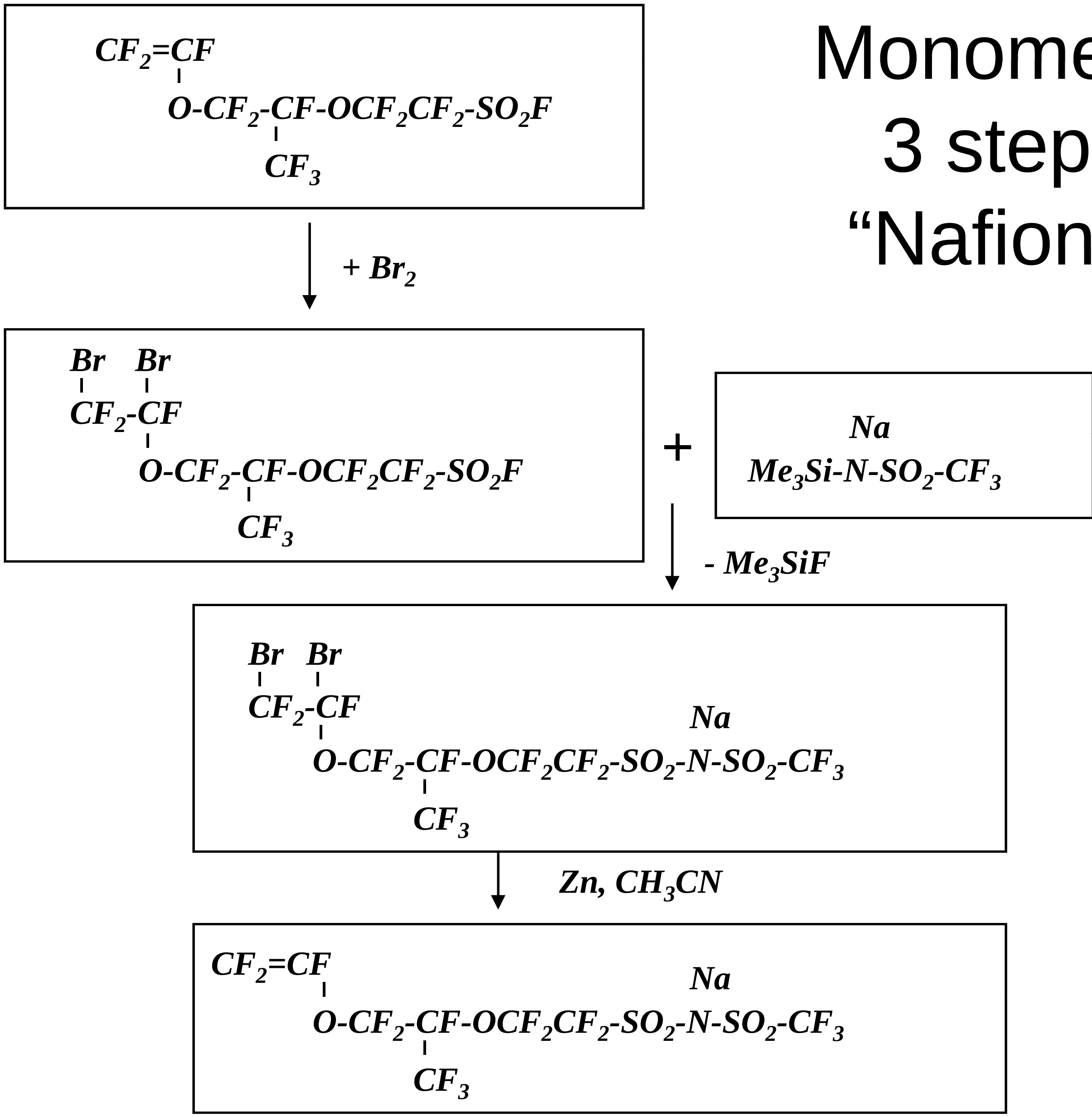
Cell Charging - Discharging

$Li_4Ti_5O_{12}$ | LiTFSI (1 M) in PEGDME | $LiCoO_2$ + Fluorolink electrolyte

- ***Cell capacity approx. 0.3 mAh***
- ***CC charging @ C/100 - 100% capacity achieved;***
- ***Discharging @ C/20 and C/10; full capacity NOT achieved***
- ***Could be due to effects of salt concentration polarization***



Monomer synthesis; 3 steps from the "Nafion monomer"



DesMarteau, D. D., Novel perfluorinated ionomers and ionenes. Journal of Fluorine Chemistry 1995, 72, 203-208.

Proposed Cathode Formulation;

• ***$LiCoO_2$***	***86 %***
• ***LHB-108P binder***	***4 %***
• ***Fluoroionomer***	***5 %***
• ***Carbon Black***	***5 %***

In NMP solvent