PROCESS DEVELOPMENT AND SCALE UP OF CRITICAL BATTERY MATERIALS

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Project ID: ES168

June 2016, Washington, D.C.

Overview

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2017
- Percent complete: on going

Budget

- Total project funding:
  - $1.2M in FY15
  - $1.2M in FY16

Barriers

- Cost: Reduce cost to manufacture materials
- Performance: Determine optimal purity for maximum performance

Partners

- Scaling materials for:
  - Oak Ridge National Lab
  - Argonne's Applied R&D Group
  - Army Research Laboratory

- **Supporting battery research for:**
  - MIT, Wildcat Discovery, Army Research Lab, CAMX Power LLC, Pacific Northwest National Lab, Sandia National Lab, 24M Technologies, Cidetek, Argonne's CAMP Facility and JCESR battery hub.

Approach - Milestones

- FY15
  - Li-FSI Impurity vs. performance study
  - GM-Polymer
  - SNL PFPBO•LiF
  - Fluorinated EMC initiated
  - Fluorinated DEC initiated
  - LBNL-PFM Si-anode binder study
- FY16
  - ORNL Li-BMFBM
  - Fluorinated EMC
  - Fluorinated DEC
  - LBNL Si-anode binders (PPy and PPyE)
  - ARL MGC
- FY17
  - 4-6 Electrolyte materials to be scaled
  - Develop specifications for battery grade materials

MILESTONE	DATE Complete
ORNL-Li-BMFBM	
Assess scalability of disclosed process	8/19/2015
Develop and validate scalable process chemistry (10g scale)	1/5/2016
Go/ No Go	**GO**
First process scale-up (100g bench scale)	2/3/16
Go/ No Go	Pending evaluation
Second process scale-up (1000g pilot scale)	Pending evaluation
FEMC	
Assess scalability of disclosed process	1/9/15
Develop and validate scalable process chemistry (10g scale)	3/16/15
Go/ No Go	**GO**
First process scale-up (100g bench scale)	6/16/15
Go/ No Go	**GO**
Second process scale-up (3000g pilot scale)	8/19/2015
DFEC	
Assess scalability of disclosed process	1/16/15
Develop and validate scalable process chemistry (10g scale)	2/19/15
Go/ No Go	**GO**
First process scale-up (100g bench scale)	5/14/2015
Go/ No Go	**GO**
Second process scale-up (1000g pilot scale)	5/27/2015
ARL-MGC	
Assess scalability of literature procedures	2/5/2016
Develop and validate scalable process chemistry (10g scale)	3/4/2016
Go/ No Go	**GO**
First process scale-up (100g bench scale)	3/24/2016
Go/ No Go	Pending evaluation
Second process scale-up (1000g pilot scale)	Pending evaluation
LBNL- Binder Study	
Synthesize polymers	ongoing

Objectives - Relevance

- The objective of this program is to provide a systematic engineering research approach to:
  - Develop **cost-effective** processes for the scale-up of advanced battery materials.
  - Provide **sufficient quantities** of these materials produced under rigorous quality control specifications for industrial evaluation or further research.
  - Determine **material purity profiles** and evaluate their influence on battery performance.
  - Evaluate **emerging manufacturing technologies** for the production of these materials.

- The relevance of this program to the DOE Vehicle Technologies Program is:
  - The program is a key missing link between discovery of advanced battery materials, market evaluation of these materials and high-volume manufacturing
    - Reducing the risk associated with the commercialization of new battery materials.
  - This program provides large quantities of materials with consistent quality
    - For industrial validation in large format prototype cells.
    - To further research on these advanced materials.

Approach And Strategy

- Discovery scientists submit promising new materials.
  - Collaborate on special requests for custom materials not commercially available.
- Prioritize materials based on level of interest, validated performance and scale up feasibility.
  - Discuss candidate materials with DOE for final approval.
- Conduct process R&D and develop performance *vs.* specification criteria.
  - Scaling to kilogram or larger takes substantial process modifications.
- Make materials available for both basic researchers and industrial evaluators.
  - Provide feedback to discovery chemists, helping guide future research.

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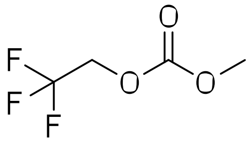
Technical Accomplishments And Progress Overview

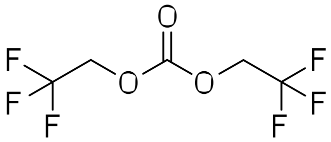
- Scalable processes were developed and several materials were investigated.
  - Trifluoroethyl methyl carbonate (FEMC) – solvent for high voltage electrolyte (complete).
  - Bis(trifluoroethyl) carbonate (DFEC) – solvent for high voltage electrolyte (complete).
  - Glycerol methyl dicarbonate (MGD) – ARL high voltage electrolyte additive (complete).
  - Trifluoropropylene carbonate (TFPC) – solvent for high voltage electrolyte (in progress).
  - Li-BMFMB – ORNL alternative to $LiPF_6$ for high voltage cells (in progress).
- Collaboration with CAMP on Si anode binders is ongoing.
  - LBNL-PPy and LBNL-PPyE binder for Gr-Si anode (in progress).
- Next Generation Anodes for Li-Ion Battery
  - "Self-healing" binders for advanced anode (in progress).
- Materials Distribution.
  - Since the program start over 120 material samples have been sent. Over 12,000 g of battery grade materials have been sampled. In FY15 alone, 23 samples totaling over 1700g were sent out.
- A total of 10 materials have now been fully distributed.
- Several materials and processes have been licensed to commercial manufacturers (Strem and Aldrich) for production and distribution for R&D use.

Technical Accomplishments And Progress: Scale Up Of Fluorinated Carbonate Solvents

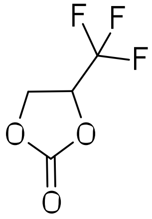
- Current electrolyte materials fail rapidly at high voltages with 5V LNMO cathode and high energy LMR-NMC cathodes.
- Three solvents with enhanced stability in high voltage electrolytes and better thermal stability were targeted.
- The materials are not commercially available.



methyl (2,2,2-trifluoroethyl) carbonate
(FEMC)



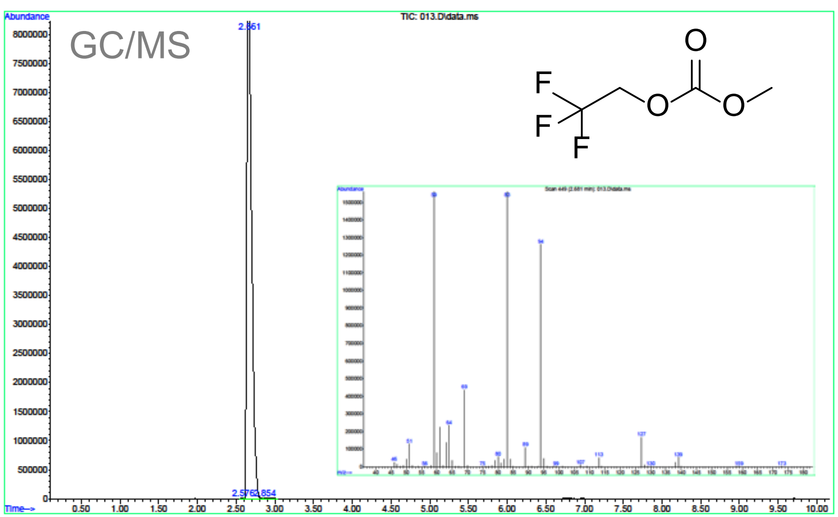
bis(2,2,2-trifluoroethyl) carbonate
(FDEC)



3,3,3-trifluoropropylene carbonate
(TFPC)

Technical Accomplishments And Progress: Scale Up Of FEMC

- The standard literature synthesis uses chlorinated solvents and tertiary amines as an auxiliary reagent.
- Traces of chlorine bearing compound (solvent and/or amine hydrochloride) may be carried over contaminating the final material. MERF developed a greener process eliminating both dichloromethane and the amine reducing number of synthesis steps and minimizing waste generation.
- Nearly 3 kg of the material was manufactured and 250 g already provided to research community.

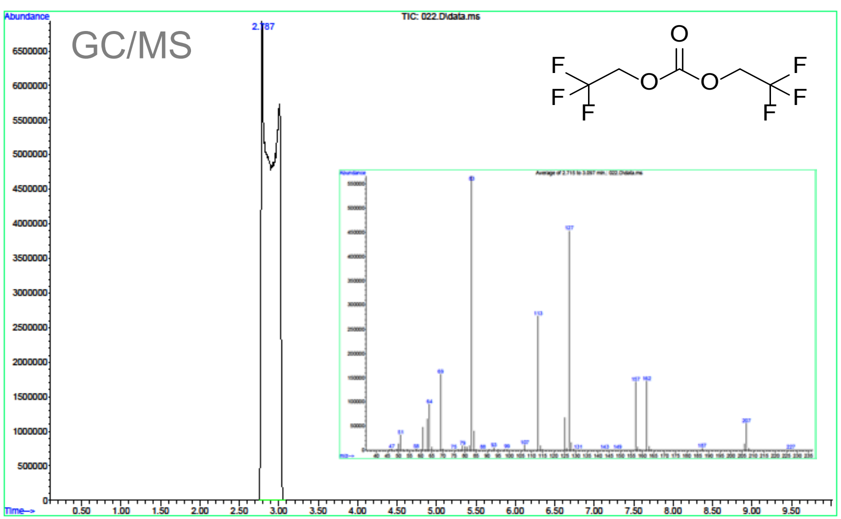


	FEMC
Description	Methyl (2,2,2-trifluoroethyl) carbonate
CAS #	156783-95-8
Formula	$C_4H_5F_3O_3$
FW	158.08
LOT #	TD7-271
Purity	99.8%[1]
Batch Size	2900 g
Manufactured	8-20-15

Analysis	Method	Results	Analysis By:
GC/MSD	Agilent DB-5MS, 0.25 um, 30m x 0.250 mm, 25 deg/min	99.8% [1,2]	T. Dzwiniel
Boiling Point	Automatic, range method (Buchi M-565)	104-106°C	T. Dzwiniel
Flash Point	Pensky-Martens Closed Cup	37°C	T. Dzwiniel
KF Moisture Titration	Coulometric (KEM MCU-610)	TBD ppm	K. Pupek
FTIR	Bruker Vertex 70, Attenuated Total Reflection	Consistent with Structure	T. Dzwiniel
NMR	^{1}H, ^{19}F, ^{13}C Bruker 500 MHz, $CDCl_3$ solution.	Consistent with Structure	T. Dzwiniel

Technical Accomplishments And Progress: Chlorine Free Synthesis Of FDEC

- The standard literature synthesis uses phosgene or triphosgene as a 2,2,2-trifluoroethanol coupling reagent.
- MERF developed novel, chlorine-free, safe and environmental friendly process. The new process provides high purity solvent in good yield.
- Scale up of the material is completed. Single batch of 1 kg was produced out of which 250 g of the material was already distributed.

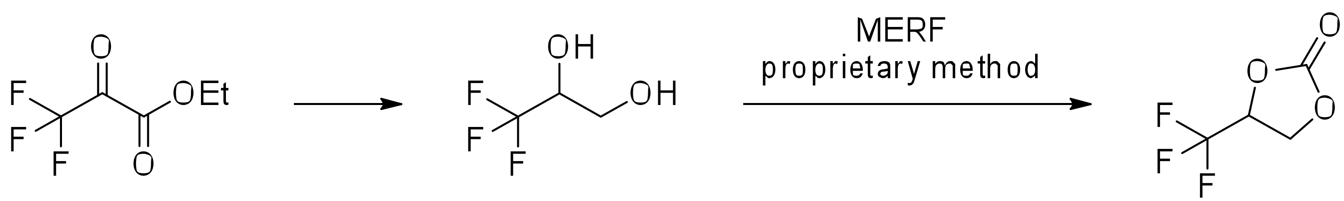


Argonne	FDEC
Description	Bis (2,2,2-trifluoroethyl) carbonate
CAS #	1513-87-7
Formula	$C_5H_4F_6O_3$
FW	226.07
LOT #	TD7-241
Purity	>99.95%[1]
Batch Size	1056 g
Manufactured	5-28-15

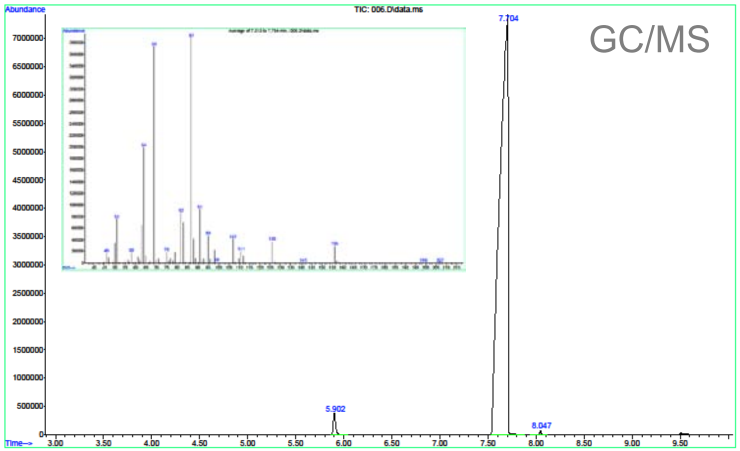
Analysis	Method	Results	Analysis By:
GC/MSD	Agilent HP-5MS, 0.25 um, 30m x 0.250 mm, 30 deg/min	>99.95% [1,2]	T. Dzwiniel
Boiling Point	Automatic, range method (Buchi M-565)	118-119°C	T. Dzwiniel
Flash Point	Pensky-Martens Closed Cup	No flash	T. Dzwiniel
KF Moisture Titration	Coulometric (KEM MCU-610)	TBD ppm	K. Pupek
FTIR	Bruker Vertex 70, Attenuated Total Reflection	Consistent with Structure	T. Dzwiniel
NMR	^1H, ^{19}F, ^{13}C Bruker 500 MHz, $CDCl_3$ solution.	Consistent with Structure	T. Dzwiniel

Technical Accomplishments And Progress: Chlorine Free Synthesis Of TFPC

- 3,3,3-Trifluoropropylene carbonate (TFPC) is a partially fluorinated cyclic carbonate that imparts higher temperature and voltage stability.
- Floating test of 0.5 M $LiPF_6$ in TFPC/FEMC, 4.9 V to 5.2 V at r.t. and 55°C revealed decrease in current leakage compared to EC/FEMC solvents blend (Meinan He et al. J. Electrochem. Soc. 2015; 162: A1725-A1729).

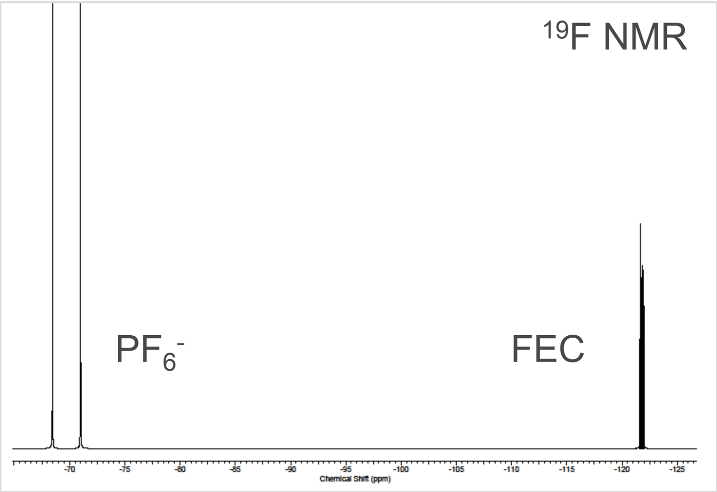


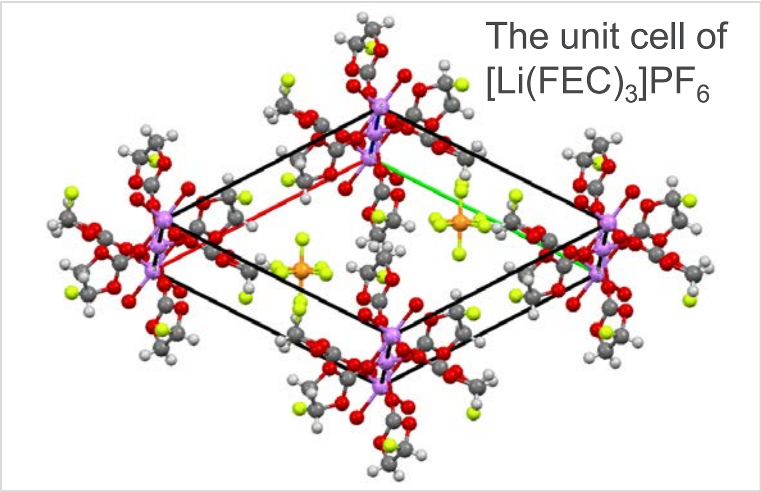
- MERF researched novel, chlorine-free, safe and environmental friendly process to manufacture the material.
- Work is currently in progress to refine the process to achieve purity greater than 99.5%.



Technical Accomplishments And Progress: Investigating Properties Of Fluorinated Carbonates

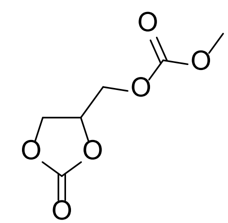
- MERF evaluates basic properties and usability of the solvents for electrolytes formulations (salts solubility, miscibility).
- Unexpected tendency for the formation, aggregation, and phase separation of lithium ion coordination polymers in certain fluorinated electrolytes containing FEC was observed.
- The crystalline aggregates were separated and studied by NMR and single crystal X-ray.
- The aggregates always have 1:3 molar ration between lithium ion and FEC.

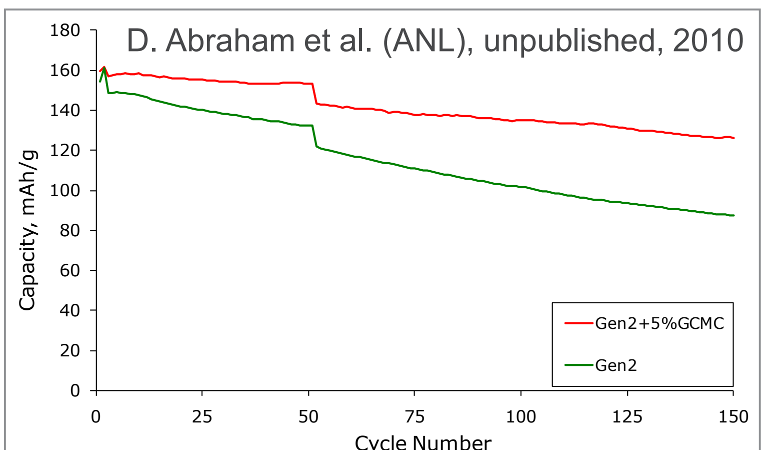




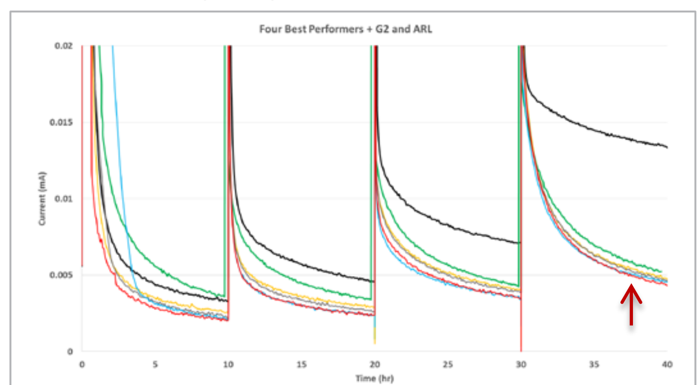
Technical Accomplishments And Progress: Synthesis Of Methyl Glycerol Carbonate

- It was previously demonstrated that addition of methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (MGC) to Gen2 electrolyte improves capacity retention (D. Abraham et al., ANL, 2010).
- More recently MGC revealed promising results in 4.9 to 5.2 V current leakage test at 0.5 % w/w (K. Xu et al., ARL, 2016).
- MERF developed proprietary process for manufacturing high purity material (>99.9%) without the need for non-scalable sublimation step.
- 300 g of the material was synthesized, analyzed and is ready for distribution.



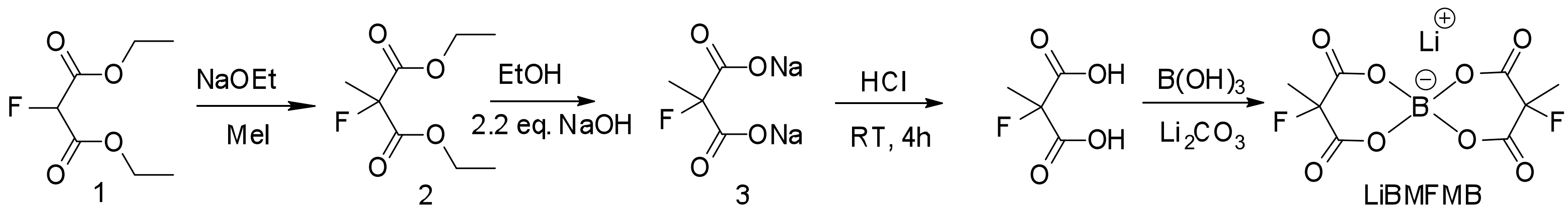


K. Xu et al. (ARL), 2016



Technical Accomplishments And Progress: Scale Up Of Alternative Li Salt

- Alternative to $LiPF_6$ for high voltage cells with better thermal stability. (*Chem. Commun.*, 2015, 51, 9817).
- Initial process development complete with several improvements.

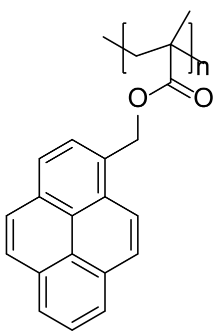


- Overall, reduced # of steps by 33%.
- Reduced time by estimated 70% (exclusive of final purification).
- Removed hazards from: alkali metals, metal hydrides, concentrated acids, and water-reactive materials.
- Eliminates the non-selective silylation procedure.

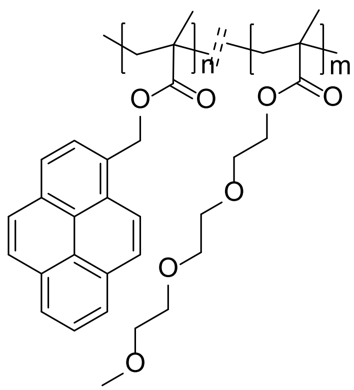
- Currently developing derivatives to support HV/HE and JCESR programs.

Technical Accomplishments And Progress: Scale Up Of LBNL Binder For Si Anode

- MERF is collaborating with CAMP on synthesis and testing of 3rd generation of LBNL conductive binder for silicon anode.
- Both homopolymer PPy and co-polymer PPyE were prepared.
- The materials were forwarded to CAMP for manufacturing of electrodes.
- NanoAmor Si nanopowder (50-70 nm) was wet coated with PPyE (90/10 w/w ratio) and ball milled.
- CAMP used the blend to make and test composite anode.



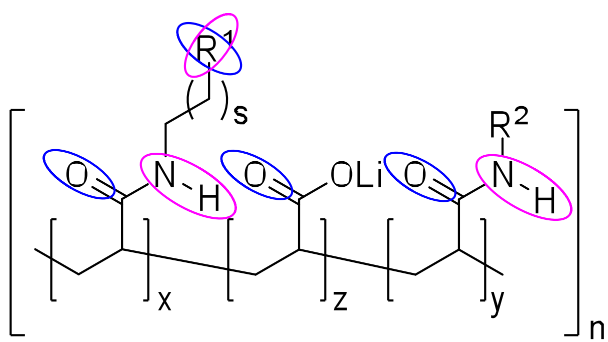
PPy		
	LBNL	MERF
Mw (kDa)		TBD
Mn (kDa)	21	TBD
PDI	2.5	TBD



PPyE		
	LBNL	MERF
Mw (kDa)		96
Mn (kDa)	34	31
PDI	2.9	3.1

Technical Accomplishments And Progress: "Self-healing" Binder For Advanced Anode

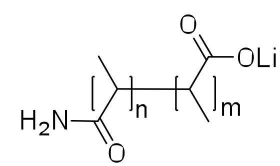
- The binders are co-polymers of acrylic acid lithium salt and acrylate based co-monomer bearing hydrogen bond donor and hydrogen bond acceptor.
- As a part of the multi-laboratory Next Generation Anode Program MERF is designing, synthesizing and testing new binders for silicon anode.
- Such co-polymers can expand and contract supramolecular structures ("self-healing") thereby improving mechanical integrity of the anode.



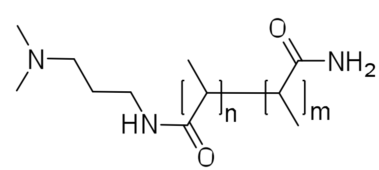
hydrogen bond donors and acceptors sites

R^1, R^2 = H, Alk, Ar, N-Het, O-Het, $CONR_2$, NR^3R^4

R^3, R^4 = H, Alk, COAlk, COAr, $CONR_2$



n:m = 1:1



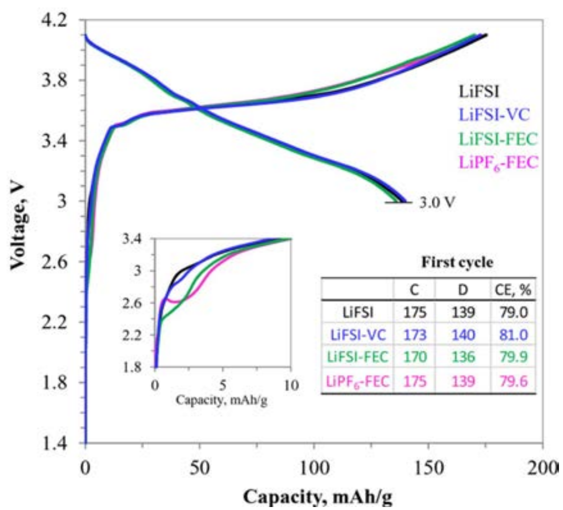
n:m = 1:2

Prepared. Pending electrochemical evaluation.

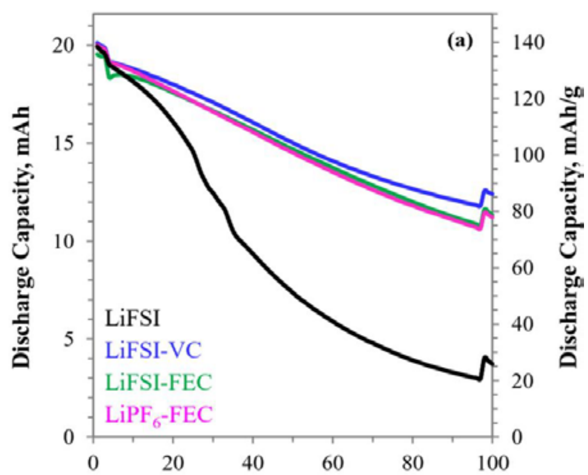
D. Dees, 2016 AMR, ES216

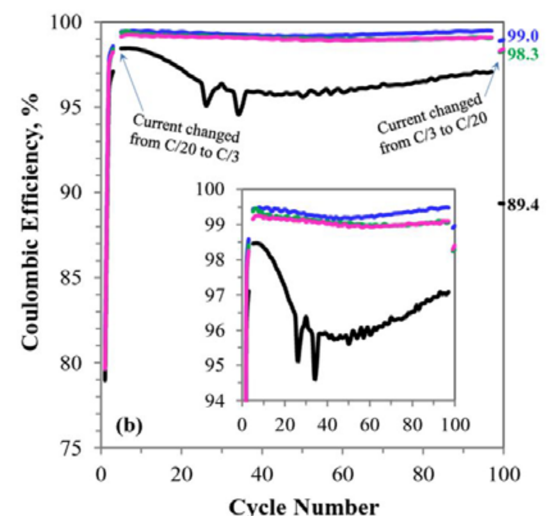
Technical Accomplishments And Progress: Investigating Performance Of LiFSI Based Electrolyte

- MERF continues to investigate LiFSI-based electrolytes in various cell chemistries.
- We examine the cycling of 20 mAh pouch cells with LiFSI-carbonate electrolytes, silicon-graphite negative electrodes, and NCM253 positive electrodes.
- The effect of FEC and VC addition on cell performance was examined and compared to baseline $LiPF_6$ cells.
- The performance of LiFSI-FEC and $LiPF_6$-FEC cells are very similar indicating that the electrolyte salts play a much smaller role in performance degradation than the electrolyte solvent.



	C	D	CE, %
LiFSI	175	139	79.0
LiFSI-VC	173	140	81.0
LiFSI-FEC	170	136	79.9
$LiPF_6$-FEC	175	139	79.6



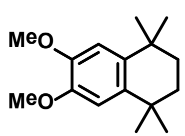


Technical Accomplishments And Progress: Materials And Processes Licensing

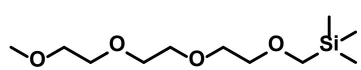
- Nine materials scaled up by MERF were licensed to Strem Chemicals and three materials to Sigma-Aldrich for manufacturing and distribution for R&D use.
- MERF provided the manufacturers with detailed Technology Transfer Packages for each material.
  - Contains detailed synthesis procedures, process schematics, material mass balances, product physico-chemical characterization, analytical and quality control data.
- The materials will soon be available to the research community via the vendor's catalogs.

STREM CHEMICALS, INC.

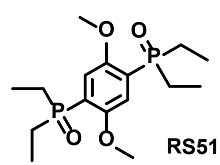
SIGMA-ALDRICH



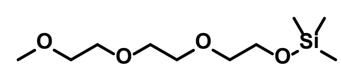
RS21



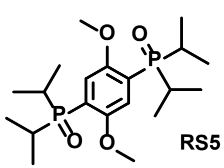
1S1M3



RS51



1NM3



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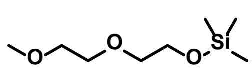

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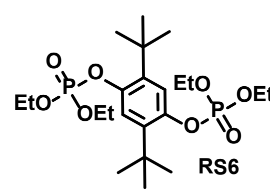

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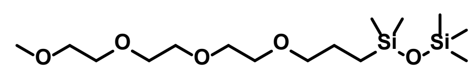
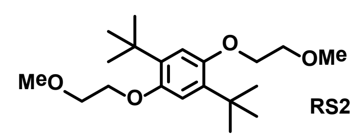


2SM3



RS2

Response To Previous Year Reviewer' Comments

- This project was not reviewed last year.

Collaborations

- Materials process R&D:
  - Lawrence Berkeley National Lab (Gao Liu) and Argonne's CAMP facility (Andrew Jansen, Bryant Polzin, Steve Trask)
    - Si-binder synthesis, anode formulation, and cell testing
  - Argonne National Lab (John Zhang)
    - Synthesis of high voltage solvents FEMC, DFEC, TFPC
  - Oak Ridge National Lab (Xiao-Guang Sun)
    - Lithium salt for high voltage applications
  - Army Research Laboratory (Kang Xu)
    - Additive for high voltage stability
- Material samples provided for further research:
    - Army Research Lab
    - Pacific Northwest National Lab
    - Sandia National Laboratory
    - MIT
    - JCESR
    - Wildcat Discovery
    - CAMX Power LLC
    - SolidEnergy Systems
    - 24M Technologies
    - Cidetek

Sandia National Laboratories

OAK RIDGE National Laboratory

BERKELEY LAB Lawrence Berkeley National Laboratory

Argonne NATIONAL LABORATORY

ARL

JCESR JOINT CENTER FOR ENERGY STORAGE RESEARCH

24m

CAMX Power

solid energy

Wildcat Discovery Technologies

MIT Massachusetts Institute of Technology

IK4 CIDETEC Research Alliance

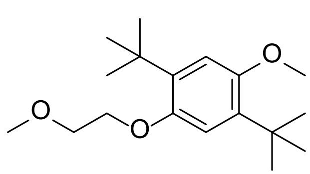
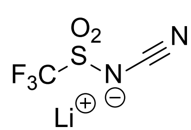
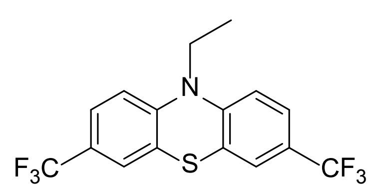
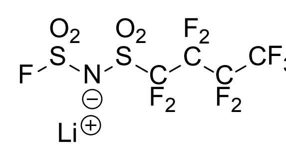
Pacific Northwest NATIONAL LABORATORY

Remaining Challenges And Barriers

- New battery materials are continually being discovered and developed, but industry is typically unable to model the cost of production using bench scale processes and obtain large samples for evaluation.
- There is a strong demand from the research community for high quality, uniform experimental materials.
- A detailed understanding of impurity profiles of experimental materials used in the battery community is needed, as well as their effect on battery performance.
- Battery grade specifications are needed for newly developed battery materials to minimize cost.
- Emerging manufacturing technologies need to be evaluated to further reduce production costs of battery materials.

Activities For Next Fiscal Year

- Target 4-6 new materials for battery development.
  - Develop scalable process, analytical methods and quality control procedures.
  - Validate the manufacturing process, analytical and electrochemical properties.
  - Characterize the impurity profile.
  - Supply material samples to the research community and industry for evaluation.
- Investigate analytical purity vs. electrochemical performance for new material.
- Evaluate new technologies/processes with a focus on Green Chemistry.
  - Continuous processes using flow chemistry.
    - Fast mass and heat transfer; accurate control of reaction.
    - Allow rapid optimization of reaction parameters.
    - Low usage of reagents in the optimization process.
- Program is open to suggestions for new, advanced materials.
  - Currently evaluating several requests for scale-up.

Summary

- This program has been developed to provide a systematic approach to process R&D and scale-up, and to provide sufficient quantities of advanced battery grade materials for industrial evaluation.

- Argonne's process R&D program enables industry to carry out large-scale testing of new battery materials and enable scientists to obtain consistent quality, next generation materials for further research.

- Integration of materials discovery with process R&D will expedite the time needed for commercial deployment.

- Over 120 samples have been presented to collaborating research entities.
  - Several materials have been fully distributed.
  - Completed licensing agreements with Strem Chemicals and Sigma-Aldrich for production and distribution of scaled materials for R&D use.

- **Technical Summary:**
  - Completed 2 fluorinated solvents for HV electrolytes: F-DEC and F-EMC.
  - Third fluorinated solvent (TF-PC) in progress.
  - Two materials (ORNL-Li-BMFBM and ARL-MGC) scaled to >100g.
  - LBNL- Si-Anode binder study (PPyE) ongoing.

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For samples and further information:

www.anl.gov/merf

Technical Backup Slides

Materials Produced

Solvents	Shuttles	Salts	Additives	Binders
ANL-1NM2	ANL-RS2*	Li-DFOB*	ARL-HFiPP*	LBNL-PFM*
ANL-1NM3*	ANL-RS5	Li-TDI	ARL-LiPFTB	LBNL-PEFM*
ANL-2SM3*	ANL-RS6	SNL-PFPBO•LiF	CWR-FRION	LBNL-PPyE*
ANL-1S1M3	ANL-RS21	Li-FSI*	GM separator*	LBNL-PPy
F-EMF	ANL-RS51	ORNL-LiBMFMB	ARL-MGC	
F-DEC				
TF-PC				

* Materials fully distributed

For samples and information:

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