

PROCESS DEVELOPMENT AND SCALE-UP OF CRITICAL BATTERY MATERIALS -CONTINUOUS FLOW-PRODUCED MATERIALS



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Overview

Timeline

- Project start date: Oct. 2011
- Project end date: Sept. 2022
- Percent complete: on going

Budget

- Total project funding:
 - \$1.08M in FY20
 - \$0.80M in FY21

Barriers

- New electrolytes are needed for advanced batteries.
- High cost of manufacturing advanced materials needs to be addressed.

Partners

- Scaling materials for:
 - Argonne's Applied R&D Group.
 - Zhang group (BAT374).
 - JCESR
- Supporting battery research for:
 - ADA Technologies
 - Brookhaven National Laboratory
 - NREL
 - University of Chicago
 - UC San Diego
 - Wildcat Discovery



Approach – FY 21 Milestones

- Flow Chemistry Development:
 - Development of new continuous processes for electrolyte materials:
 - Lithium tricyanoimidazole (Li-TCI) via diazotiation chemistry is **ongoing**.
 - Continuous flow process for 3,3,3-trifluoropropylene carbonate (TFPC) is **complete**.
 - Continuous flow process for methyl (2,2,3,3-tetrafluoropropyl) carbonate (MTFPC) is ongoing.
- Scale-up Programs:
 - Scale-up of methyl bis(fluorosulfonylimide) (MeFSI) is complete to 100g level.
 - Scale-up of 3,3,3-trifluoropropylene carbonate (TFPC) is complete to kilo level.
 - Scale-up of lithium 4,5-dicyano-1,2,3-triazole (Li-DCTA) is ongoing.



Objectives and Relevance

- The **objective** of this program is to provide a systematic research approach to:
 - Develop cost-effective, scalable processes for manufacturing of advance materials by more efficient use of feedstock and energy, improved safety and reduced environmental impact.
 - Evaluate **emerging synthesis technologies** for production of experimental materials.
 - Produce and provide high quality and sufficient quantities of these materials for industrial evaluation and in support of further research.
- The **relevance** of this program to the DOE Vehicle Technologies Program is:
 - The program is a key missing link between invention of new advanced battery materials, evaluation at multiple R&D organization, 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 and prototyping in large format cells.
 - To allow battery community access to new materials and advance further research.
- Continuous flow chemistry is an emerging technology that promises to outperform traditional batch manufacturing processes in cost and time.



Approach and Strategy







- Researchers in a basic science invent new materials, synthesize small amounts and evaluate electrochemical performance in small cell formats. This project forms half of the Materials Engineering Research Facility (MERF) at Argonne.
 - MERF collects information about new materials, prioritizes them based on level of interest, validated performance and scale up feasibility. Discuss candidate materials with DOE program managers for final approval.
 - MERF evaluates emerging manufacturing technologies, conducts process R&D, develops and validates optimal process parameters for new material production.
 - Proof of concept in stages from milligrams to 10g to 100g to kilograms.
 - Validate electrochemical performance.
 - Develop performance *vs.* purity and impurity profile relationship (material specification).
- Provide feedback to discovery scientists helping promote future research.
- MERF makes promising new materials available to assist basic researchers and to facilitate industrial evaluation.



Approach and Strategy

- In the quest for better, advanced electrolyte materials (solvents, salts, additives) scientists design, synthesize and evaluate more and more complex molecules.
- The complexity of the molecular structure is frequently translated into increased complexity and cost of the manufacturing processes.
- The program evaluates emerging synthesis techniques to address the cost issue.
- Continuous Flow Chemistry enables the synthesis of materials from discovery through process development and (possible) production scale in a cost effective manner.
- Continuous flow reactors can be used for rapid screening of reaction conditions to better understand fundamentals of process kinetics and thermodynamics.
- MERF demonstrates the feasibility of new continuous processes by scaling material manufacturing.





Technical Accomplishments carbon dioxide CF **TFPC Scale-Up** Process scaled up for manufacture of over 1kg TFPC, >99.5% purity. - Simple distillation provided pure material. Microfluidic Improved, larger scale tubular reactor design is in progress. chip Mass flow Heating/chilling Temperature circulator controller for gas controller Back pressure controller CORNING CORNING Microfluidic Product Liquid High pressure Compressed collection chip housing CO₂ cylinder reagents pump Argonne 🧲

Diazotization Reactions in Flow Synthesis: Li-TCI

- Reported effect of Li-TDI in preventing anodic dissolution when used with Li-FSI¹ prompted a search into other imidazole derivatives.
 - Possible targets include:
 - Tricyanoimidazole (TCI)²
 - Fluorodicyanoimidazole (F-DCI)
- Diazonium intermediates (TCI route) are particularly hazardous and illsuited for large scale reactions, but suitable for flow reactions.
- Development required to adapt literature procedures to flow.





- Challenges: limited solubility of the starting amine in most solvents, diazonium intermediate also has limited solubility, smooth reaction with CuCN, KCN (water soluble).
- Able to run in DMF or other highly polar aprotic solvents.
- Several grams of Li-TCI was produced.

¹See: a) Journal of Physical Chemistry Letters (2017), 8(15), 3678-3682. b) Journal of Physical Chemistry C (2016), 120(50), 28463-28471. c) LiTDI: An electrolyte additive for extended battery life and fast charging. Charged Magazine March 30, 2020. ²See: a) World Intellectual Property Organization, WO2015136199 A1. b) World Intellectual Property Organization, WO2016203390 A1



Li-TCI Proof of Concept: Semi-Batch

- Use of flow chemistry needed to address safety issues.
- Preformed diazonium was reacted in simple flow tube with T-mixers using syringe pumps.
 - Investigated metal loading, temperature, flow rate.
 - No plugging. $72 \pm 1\%$ purity by HPLC.
 - DCI-NH₂ is insoluble in most solvents- challenging for flow processes.









Li-TCI Full Flow Development

- Mixtures of MeCN: DMSO: water (6:1:1) or similar polar solvents required for 1M DCI-NH₂ feed solution.
 - DMSO suboptimal for reaction- MeCN very good, but not soluble.
- Analysis: HPLC quantifies all species, but is too slow for monitoring. FTIR?
 - Syrris system programmed for 6 reactions.
 - v = 1140 cm⁻¹ appears to be product.





DCI-NH₂



Diazo Formation time scale determination

- Solvent: MeCN: DMSO: water (6: 1: 1).
 - NMR (DMSO) shows rxn with t-Bu-NO₂ is over in 5-6 minutes.
 - ReactIR analysis* (MeCN: DMSO : H_2O , 1150 cm⁻¹) agrees.
 - *Solution prepared and injected directly to the probe.



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TCI Full Flow Synthesis

- Flow system: DCI-NH₂, tBu-NO₂, quench: KCN/CuCN.
- No significant time dependence on diazonium hold >10 min.
 - \rightarrow Diazonium is relatively stable in solution.
 - Lower [K] gives poor conversion- higher [K] has no benefit.
 - Lower [Cu] and higher [Cu] give poor conversion
 - Temperature (20 vs 40°C) had no effect. 0°C plugged.
- New conditions improve yield and color.
 - Air vs N₂ atmosphere.
 - Extraction solvent or none.
 - Base vs none.









Improved process by

- 1) Minimal to no suspended solids; Removes filtration step.
- 2) Lighter solution color; better visibility for work-up separation.
- 3) Better extraction efficiency and yields.



N-Methyl Bis(fluorosulfonyl)imide (Me-FSI): Unique electrolyte solvent

- Safety is still a main concern in widespread use of lithium-ion batteries.
- Nonflammable solvents increase the safety margins of LIB operation.
- Originally developed as new Ionic Liquid (IL) precursor (Zhang group, ANL).
- MeFSI can be repurposed as a non-flammable electrolyte solvent.
- Technical Difficulties:
 - Most synthetic methods not scalable due to expense or safety.
 - Huge excess of dimethyl sulfate required.
 - Highly exothermic work-up procedure.
 - Use of toxic dioxane.
 - Difficult to completely remove dioxane from the product.



MeFSI

N-Methyl Bis(fluorosulfonyl)imide (Me-FSI): Synthesis Screening Experiments

- Objective: remove large excess of Me₂SO₄ and dioxane. Monitor reaction.
- Less Me_2SO_4 (10 vs 15 eq) as the sole solvent gels.
- ¹⁹F NMR distinguishes Me-FSI and K-FSI: ability to monitor reaction.
- Best conditions: 3-5 eq. Me₂SO₄, DME, 80°C, no dioxane needed.
- LiFSI works well when replacing DME with EtOAc.





N-Methyl Bis(fluorosulfonyl)imide (Me-FSI): Scale-up

- 100g scale up completed using DME, only 4 equivalents Me₂SO₄, 80°C, 10h, no dioxane.
- Highly pure material (99.9% GC/MS) after modified workup and purification.

¹⁹F NMR

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55

50

0 0 0 0 F⁻S[']N⁻S[']F

45

40 fl (ppm) _ں_s_c 0´ `0

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MeFSI

Technical Accomplishments Me-FSI with GBL or EC + 5 % VC Full Cell Results

- Li-FSI can replace LiPF₆ in Me-FSI plus 20% co-solvents.
 - More stable to water.
- Solution benefits from passivation additives (LiDFOB, VC).
- Full cell analysis: NMC622 (C023)/Gr (A002B); 1C = 2 mA; 4.1-3.0 V.
- Solvent: 0.8M LiFSI in Me-FSI:GBL (8:2) + 0.2M LiDFOB.
- Solvent: 0.8M LiFSI in Me-FSI:GBL (8:2) + 0.2M LiDFOB + 5% VC.
- Solvent: 0.8M LiFSI in Me-FSI:GBL (8:2) No additive.
- Additives are required to prevent electrochemical decomposition of Me-FSI and get good cycling performance.
- All formulations are non-flammable.
- Work on other cathode materials and wider voltage ranges are in progress.

Methyl 2,2,3,3-Tetrafluoropropyl Carbonate (M-TFPC): Safer electrolyte solvent

- We previously reported on methyl 2,2,2-trifluoroethyl carbonate. o¹/_c
- M-TFPC targeted for high voltage and extreme temperature use.³
- Good candidate for flow chemistry: Fast, exothermic reaction
 - Heat of reaction is high at 15.8 kJ or 210 kJ/mol.
 - Reaction has no induction period and little accumulation (i.e. reacts as the MCF is added).
 - Optimize reagents, time and temperature for flow conditions.
 - In-line analysis required.

⁺ HO $C_{F_2} \xrightarrow{CF_2H} \longrightarrow O \xrightarrow{O} O \xrightarrow{CF_2H} F_2$

Lithium 4,5-dicyano-1,2,3-triazole (Li-DCT)

- Thermally stable, may be useful in preventing anodic dissolution with high voltage Li-FSI, like Li-TDI.¹
- Previously reported synthesis.⁴
- 2032 Coin Cell, NMC622// Graphite, 30°C
- Electrolyte: 1.0M LiFSI + 0.2M LiDCT in EC/EMC 3/7
- 1C: 2mA, 3-4.1V, C/20 3X, HPPC, C/3 92X, HPPC, C/20 3X.

⁴Savateev et. al. Chem. Commun. 2017, 53(73) 10192. Sabate et.al, Dalton Trans. 2012,41,3817. Scheers, et. al. J. Power Sources 251 (2014) 451. Kerner, Manfred; et. al. Journal of Power Sources (2016), 332, 204-212.

Technical Accomplishments: Feedback

ADA evaluation of fluoro-solvents (Courtesy D. Yanga, W. Xing and B. Almeida)

- Although we distribute numerous samples, due to possible IP and confidentiality concerns, are unable to show most results.
- Project goal: Develop high voltage, non-flammable electrolyte.
- Figure 1 shows discharge voltage profiles of Li/LiNMO cells with various electrolytes.
- Figure shows discharge voltage profiles of LTO/LNMO full cells during formation for NSE2b-e and NSE5b electrolyte candidates and the baseline electrolyte control. The NSE2e electrolyte based full cells displayed similar discharge voltage profiles and similar specific capacity (100 mAh/g) compared with the control electrolyte based cell. The NSE2b-d and NSE5b electrolyte based full cells displaced smaller specific capacity (100 mAh/g).

LTO/LNMO Cells: Formation Discharge

Response To Previous Year Reviewer' Comments

There were no comments from last years reviewers.

Collaborations

Process R&D and material scale up:

- Argonne National Laboratory
- High voltage solvents, Me-FSI (Zhang, ANL)
- Ionic liquids for batteries (Zhang, ANL)
- Fluorinated Electrolytes (Amanchukwu, U of Chicago)
- Material samples provided for further research:
 - ADA Technologies
 - Argonne National Laboratory
 - Brookhaven National Laboratory
 - NREL
 - University of Chicago
 - UC San Diego
 - Wildcat Discovery

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Remaining Challenges And Barriers

- New advanced battery chemistries call for new and/or reformulated materials.
- New electrolyte materials are being continuously invented and tested in laboratories but only limited quantities are available to evaluate basic properties and performance.
- There is a strong demand from the research community for high quality, uniform experimental materials.
- Large quantities of these high quality experimental new materials are needed for industrial validation and prototyping.
- Industry is typically unable to accurately model the cost of production based on bench scale procedures.
- New materials also need to be evaluated for performance to be successfully introduced to the market.
- Emerging manufacturing technologies need to be evaluated to address production costs of battery materials.
- MERF has the capability to evaluate, manufacture, and distribute large quantities of new materials to assist the battery community as well as develop and evaluate technologies for more efficient manufacturing of advanced materials.

Proposed Research For Next Fiscal Year

- In collaborations with other researchers we will complete electrochemical testing on new imidazole-based salts and non-flammable, Me-FSI based electrolytes for Li-ion batteries.
- Continue to evaluate new technology platforms focused on Green Chemistry and economy of the process.
- Continuous flow chemistry (CFC) will continue to be a major focus due to advantages over batch in:
 - Fast mass and heat transfer; accurate control of reaction conditions.
 - Rapid optimization of reaction parameters.
 - Low usage of reagents in the optimization process.
 - Dramatically increased process safety.
 - Integrate CFC with inline analytical and AI/ML to enable autonomous process optimization.
- Process R&D and Scale Up Target 2-3 new materials for development and scale-up.
 - Evaluate and select the best synthesis technique and route for each new material.
 - Develop scalable process, analytical methods, quality control procedures, and characterize the impurity profile.
 - Validate the manufacturing process for material quality consistency.
 - Supply material samples to the research community and industry for their evaluation.
 - Investigate chemical purity vs. electrochemical performance for new materials.
- This program is open to suggestions for scaling up newly invented, promising battery materials.
- ²⁹ Any proposed future work is subject to change based on funding levels.

Summary • Accomplishments

- We have scaled up both Me-FSI and TFPC.
- We have synthesized and are testing three nitrogen heterocycle- based lithium salts:
 - Li-TCI
 - Li-F-DCI
 - Li-DCT
- Efficient continuous methods for advanced electrolyte materials (Li-TCI, MTFPC) are in development.
- To date, hundreds of samples totaling over 21 kilograms have been provided to battery research groups.

Technical Highlights

- New materials, in particular, TFPC have been shown to have a beneficial impact in battery programs.
- Partners developed nonflammable electrolytes with similar discharge voltages using MERF materials.

Impact

- Continuous flow reactor technology continues to be developed and evaluated. This emerging manufacturing technology platform permits expedited process R&D and rapid "proof of concept" materials production. Flow reactor systems reduce time and cost associated with process R&D. Scope, limitations and benefits of producing other advanced materials in continuous flow process continue to be investigated.
- Sample of all materials produced at MERF are available to support basic research and for industrial validation.

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Technical Back-up Slides

Technical Back-up Slides: Me-FSI Flame Tests

Technical Back-up Slides: Approach Flowchart

Work with discovery chemists to learn about promising new materials. Collaborate on special requests for custom materials not commercially available.

Maintain a database of potential materials to scale.

Prioritize materials based on systematic approach including level of interest, validated performance and feasibility. Discuss candidate materials with DOE for final approval.

Conduct process R&D and take materials through the stages of scale-up.

Develop material specifications that meets electrochemical performance at the lowest cost.

Make materials available for industrial evaluation and to the R&D community for basic research.

Provide feedback to discovery chemists, helping guide future research.

Technical Back-up Slides: Candidate Materials

- Establish candidate materials by interaction with battery researchers in:
 - ABR/BATT funded programs to add novel materials.
 - Organizations looking to have known materials scaled.
 - DOE programs who want to use novel materials in their own research programs.
- Add materials by closely monitoring the trends in the battery research community.
 - e.g., high voltage materials.
- Prioritize materials Ranking based on:
 - Level of interest and guidance from stakeholders from ACCESS advisory board.
 - Material performance and impact.
 - Prioritization criteria.
 - DOE guidance.

Technical Back-up Slides: Available Samples

Abbreviation	Chemical Name	Uses	Sample Size (g)	Abbreviation	Chemical Name	Uses	Sample Size (g)
ANL-1NM2	2,2-dimethyl-3,6,9-trioxa-2-siladecane	Low Flammability Solvent	100s		lithium 4.5-dicvano-2-		
ANL-1NM3	2,2-dimethyl-3,6,9,12-tetraoxa-2-	Low Flammability Solvent	0	Li-TDI	(trifluoromethyl)imidazol-1-ide	Lithium Salt	10s
	2.2 dimethyl 4.7.10.12 tetreove 2			ARL-LIPFTB	Lithium perfluoro-tert-butoxide	Lithium Salt	100s
ANL-1S1M3	silatetradecane	Low Flammability Solvent	0	Li-PFPBO	lithium 2-fluoro-4,5-dioxo-2- (perfluorophenyl)-1,3,2-dioxaborolan-2-uide	Electrolyte Additive	100s
ANL-2SM3	2,2,4,4-tetramethyl-3,8,11,14,17-pentaoxa- 2,4-disilaoctadecane	Low Flammability Solvent	0				
FDEC	Bis (2,2,2-trifluoroethyl) carbonate	Fluorinated Solvent	10s	ARL-HFiPP	Tris (1,1,1,3,3,3-hexafluoro-2-propyl)	Electrolyte Additive	0
FEMC	Methyl (2,2,2-trifluoroethyl) carbonate	Fluorinated Solvent	100s				
TFPC	3,3,3-Trifluoropropylene carbonate	Fluorinated Solvent	100s	MGC	methyl ((2-oxo-1,3-dioxolan-4-yl)methyl)	Electrolyte Additive	10s
ANL-RS2	1,4-di-tert-butyl-2,5-bis(2- methoxyethoxy)benzene	Flow Battery Catholyte/ Shuttle	0	LiBAFMB	lithium 3,9-diallyl-3,9-difluoro-2,4,8,10- tetraoxo-1,5,7,11-tetraoxa- 6- boraspiro[5.5]undecan-6-uide	Electrolyte Additive	1s
ANL-RS5	(2,5-dimethoxy-1,4- phenylene)bis(diisopropylphosphine oxide	Flow Battery Catholyte/ Shuttle	1s				
ANL-RS6	2,5-di-tert-butyl-1,4-phenylene tetraethyl bis(phosphate	Flow Battery Catholyte/ Shuttle	100s	CWU-FRION Li[B(DPC)(Ox)]	Lithium [(3,6-diethoxyphosphoryl)-1,2- catecholato][oxalato]borate	Electrolyte Additive	1s
ANL-RS21	6,7-dimethoxy-1,1,4,4-tetramethyl-1,2,3,4- tetrahydronaphthalene	Flow Battery Catholyte/ Shuttle	100s	MTMSMC	Methyl (trimethylsilylmethyl) carbonate	Low Flammability Solvent	10s
ANL-RS51	(2,5-dimethoxy-1,4- phenylene)bis(diethylphosphine oxide)	Flow Battery Catholyte/ Shuttle	1s	ETMSMC	Ethyl (trimethylsilylmethyl) carbonate	Low Flammability Solvent	10s
				BTMSMC	Bis-(trimethylsilylmethyl) carbonate	Low Flammability Solvent	10s

• Although Me-FSI was scaled up this year, all material made was obligated to current projects.

