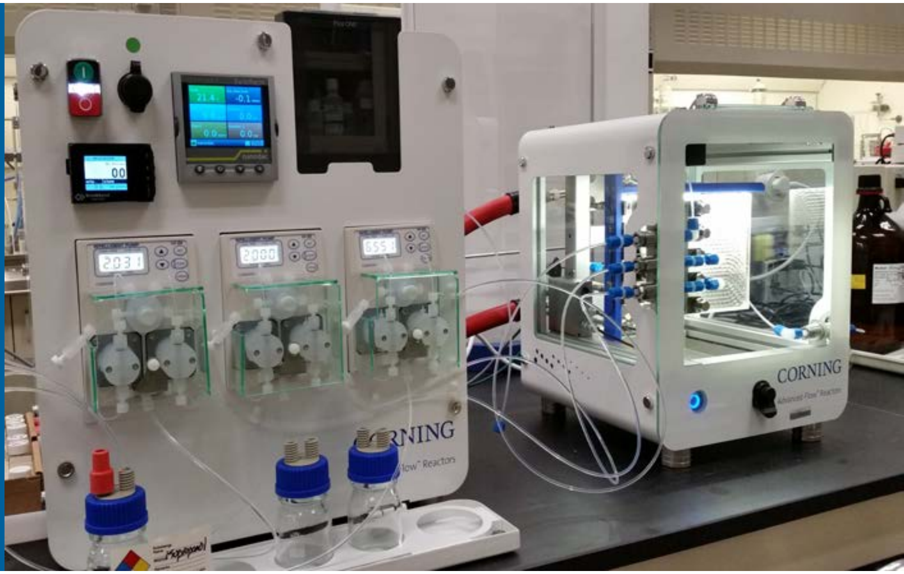
Process Development and Scale up of Critical Battery Materials – Continuous Flow Produced Materials



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Project ID: BAT168

June 19, 2018, Arlington, VA

Overview

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2018
- Percent complete: on going

Budget

- Total project funding:
  - $1.5M in FY17
  - $950k in FY18

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
  - Next Generation Anodes for Lithium-ion Batteries Project
  - Enabling High-Energy/High-Voltage Lithium-ion Cells Project
- **Supporting battery research for:**
  - ADA Technologies
  - General Motors
  - SilLion
  - Army Research Laboratory
  - Lawrence Berkeley National Laboratory
  - Pacific North National Laboratory
  - Purdue University

Approach - Milestones

- FY17
  - Process development and scale up of 3,3,3-trifluoropropyl carbonate was completed.
  - Scale up of 1,2-bis(trifluoromethyl)ethylene carbonate (BTFMEC). Photosynthesis of intermediate glycol completed in hundred gram scales. Process development for BTFMEC is in progress.
  - Stability and impurity study of LiFSI.
  - Work on scale up of lithium iron oxide (Li_5FeO_4) for Next Generation Anodes is in progress.
  - Modular continuous flow reactor system is set up and operational.
  - Develop green, safe and cost efficient manufacturing processes for advanced electrolyte materials.
  - Design, synthetize and evaluate advanced binders for next generation anodes for LIBs.
- FY 18
  - Scale up of ethyl and propyl trifluoromethyl sulfones in continuous flow and batch.
  - Synthesis of Si-containing carbonate solvents in continuous flow and batch.
  - Continuous flow synthesis of HTDI (LiTDI) a parent acid for LiTDI salt.
  - Continue work on scalable process development for synthesis of lithium iron oxide (Li_5FeO_4) for Next Generation Anodes project.
  - Large scale synthesis of Al-LLZO precursors to support FSP facility.

Objectives and Relevance

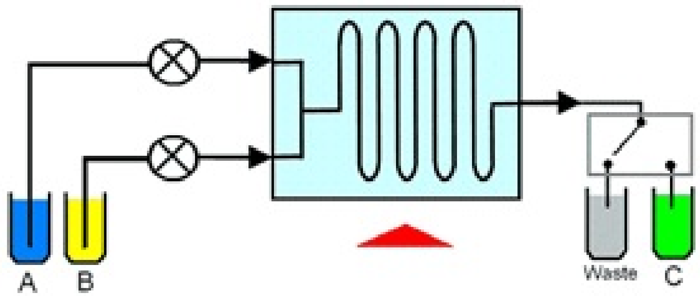
- The objective of this program is to provide a systematic research approach to:
  - Develop **cost-effective, scalable** processes for manufacturing of advance materials by more efficient use of feedstock and energy, improve safety and reduce environmental impact.
  - Evaluate **emerging synthesis technologies** for the production of experimental battery materials.
  - Produce and provide **high quality and sufficient quantities** of these materials for industrial evaluation and to support further research.
  - Investigate effect of **material purity** and **impurity profiles** on battery performance.
- 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, 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.

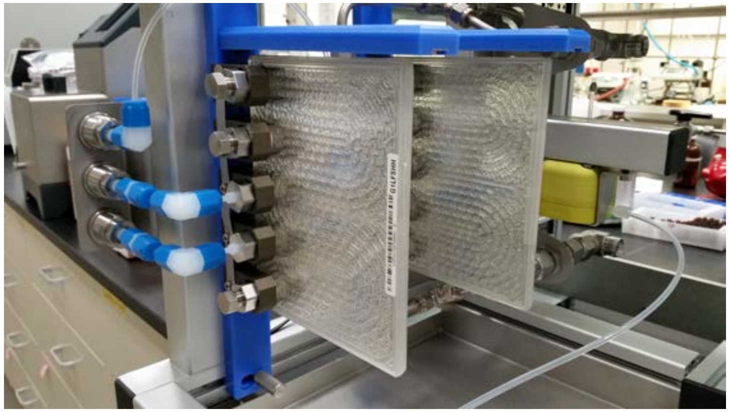
Approach and Strategy

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

Approach and Strategy

- In the quest for better, advanced electrolyte materials (solvents, salts, additives) scientists design, synthetize 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.
- Feasibility of the new process is demonstrated by material manufacturing in continuous flow mode.





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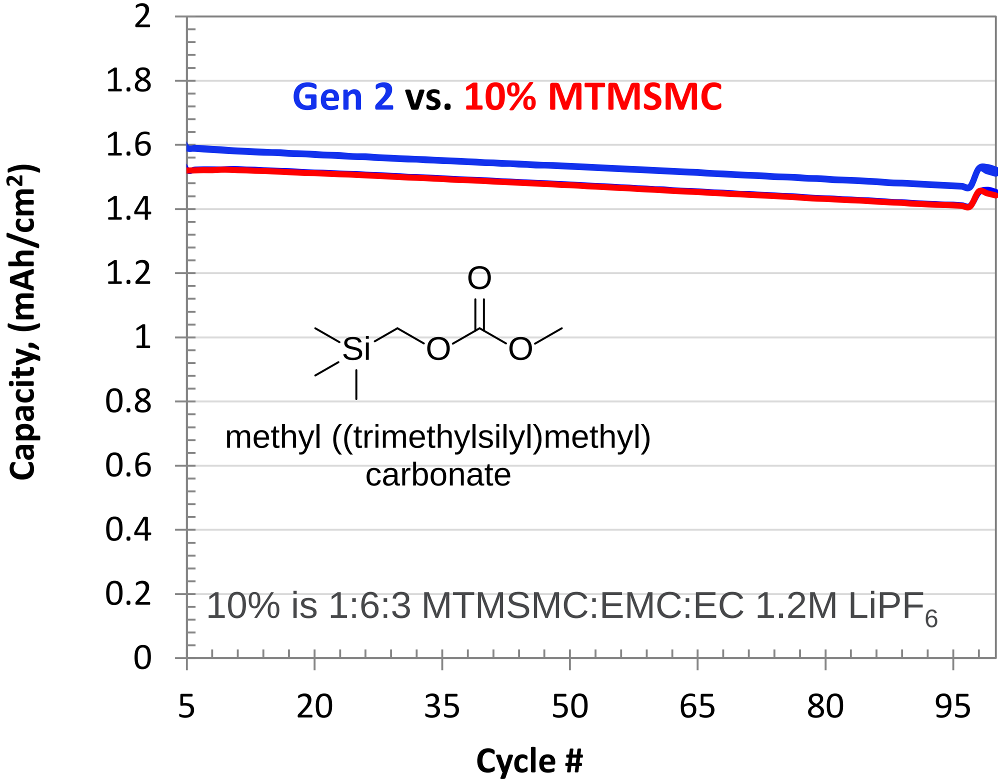
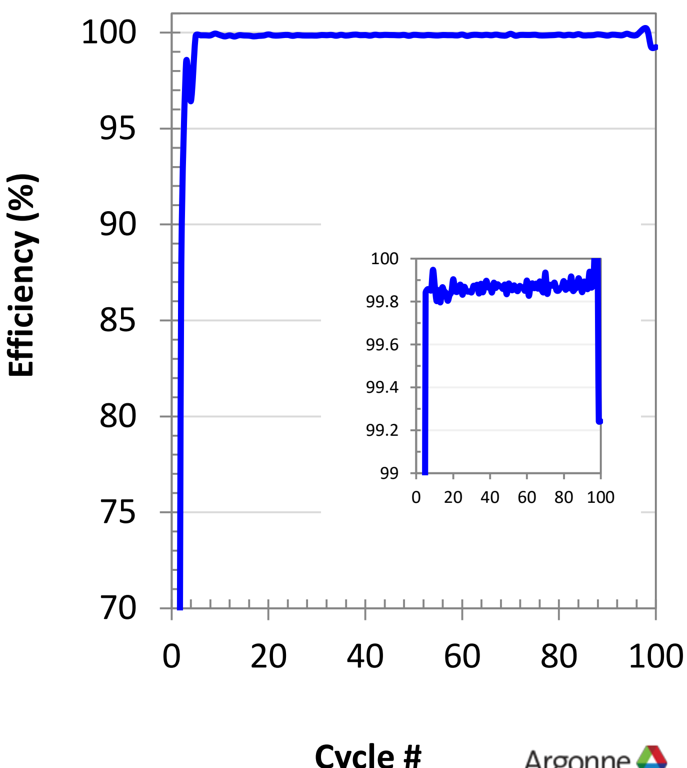
Technical Accomplishments

Si-containing carbonate solvents

- Continuous flow synthesis of MTMSMC was reported in 2017 AMR.
- The material is reported to be a flame retardant. The goal is to improve battery safety without performance degradation.
- Preliminary electrochemical evaluation (CR2032, graphite/NCM523, 3.0 - 4.4 V, C/3, 30ºC) revealed a slightly lower capacity compared to Gen2.

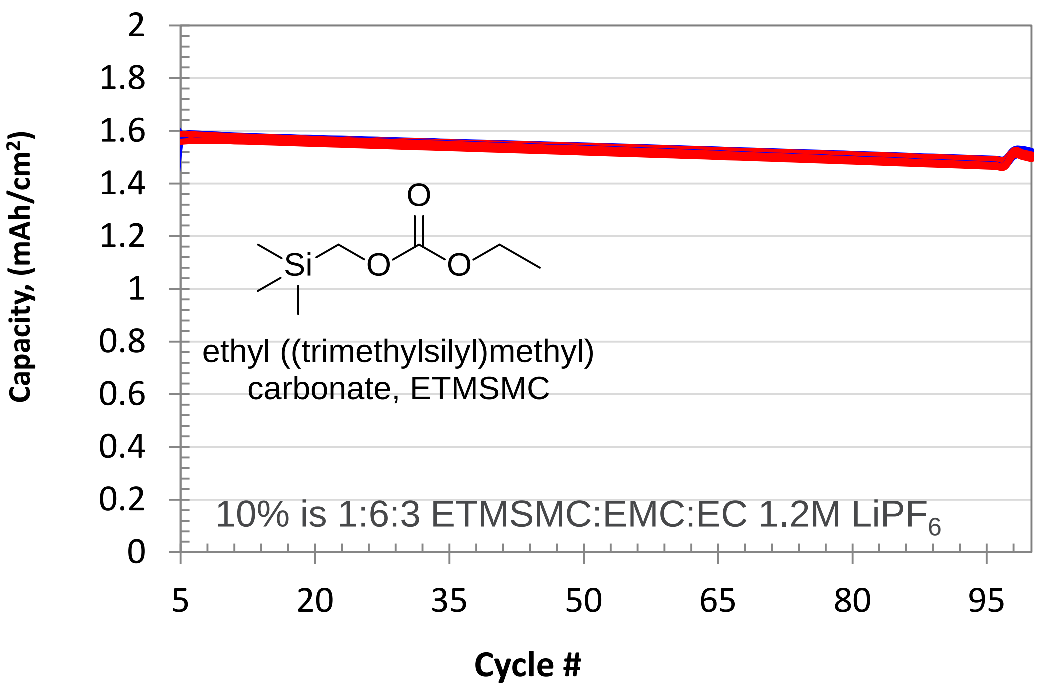


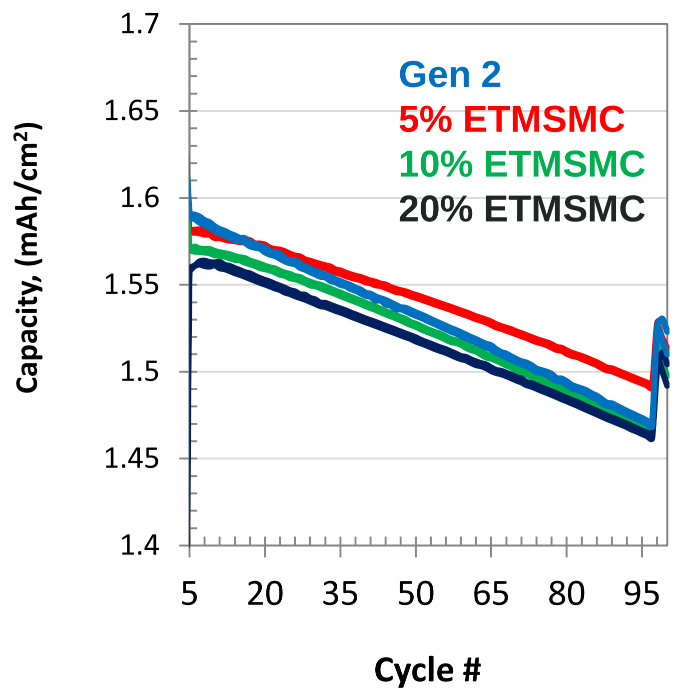


Technical Accomplishments

Si-containing carbonate solvents

- The catalytic synthesis in continuous flow developed for MTMSC provided a low yield of ETMSMC.
- Batch synthesis in the presence of a homogenous catalyst gave better results.
- Preliminary evaluation revealed better performance than MTMSC electrolyte.
- **The material is available for sampling.**

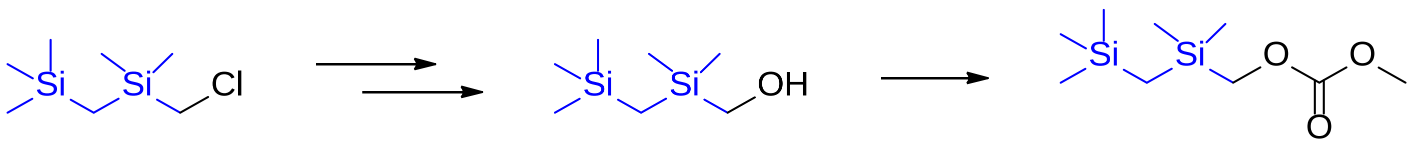


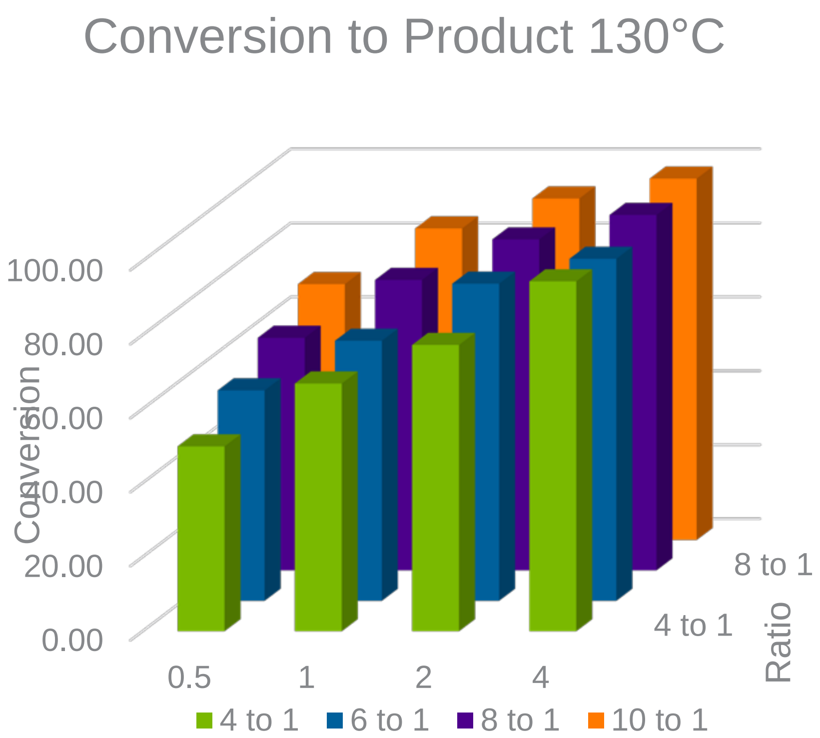


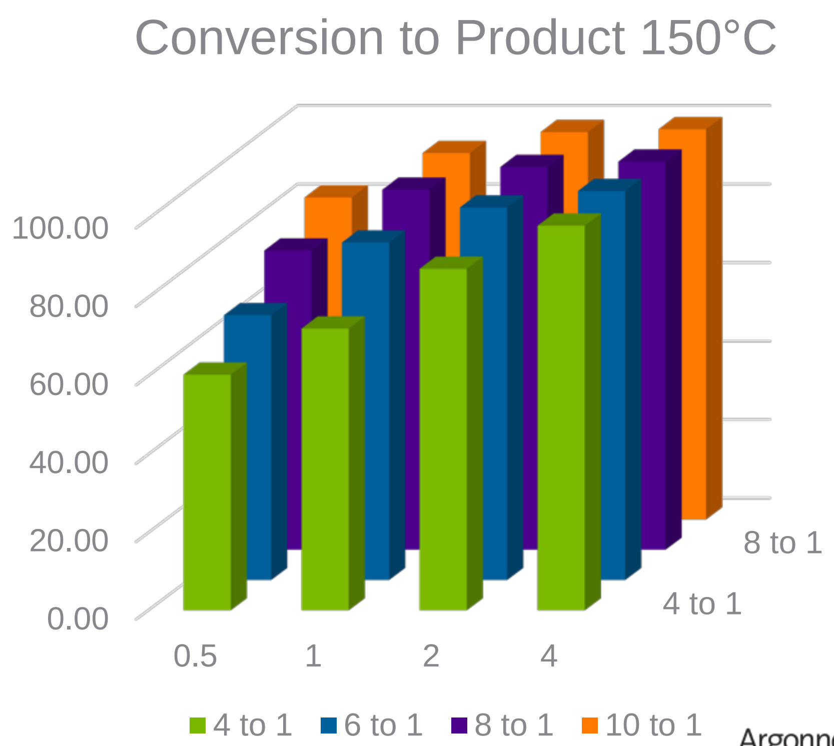
Technical Accomplishments

Si-containing carbonate solvents

- The continuous flow procedure developed for MTMSMC was evaluated and re-optimized for the synthesis of analogue with two Si atoms in the molecule.







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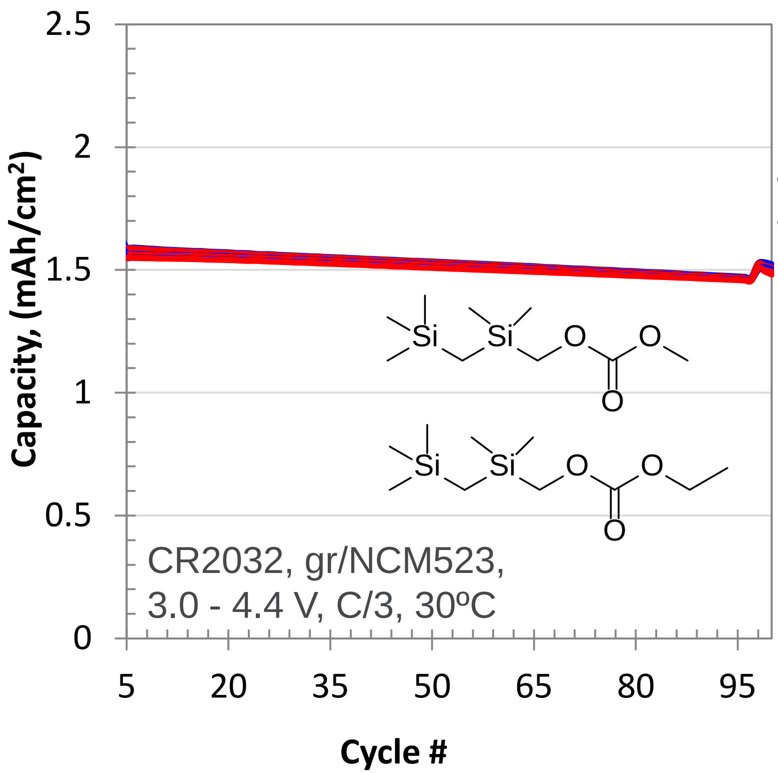
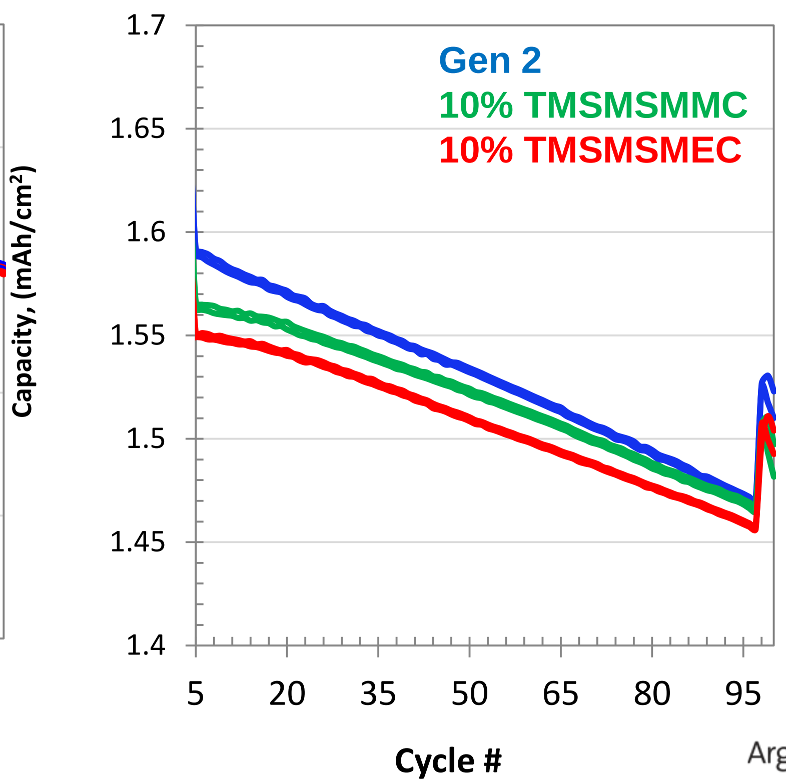
Technical Accomplishments

Si-containing carbonate solvents

- We assume that increasing number of Si atoms in the molecule should enhance the desired property of the material (flame retarding/propagation).
- The preliminary data indicate that replacing 10% (by weight) of EMC with Si-containing carbonates results in only slightly lower initial capacity for both methyl and ethyl derivative.





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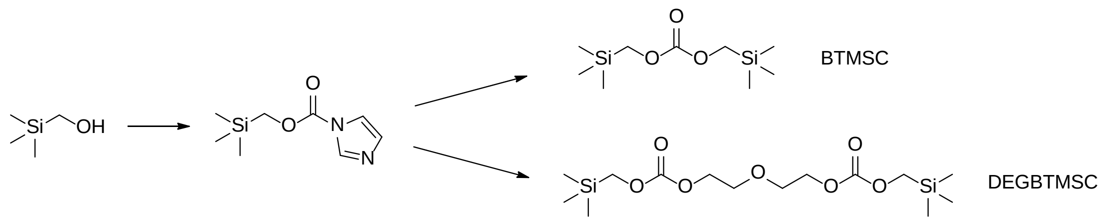
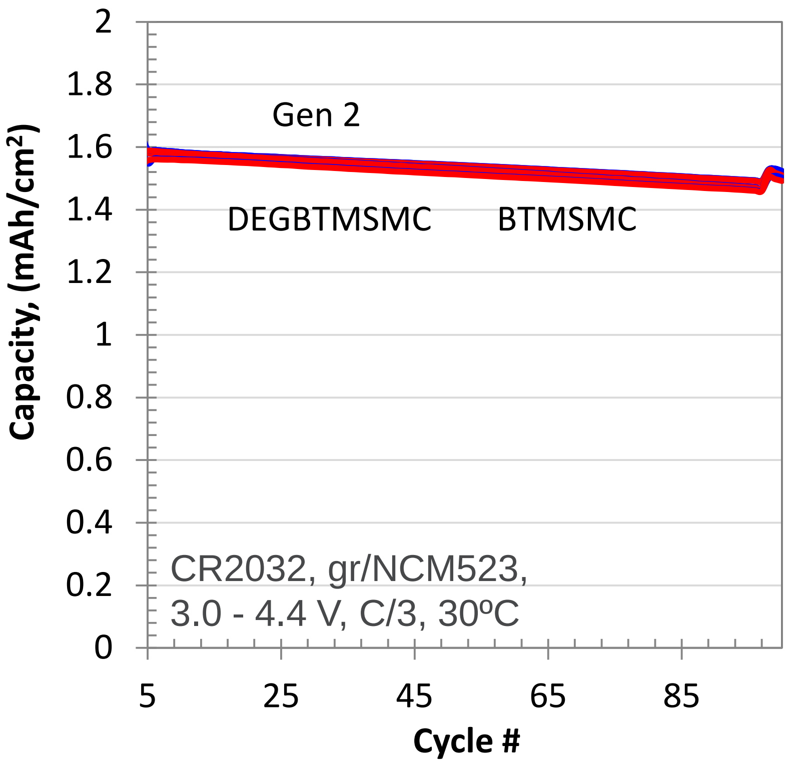
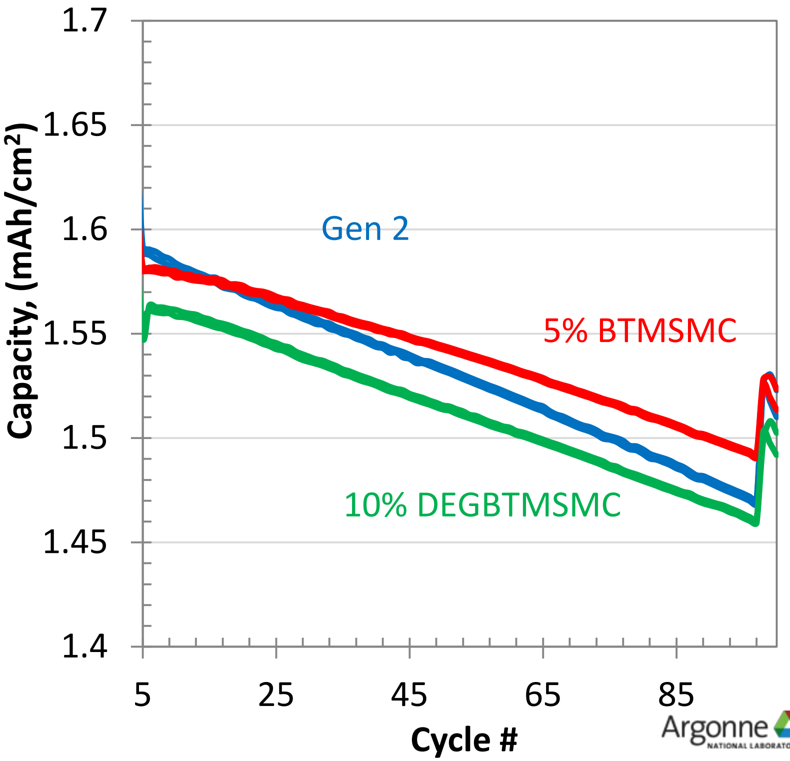
Technical Accomplishments

Si-containing carbonate solvents

- Several other Si-containing carbonates were prepared and preliminary electrochemical performance data show promise.



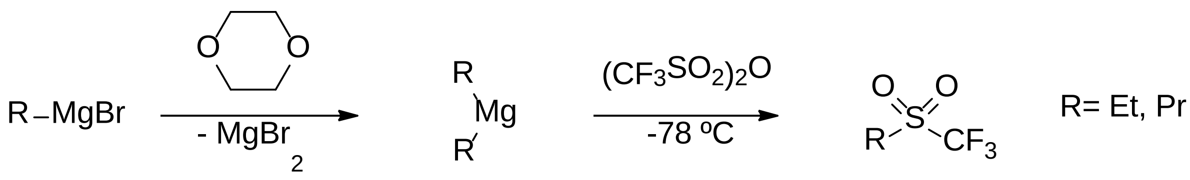




Technical Accomplishments

Trifluoromethyl sulfones

- Ethyl trifluoromethyl sulfone and propyl trifluoromethyl sulfone have been reported as promising candidates for high voltage electrolytes.
  - S. Burkhardt at al., PCT Int. Appl. (2017), WO 2017209762.
  - Z. Zhang at al., Energy and Environ. Sci. 2017, 10, 900.
  - W. Li, PCT Int. Appl. (2015), WO 2015073419.



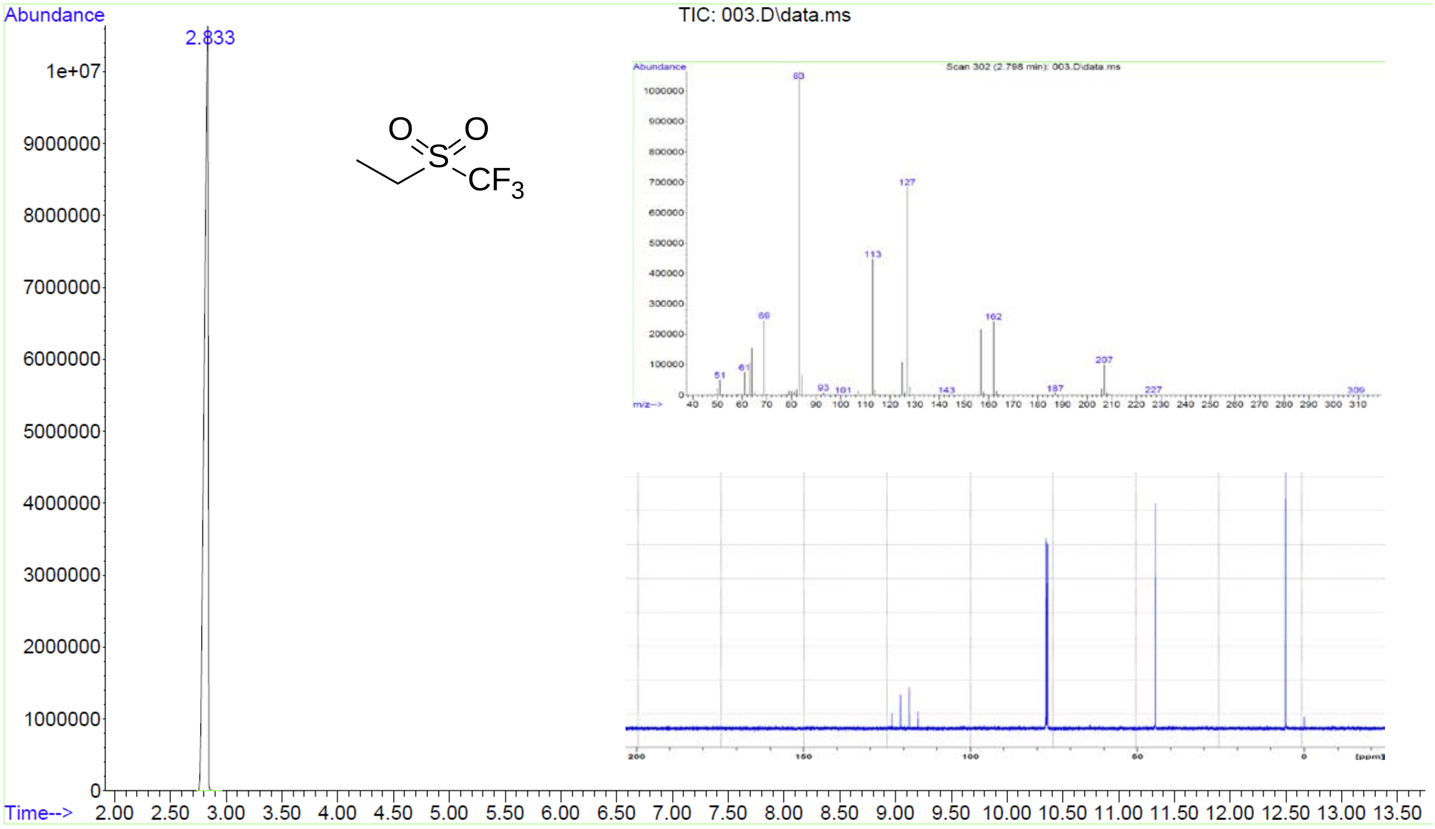
- Initial procedure was investigated with the goal to:
  - Eliminate dioxane use and subsequent centrifugation procedure to remove magnesium bromide.
  - Eliminate cryogenic temperature requirement (extreme exothermal effect).
  - Successfully in removing the centrifugation step.

- Dioxane as a co-solvent seems to be essential for the successful reaction.

Technical Accomplishments

Trifluoromethyl sulfones

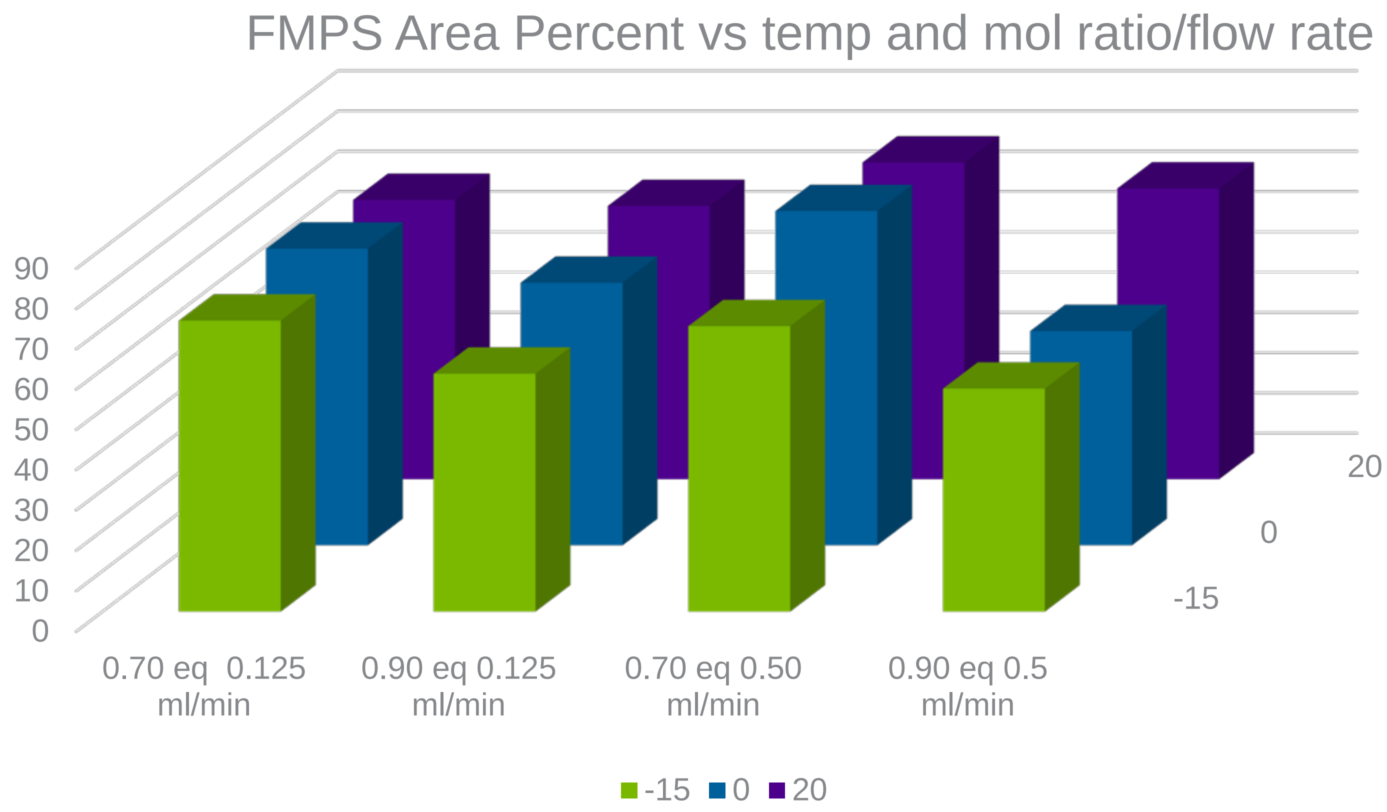
- Alternative syntheses route, reagents and reaction conditions were extensively investigated in a batch mode.
- The process has been simplified and optimized for best yield and product purity.
- **Both materials (FMES and FMPS) are available for sampling.**



Technical Accomplishments

Trifluoromethyl sulfones in continuous flow mode

- Continuous flow mode was investigated in order to mitigate the extreme exothermic effect of the reaction (better heat transfer rate due to very high surface to volume ratio).
- Continuous flow mode allowed the reaction to be run essentially at room temperature that make it a viable process for large scale production.



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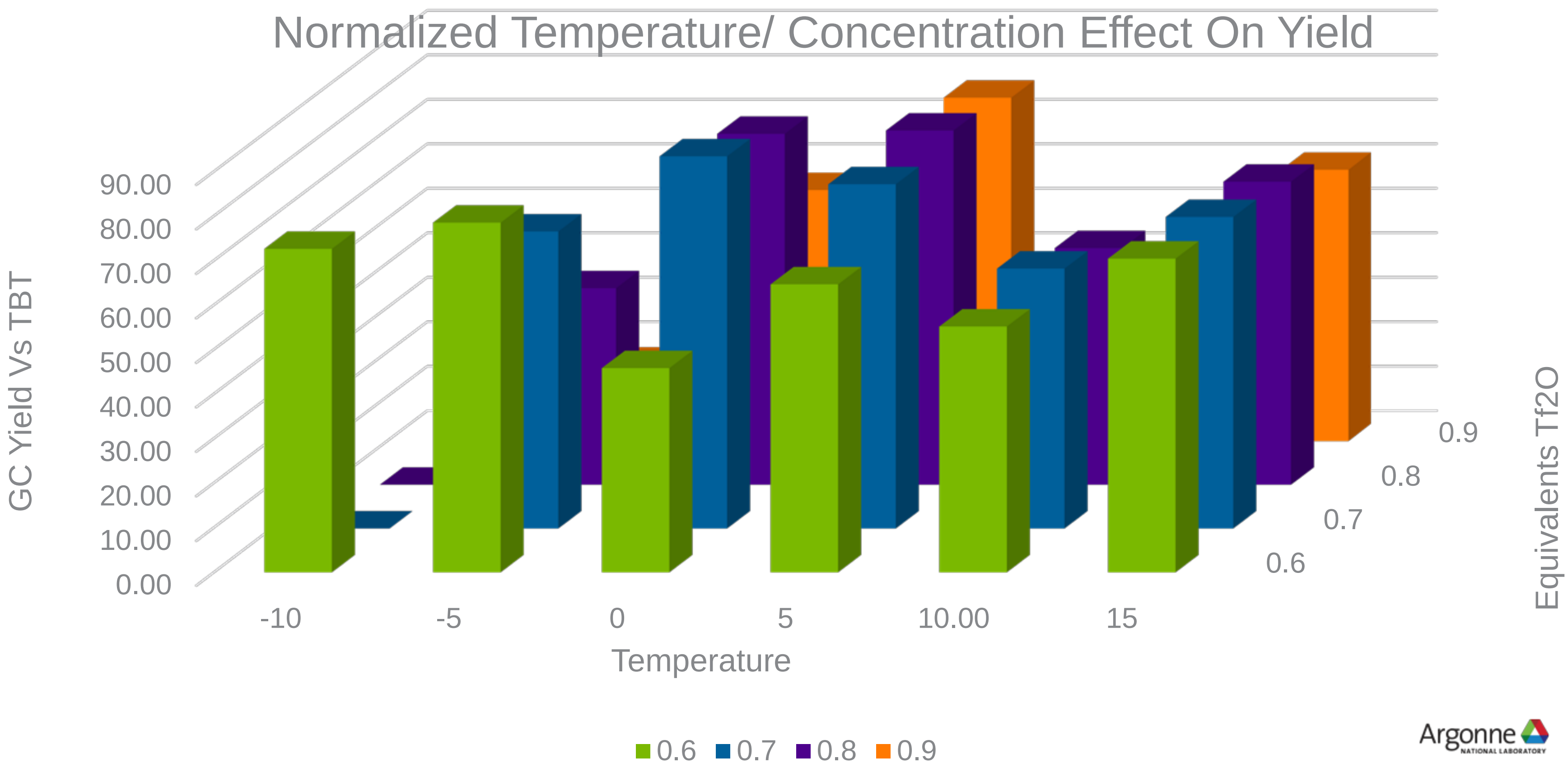
Technical Accomplishments

Trifluoromethyl sulfones in continuous flow mode

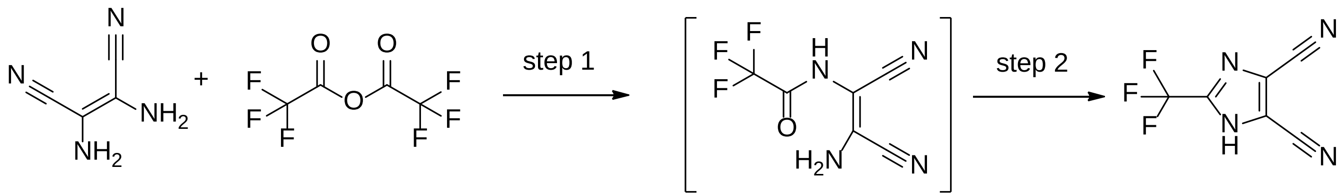
- Further optimization of the process refined the optimum process parameters.
- Replacing alkyl magnesium bromide with alkyl magnesium chloride allow for elimination of auxiliary solvent (dioxane).
- Dioxane is expensive, toxic and difficult to remove from the final product.



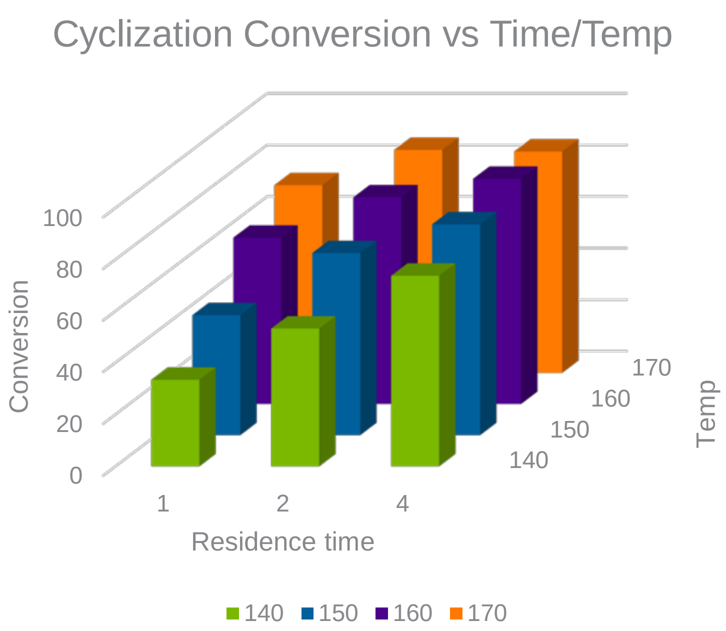
Technical Accomplishments

LiTDI revisited - continuous flow mode

- Batch synthesis of parent acid for LiTDI is a two step process.
- The modular, two microfluidic reactors cascade allow for one pass synthesis to greatly simplify the process.



H-TDI



first microfluidic reactor (step 1, reactor hold at 40 C to control exotherm)

second microfluidic reactor (step 2, hold at 170 C to facilitate cyclization)

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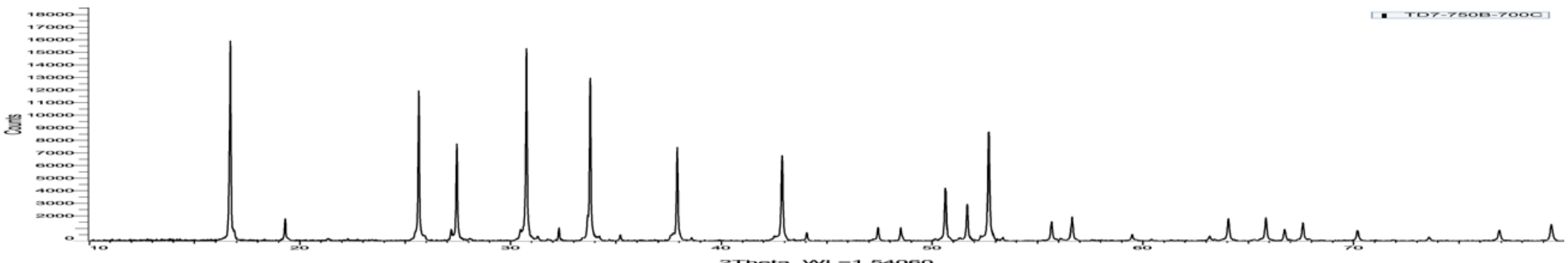
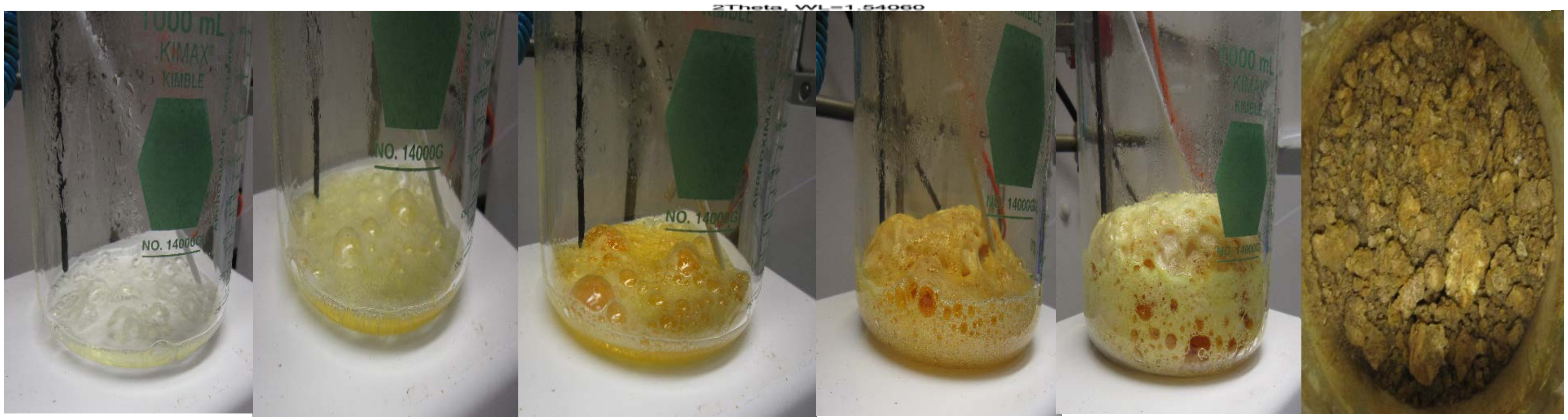
Technical Accomplishments

Al-LLZO – Sol-gel process investigation

- MERF investigated various processed for making Al doped lithium-lanthanum-zirconium oxide; garnet-type solid electrolyte for lithium batteries.
- The material is commonly produced by sol-gel process.
- After several experiments and process parameter variation we deemed sol-gel procedure non-scalable due to excessive foaming and toxic off gassing.



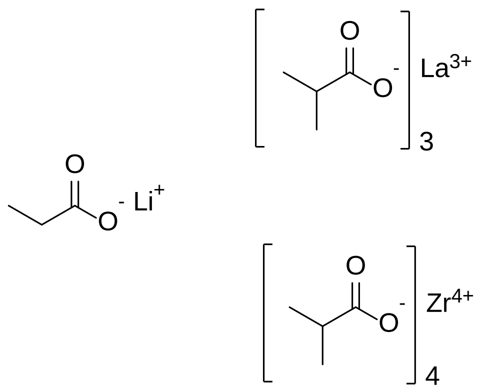


Technical Accomplishments

Al-LLZO –Precursor for FSP synthesis

- Alternative precursors were developed at MERF.
- Two separate sets (literature and MERF) of precursor formulations were prepared.
- All six materials were made on hundred gram scales.

- Literature set: based on propionic or isobutyric acid salts.
- Isolated solids.
- Soluble in alcohols.
- Unpleasant odor.



- MERF set
- Ease of preparation.
- Soluble in hydrocarbons.
- Stable in solution.
- Odorless.

Pending patent application

Response To Previous Year Reviewer' Comments

- There were no negative comments or questions that require addressing.

- Question 1: Approach to performing the work
- Reviewer 3: The reviewer acknowledged that this is very relevant work for materials development, and the approach is relatively unique in being agnostic to the source and targets of the proposed materials.
- Reviewer 4: This reviewer liked the stated concept of trying to develop new processes that will take some risk away from industry and also provide small quantities of new materials for testing.
- Question 2: Technical accomplishments and progress
- Reviewer 1: The reviewer pointed out that this program meets a critical need by linking the discovery of advanced battery materials with market volume and high volume manufacturing.
- Reviewer 2: The reviewer said that the development of a cost-effective process for the synthesis of organic solvents, screening the effect of various catalysts, and evaluation of several new solvents for LIBs is the main accomplishments of the project. The outcome of the project at this point is toward the development and scale-up of novel manufacturing processes for battery materials.
- Question 3: Collaboration and coordination with other institutions.
- Reviewer 1: The reviewer noted that the project team has various collaborations with DOE national laboratories, Army laboratories, and leading companies. The collaborations are at both scale-up and materials evaluation levels.
- Reviewer 5: This reviewer commented that adding industrial collaborators would strengthen this project.
- Answer: We agree. We are actively looking for additional industrial partners.

Collaborations

Process R&D and material scale up:

- Argonne National Laboratory
  - High voltage solvents (John Zhang)
  - Lithium iron oxide (Chris Johnson)
- Battery500 Consortium
  - Precursors for Al-LLZO
- Next Generation Anodes For LIB Project
  - Binary in-situ cross-linking binder

Material samples provided for further research:

- Army Research Lab
- Lawrence Berkeley National Lab
- Pacific Northwest National Lab
- ADA Technologies, Inc.
- General Motors
- SilLion, Inc

Other Collaboration:

- Advano
  - SBV to produce surface modified silicon NP for advanced anode.

Remaining Challenges And Barriers

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

Activities For Next Fiscal Year

- Process R&D and Scale Up - Target 3-5 new materials.
  - Evaluate and select the best synthesis technique and route for each new material.
  - Develop scalable process, analytical methods and quality control procedures.
  - Validate the manufacturing process for material quality consistency.
  - Characterize the impurity profile.
  - Supply material samples to the research community and industry for their evaluation.
- Investigate chemical purity vs. electrochemical performance for new materials.
- Continue evaluate new technology platforms with a focus on Green Chemistry and economy of the process.
  - Continuous processes using flow chemistry.
    - Fast mass and heat transfer; accurate control of reaction condition.
    - Allow rapid optimization of reaction parameters.
    - Low usage of reagents in the optimization process.
- Program is open to suggestions for scaling up newly invented, promising battery materials.

Summary

- Continuous flow reactor systems were acquired and installed.
- The modular system allows for flexible configurations to accommodate a wide range of chemistries with operating temperature range -20 to +200 ºC.
- This emerging manufacturing technology platform permits expedited process R&D and “proof of concept” materials production.
- Flow reactor systems reduce time and cost associated with process R&D.
- Efficient methods for manufacturing several advanced electrolyte materials were developed.
- Scope, limitations and benefits of producing other advanced materials in continuous flow process are investigated.
- Design, synthesis and evaluation of binary in-situ cross-linking binders to enable next generation Si-containing anodes for LIB was continued.
- Investigation of scale up procedure for lithium iron oxide (Li_5FeO_4) for Next Generation Anodes project is in progress.
- Several precursors for FSP production of Al-LLZO were scaled up.
- **Sample of all materials produced at MERF are available to support basic research and for industrial validation.**

Acknowledgements And Contributors

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- Argonne National Laboratory

  - Daniel Abraham
  - Joseph Libera
  - Christopher Johnson
  - Andrew Jansen
  - Brian Polzin
  - Steven Trask
  - Allison Dunlop
  - John Zhang
  - Wenquan Lu
  - Gerald Jeka

- Next Generation Anodes for Lithium-ion Batteries Project Team
- Enabling High-Energy/High-Voltage Lithium-ion Cells Project Team

Samples request and further information:

www.anl.gov/merf