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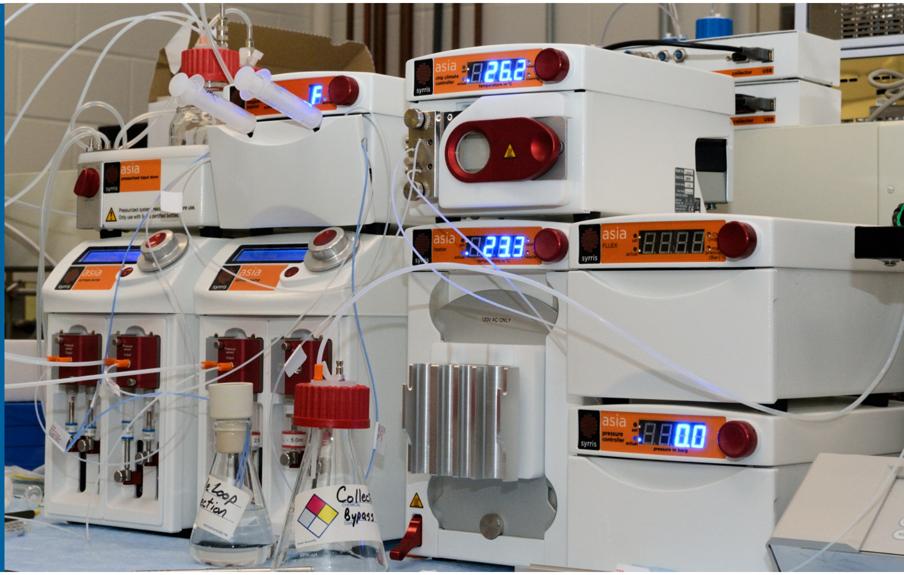
Process Development and Scale up of Critical Battery Materials – Continuous Flow Produced Materials



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Project ID: ES168

June 2017, 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 FY16
  - $1.5M in FY17

Barriers

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

Partners

- Scaling materials for:
  - Oak Ridge National Laboratory
  - Argonne's Applied R&D Group
  - Next Generation Anodes for Lithium-ion Batteries Project
  - Enabling High-Energy/High-Voltage Lithium-ion Cells Project
  - DellaTech

Supporting battery research for:

- Army Research Laboratory
- Lawrence Berkeley National Laboratory
- Pacific North National Laboratory
- SolidEnergy Systems
- Toyota Technical Center

Approach - Milestones

- FY16
  - The following materials have been scaled up and samples distributed to researches:
    - ORNL Li-BMFBM (stable, high temperature lithium salt).
    - Methyl 2,2,2-trifluoroethyl carbonate (solvent for HV electrolyte).
    - Bis(2,2,2-trifluoroethyl) carbonate (solvent for HV electrolyte).
    - Various polymers (binders for Si-graphite composite anode).
    - Glycerol methyl dicarbonate (additive to HV electrolyte).
- 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 hundreds gram scale. Process development for BTFMEC is in progress.
  - Stability and impurity study of LiFSI.
  - Scale up of lithium iron oxide (Li_5FeO_4) and lithium cobalt oxide (Li_6CoO_4) for Next Generation Anodes project 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.

Objectives and Relevance

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

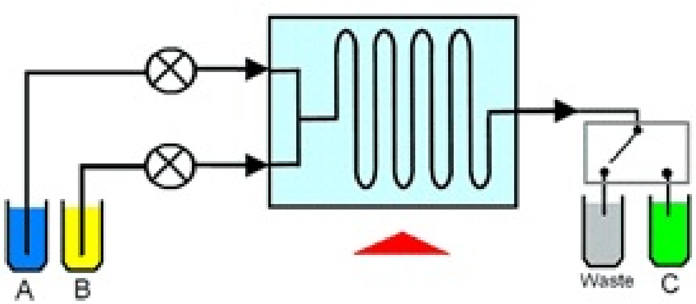
- The relevance of this program to the DOE Vehicle Technologies Program is:
  - The program is a key missing link between discovery of new advanced battery materials, market evaluation of these materials and high-volume manufacturing
    - Reducing the risk associated with the commercialization of new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

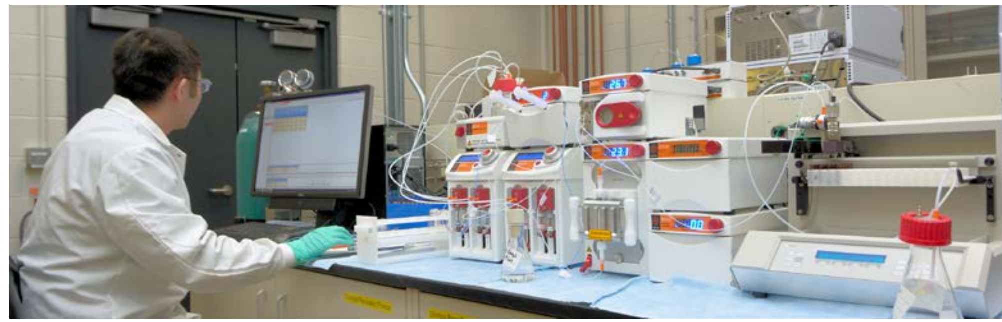
Approach and Strategy

- Discovery scientists invent new material, synthesize small amount in a batch system and evaluate basic properties.
- MERF prioritize new materials 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, develop and validate optimal process parameters for production of new materials.
- Proof of concept production in kilograms scale
  - Validate electrochemical performance.
  - Develop performance *vs.* purity and impurity profile relationship (material specification).
- Make materials available to support basic research and to industry for evaluation.
- Provide feedback to discovery chemists, helping guide future research.

Approach and Strategy

- Flow Chemistry enables the continuous synthesis of materials from discovery through process development and (possible) production scale.

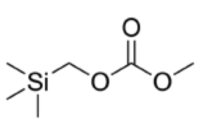




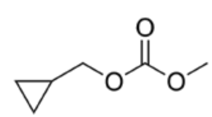
- Benefits of flow reactor:
  - Excellent mass and heat transfer improve kinetics, reduces reaction time and results in better selectivity and yield.
  - Reaction can be run in conditions not practical in batch process.
  - Allow for an on-line monitoring and analysis in a real time.
  - Improve process safety by minimizing volume of active reacting zone.
  - Improve economy of the process.
- Continuous flow reactor can be used for rapid screening of reaction condition to better understand fundamentals of process kinetic and thermodynamic.
- Feasibility of the new process is demonstrated in a proof-of-concept material manufacturing in continuous flow mode.

Technical Accomplishments And Progress Overview

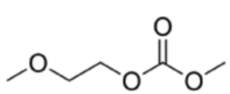
- Modular Continuous Flow Reactor System (Syrris Asia model) has been procured and installed.
- The flow reactor technology platform allows for rapid screening of reactions condition to better understanding impact on the product quality and quantity and for quick optimization to make manufacturing process as effective as possible.
- Flow reactor system reduces time and cost associated with process R&D.
- Continuous processes for production of several advanced solvents for LIB electrolyte have been evaluated and optimized.
  - Catalytic process for manufacturing of advanced non-symmetrical carbonates.
  - Catalytic process for production of siloxane solvent ANL-2SM3.



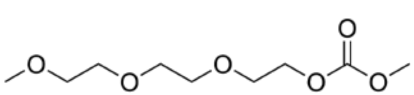
methyl ((trimethylsilyl)methyl) carbonate
(MTMSMC)



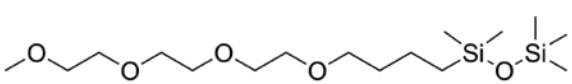
cyclopropylmethyl methyl carbonate
(CPMMC)



2-methoxyethyl methyl carbonate
(MEMC)



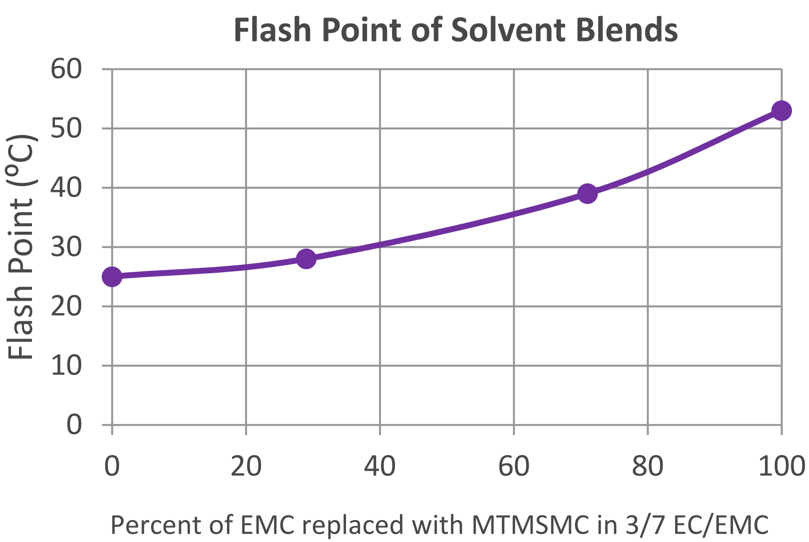
2-(2-(2-methoxyethoxy)ethoxy)ethyl methyl carbonate
(TEGMMC)

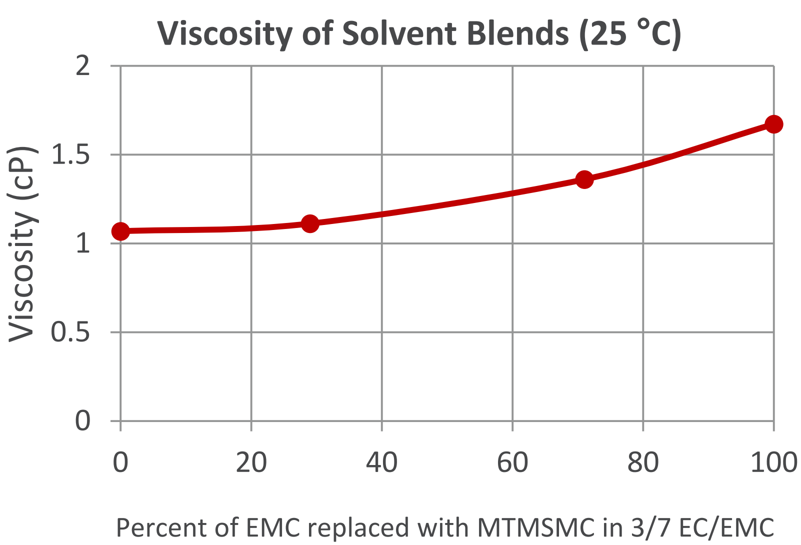


2,2,4,4-tetramethyl-3,9,12,15,18-pentaoxa-2,4-disilanonadecane
(ANL-2SM3)

Technical Accomplishments And Progress
MTMSMC: Basic Properties of the Material

- Preliminary investigation of basic physicochemical and electrochemical properties indicates that MTMSMC is a promising solvent for LIB electrolyte.
- Partial replacement of EMC with MTMSMC in EC/EMC solvent mixture increase flash point potentially improving safety of the battery.
- Moderate increase in viscosity was observed with increased contents of MTMSMC in the solvents blend.

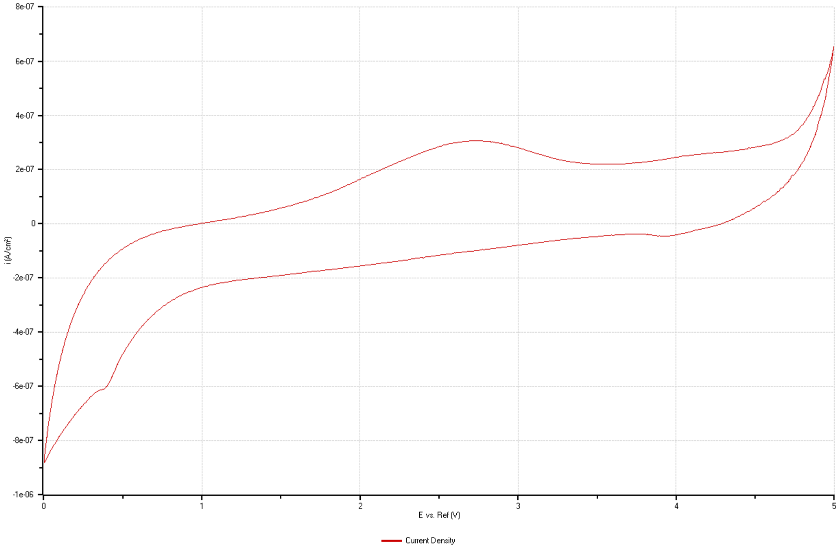




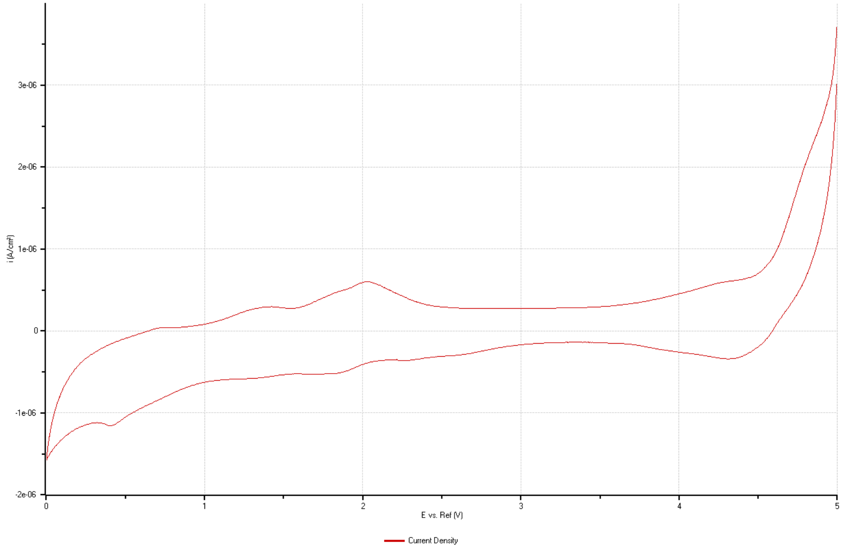
Technical Accomplishments And Progress
MTMSMC: Basic Properties of the Material

- Salt solubility, chemical compatibility and electrochemical stability of MTMSMC formulated electrolytes were examined.
- Investigation of performance of half- and full-cells (coin format) with electrolytes containing MTMSMC is in progress.

1.0 M $LiPF_6$ in MTMSMC/EMC/EC 2/5/3 w/w



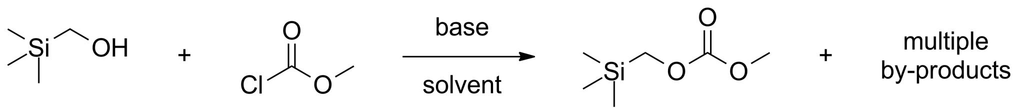
1.0 M LiFSI in MTMSMC/EMC/EC 2/5/3 w/w



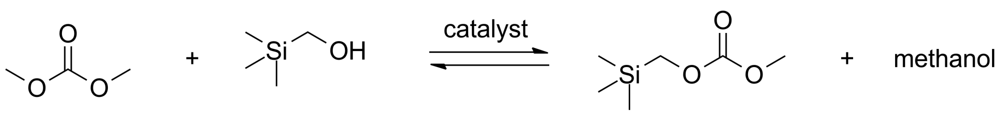
- CV condition: Pt/Li/Li, 0 – 5 V vs. Li/Li^+, 20 mV/s, 22 °C

Technical Accomplishments And Progress: Methyl (trimethylsilyl)methyl Carbonate (MTMSMC)

- The material has been referred in the literature as a flame retarding component for safer LIB electrolyte formulation.
- The single reference does not disclosure source or technique used to obtain the material.
- Standard reaction procedure for synthesis of MTMSMC failed. The reaction produced multiple by-product difficult to remove.

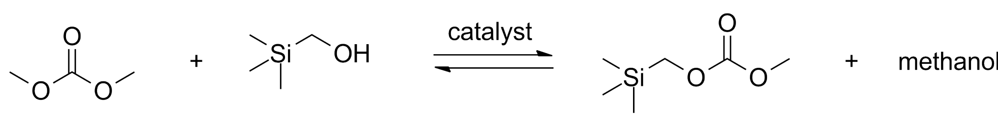


- Transesterification of dimethyl carbonate with (trimethylsilyl)methanol was investigated as an attractive alternative and good candidate for continuous manufacturing process.

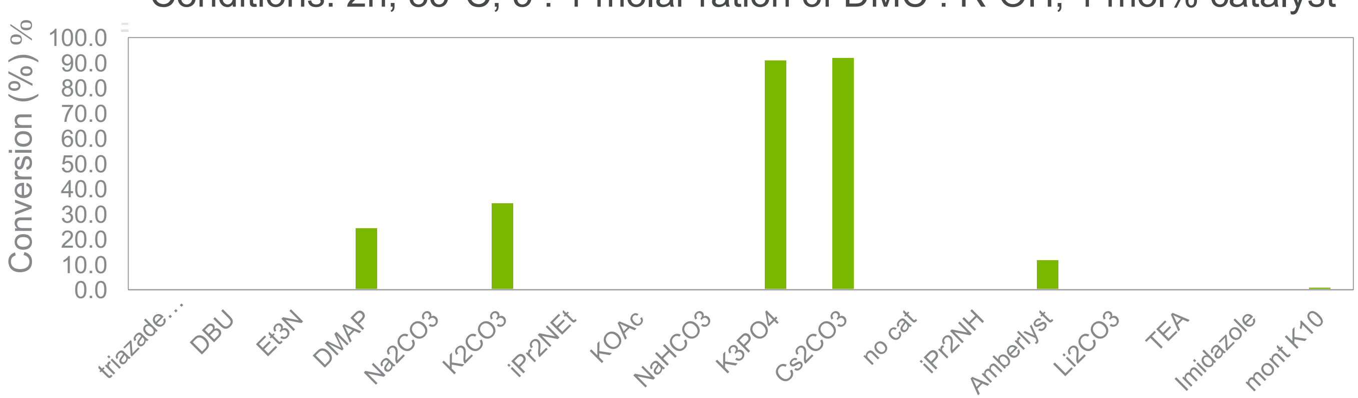


Technical Accomplishments And Progress: MTMSMC - Initial Catalyst Screening in Batch

- Catalyst screening revealed wide variation in activity.
- Loose correlation with base strength, but other factors apply.
- Reaction temperature and kinetics limited in batch system by boiling point of the solvent (DMC) – inefficient.
- Long reaction time (more than 2h) required to achieve good conversion ratio - energy wasteful.
- Catalyst needs to be removed after each batch – increase in operation costs.
- Conclusion: batch process is not suitable for manufacturing.

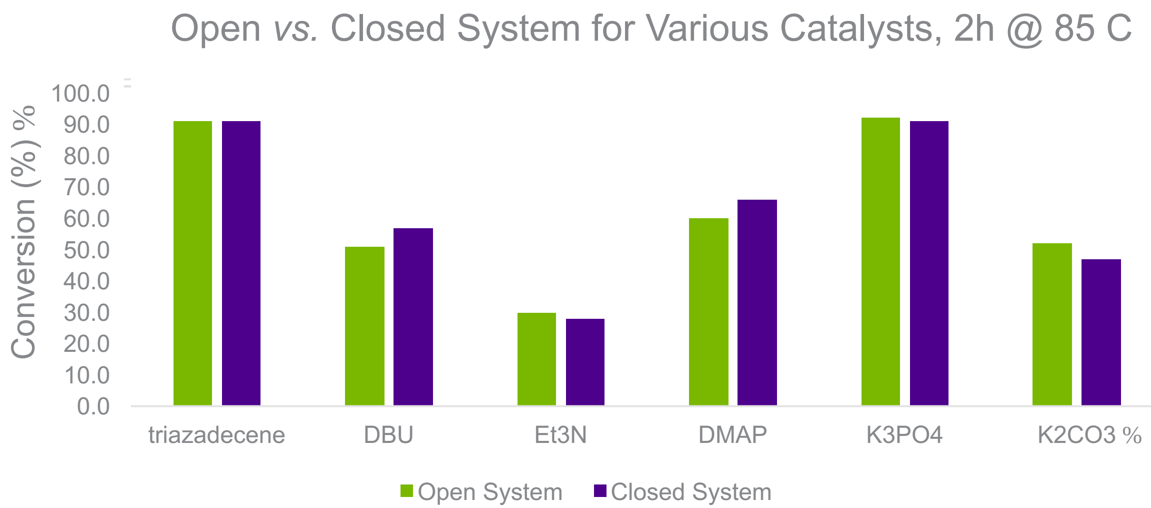


Conditions: 2h, 85°C, 5 : 1 molar ration of DMC : R-OH, 1 mol% catalyst



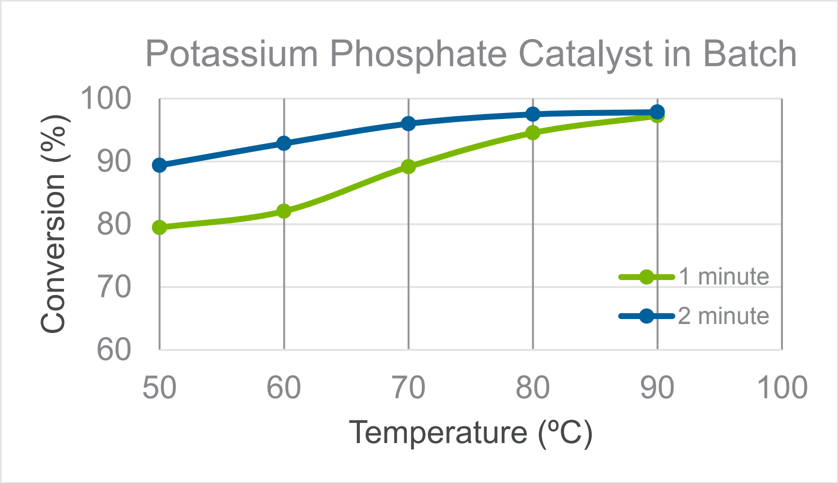
Technical Accomplishments And Progress: Can the Reaction be Adopted for Continuous Flow?

- The reaction is potentially reversible preventing complete conversion.
- Batch closed system (methanol is not removed) mimics flow reactor system.
- Closed system experiments provide results almost identical to open (ventilated) system.
- Conceivable to develop a successful flow process (which is a closed system).
- Further development focused on solid catalyst (no need to remove catalyst after reaction – simplify and lower cost of production).



Technical Accomplishments And Progress: Catalyst Activity – Batch *vs.* Flow

- Potassium phosphate (K_3PO_4) showed good conversion ratio in batch experiment at a much lower temperature then other catalysts but it slowly dissolved in the reaction mixture.
  - The residual catalyst needs to be removed adding additional step and cost to the process (big disadvantage!).
- Potassium carbonate (K_2CO_3) performance was acceptable in batch but very inefficient in the flow reactor.
  - Only 3% conversion at 120°C, 4 minute residence time (not shown on the graph).
- Neither catalyst is suitable for continuous flow process.
  - Process parameters optimized for batch need to be validated and re-optimized for flow system.



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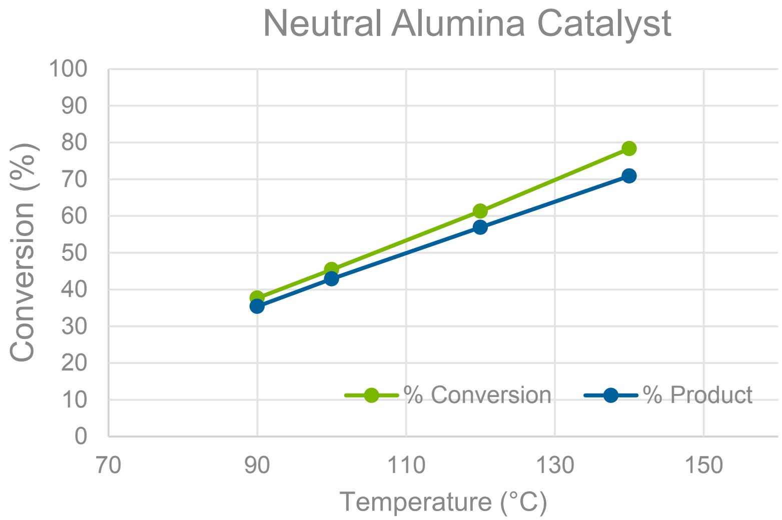
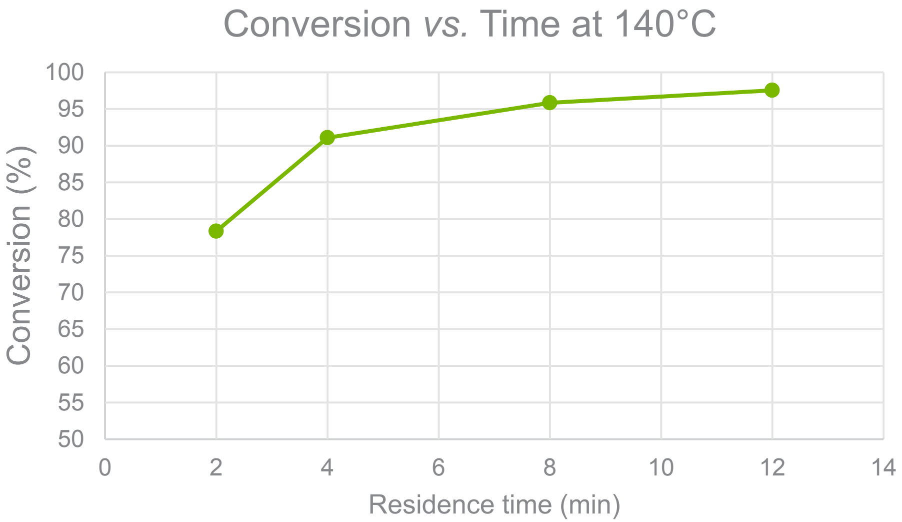
Technical Accomplishments And Progress: Solid Catalyst Evaluation in Flow System

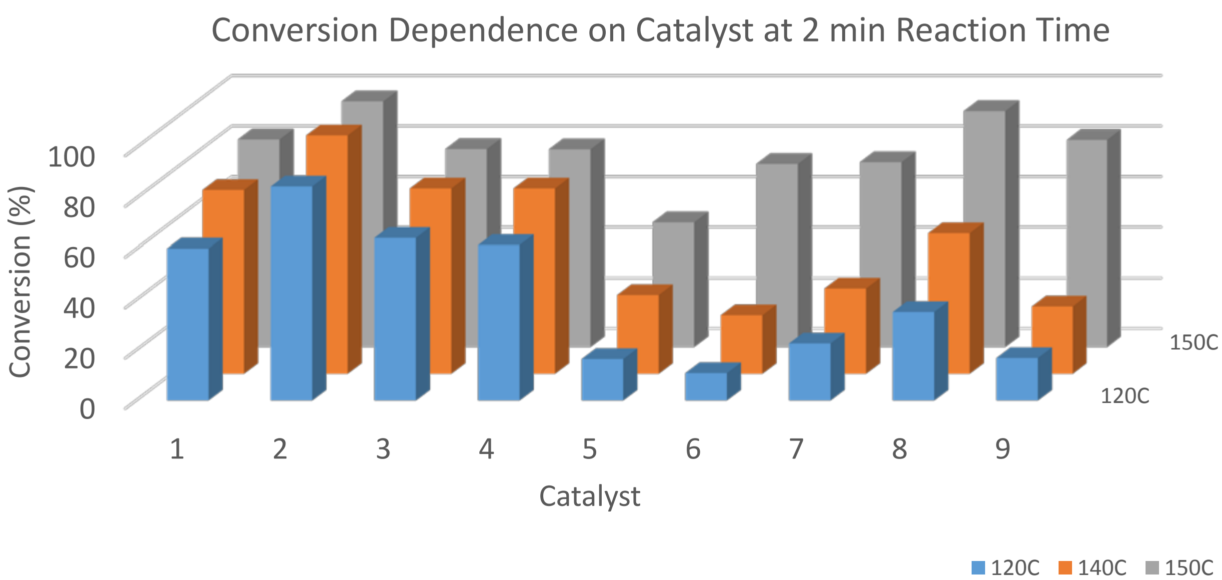
- Alumina is an inexpensive material with catalytic properties.
- Various grades and formulations are commercially available.
- Alumina is not soluble in organic solvents, no need for after-treatment.
- Neutral alumina showed slightly lower activity in a flow system than other catalyst at the same temperature.
- Near 100% conversion can be achieved at elevated temperature and extended residence time.





Technical Accomplishments And Progress: Solid and Solid-Supported Catalysts.

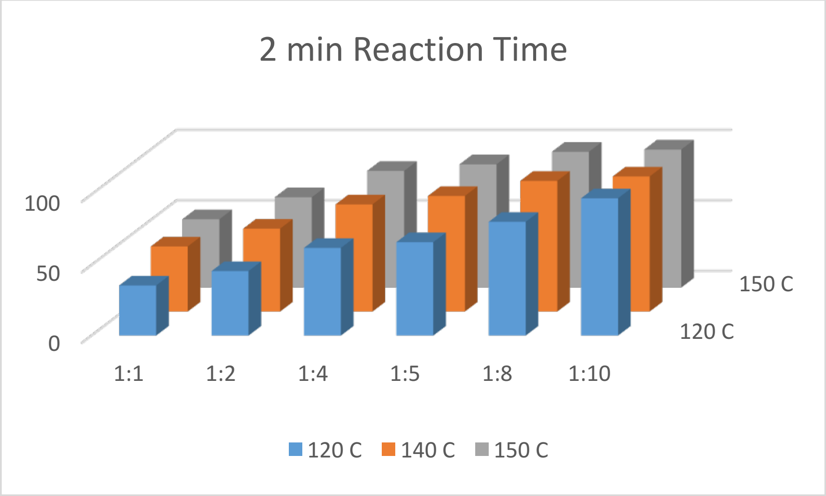
- Can modified alumina exchange catalytic activity?
- Can temperature and reaction time be lowered to make the process more energy and cost efficient?
- Several catalyst were prepared and screened in continuous flow system.
- Basic alumina (commercially available material) demonstrated the best activity at lowest temperature.

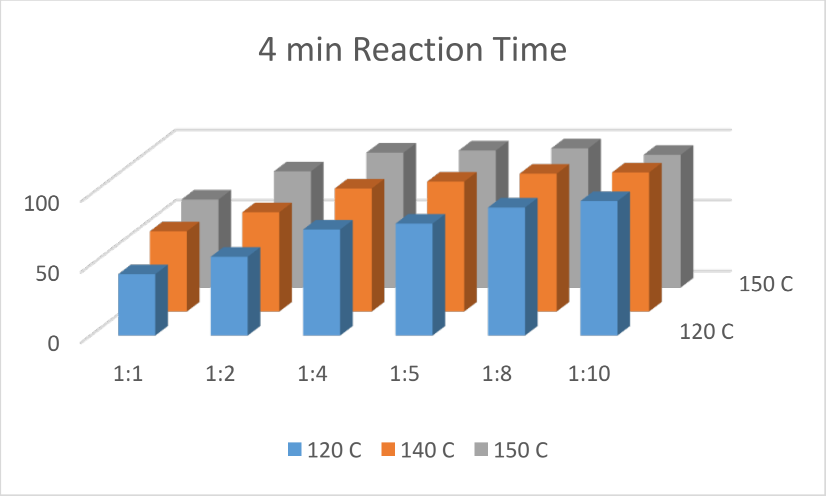


1. Alumina with 10 wt % $Zn(OH)_2$
2. Basic Alumina
3. Alumina with 10 wt % $Mg(OH)_2$
4. Neutral Alumina
5. Alumina with 5 wt% K_3PO_4
6. Alumina with 5 wt% KOH
7. Alumina with 5 wt% NaOH
8. Alumina with 5 wt% $Ca(OH)_2$
9. Alumina with 5 wt% KF

Technical Accomplishments And Progress: Reagents Ratio – Final Optimization.

- All initial reactions were run at 1:5 (trimethylsilyl)methanol to dimethyl carbonate (TMSM:DMC) ration to achieve near quantitative conversion.
- Series of experiments were run to investigate the effect of reagent ratio on conversion rate at different temperatures and reaction times.
- The experiments run at 2 and 4 min residence time (basic alumina catalyst) revealed that further increase in dimethyl carbonate ratio did not improve overall conversion ratio.





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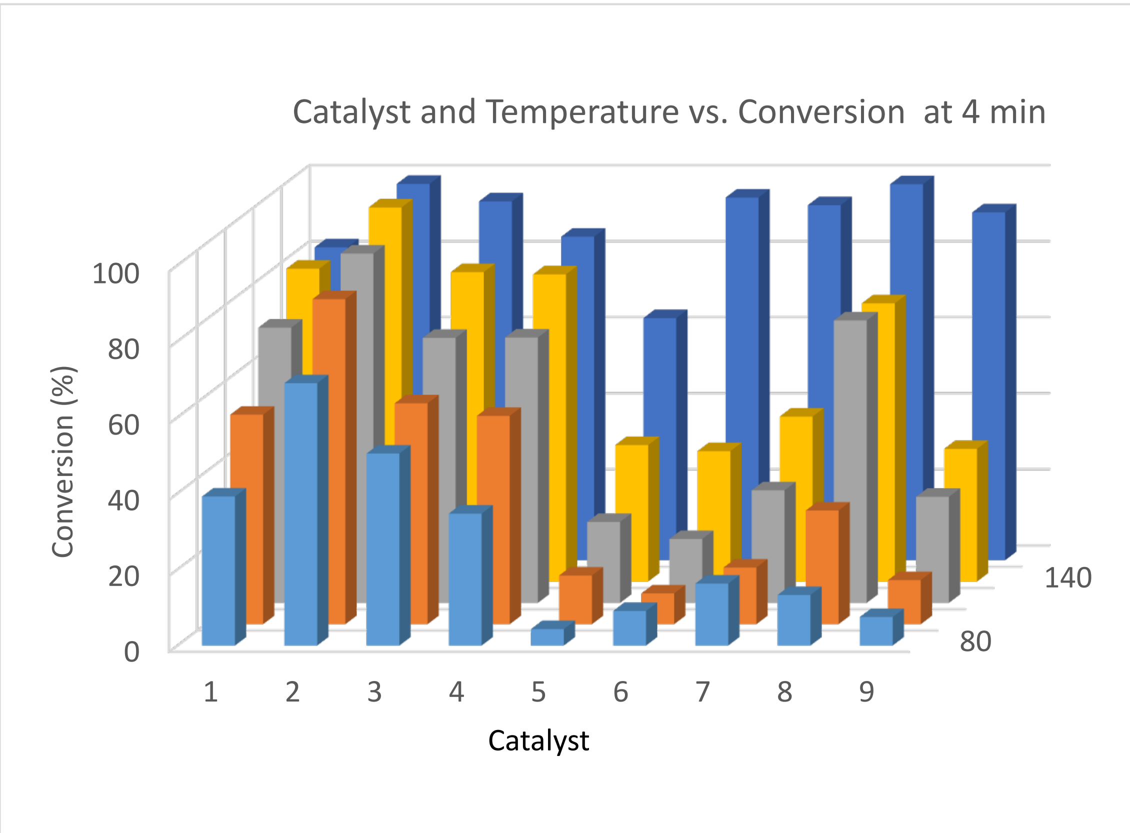
Technical Accomplishments And Progress: Solid Catalysts – Final Optimization.

- Basic alumina as a catalyst, reaction temperature of 150 °C, 4 min reaction time and 1:5 TMSM:DMC ratio were selected as optimum reaction conditions for scale up.



1. Alumina with 10 wt % $Zn(OH)_2$
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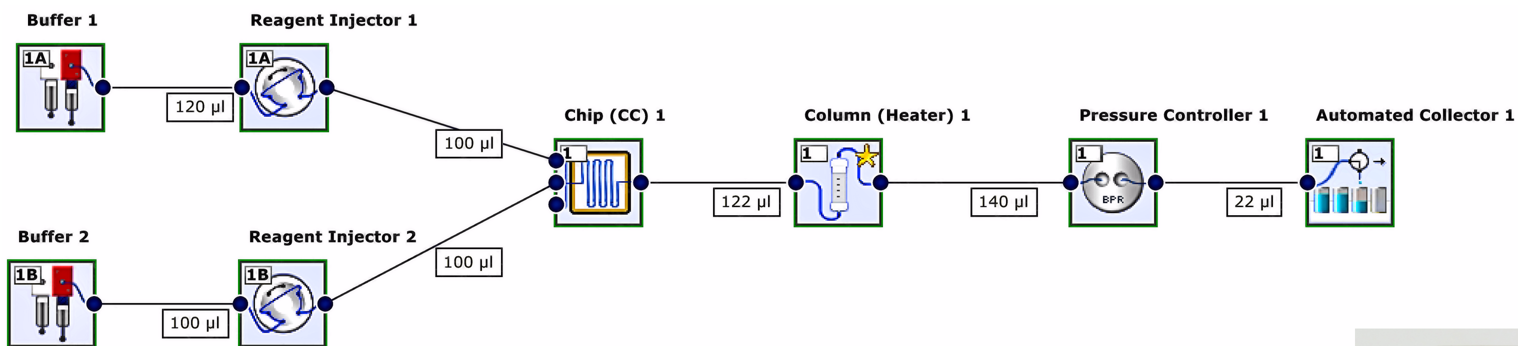
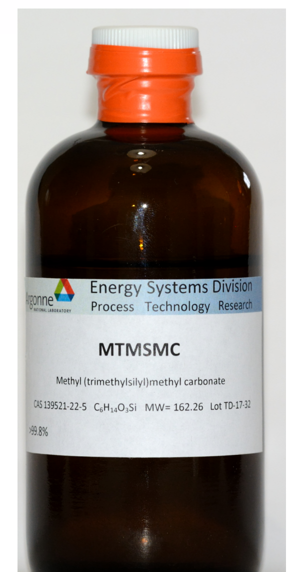
4. Neutral Alumina
5. Alumina with 5 wt% K_3PO_4
6. Alumina with 5 wt% KOH
7. Alumina with 5 wt% NaOH
8. Alumina with 5 wt% $Ca(OH)_2$
9. Alumina with 5 wt% KF

Technical Accomplishments And Progress: Scaled up Synthesis in Continuous Flow

- 250 mL of reaction mixture was processed in 16 h in fully automated catalytic continuous flow process.





- Single distillation provided methyl (trimethylsilyl)methyl carbonate with 99.8 purity.

- **Conclusion**: Catalytic transesterification in a flow reactor system offers green, cost effective process for manufacturing advanced carbonate solvents for LIBs.

- The material is available for sampling.

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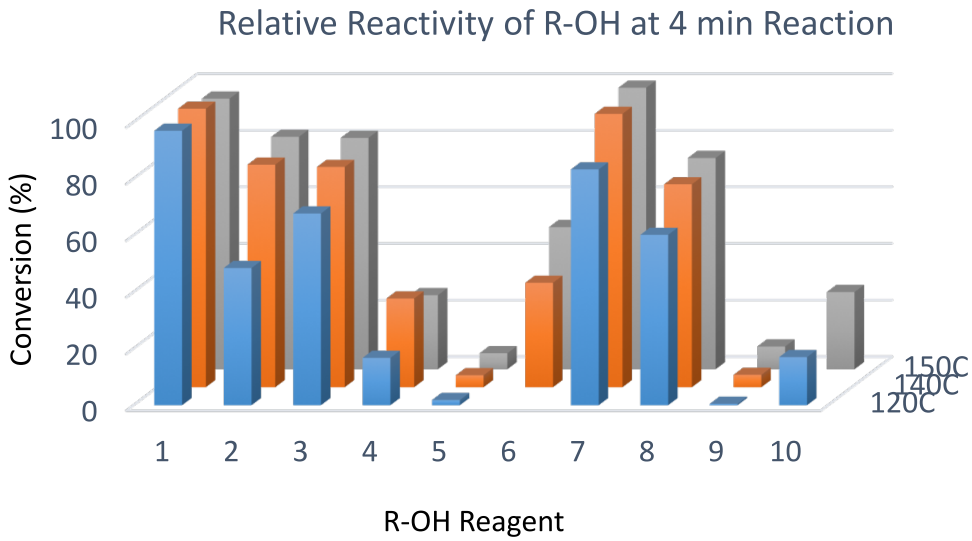
Technical Accomplishments And Progress Evaluation of Additional Material

- Synthesis of several other electrolyte solvents were investigated in the catalytic transesterification reaction in the continuous flow reactor.
- Primary alcohols with sufficient nucleophilicity revealed good conversion ratio into carbonates.
- Secondary alcohols and fluorinated alcohols (with low nucleophilicity) did produced alkyl methyl carbonate solvent at this condition.



1. Cyclopropylmethanol
2. 2-Methoxyethanol
3. Diethyleneglycol methyl ether
4. Pentafluoropropanol
5. Tetrafluoropropanol
6. Diethyleneglycol
7. TrimetylsilyImethanol
8. Triethyleneglycol methyl ether
9. Trifluoroethanol
10. 1-Cyclopropylethanol

Response To Previous Year Reviewer' Comments

- There were no negative comments or questions that require addressing.
- Question 1: Approach to performing the work…
  - Reviewer 1: The reviewer remarked impressive systematic engineering approach, sharp focus on the objectives
  - Reviewer 2: The reviewer pointed out that in order to provide critical advanced materials to the community, critical process developments must occur in areas where common material will be made.
- Question 2: Technical accomplishments and progress…
  - Reviewer 1: The reviewer said that the numbers of unique materials were developed that can be applied to the advanced development efforts.
  - Reviewer 2: The reviewer commented that the program meets DOE's needs and fills in the gaps between R&D and commercial efforts.
- Question 3: Collaboration and coordination with other institutions.
  - Reviewer 1: The reviewer remarked that bringing on board large scale manufacturer will further increase the project value, and that establishing licensing revenue is impressive.
- Question 4: Proposed future research…
  - Reviewer 1: The reviewer said that the pipeline is well balanced.

Collaborations

Process R&D and material scale up:

- Lawrence Berkeley National Laboratory (Gao Liu)
  - Binder for Si anode
- Argonne National Laboratory
  - High voltage solvents (John Zhang)
  - Lithium iron oxide and lithium cobalt oxide (Chris Johnson)
- Oak Ridge National Lab (Xiao-Guang Sun)
  - Lithium salt for high voltage applications
- Next Generation Anodes For LIB Project
  - Supramolecular binder
- DellaTech
  - LiFSI stability and impurity study

Material samples provided for further research:

- Army Research Lab
- Lawrence Berkeley National Lab
- Pacific Northwest National Lab
- SolidEnergy Systems
- Toyota Technical Center

Collaboration in development:

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

Remaining Challenges And Barriers

- A new materials need to balance cost and performance to be successfully introduce into market.
- New battery materials are being continuously invented and tested in laboratories but industry is typically unable to model the cost of production based on bench scale procedures.
- Large quantity of high quality new material is needed for industrial validation and prototyping.
- There is also 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.
- 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 process R&D.
  - 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 chemical purity vs. electrochemical performance for new materials.
- Continue evaluate new technology platform 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 process R&D and scaling up newly invented, advanced materials.
  - Currently evaluating several requests for scale-up.

- Any proposed future work is subject to change based on funding levels.

Summary

- Continuous flow reactor system was acquired and installed.
- The modular system allows for flexible configuration to accommodate a wide range of chemistries.
- This emerging manufacturing technology platform permits for expedited process R&D and “proof of concept” materials production.
- Flow reactor system reduces time and cost associated with process R&D.
- Efficient method for manufacturing methyl (trimethylsilyl)methyl carbonate (MTMSMC) was developed.
- Scope and limitation of producing other advanced carbonate solvents in continuous flow process was investigated.
- Methyl (trimethylsilyl)methyl carbonate (MTMSMC) is available for sampling.
- Design, synthesis and evaluation of supramolecular binders to enable next generation anodes for LIB is in progress.
- Scale up of lithium iron oxide (Li_5FeO_4) and lithium cobalt oxide (Li_6CoO_4) for Next Generation Anodes project is in progress.
- Sample of materials produced at MERF are available to support basic research and for industrial validation.

Acknowledgements And Contributors

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  - John Zhang
  - Wenquan Lu
  - Gerald Jeka
  - Mike Kras
  - Jessica Dunham
  - Ira Bloom

- 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