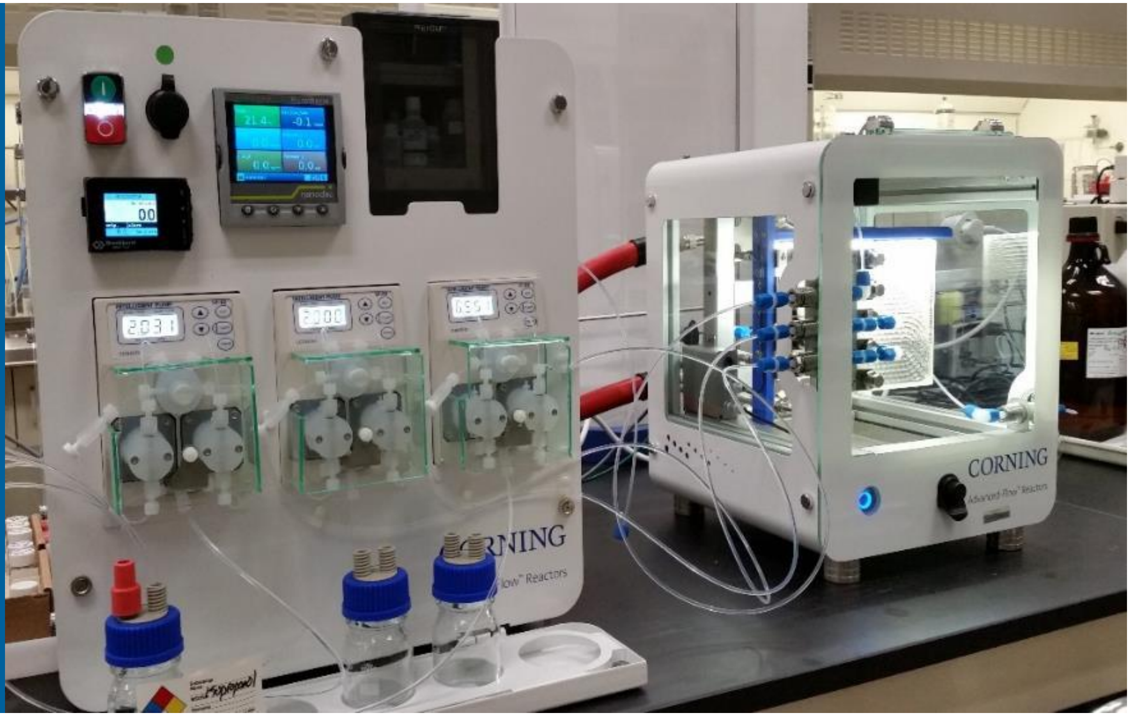
PROCESS DEVELOPMENT AND SCALE-UP OF CRITICAL BATTERY MATERIALS - CONTINUOUS FLOW-PRODUCED MATERIALS



Krzysztof Pupek **Trevor Dzwiniel**

Project ID: BAT168

June 1-4, 2020, Arlington, VA

Overview

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2021
- Percent complete: on going

Budget

- Total project funding:
  - $1.00M in FY19
  - $1.08M in FY20

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).
- Supporting battery research for:
  - 24M Technologies
  - ADA Technologies
  - Army Research Laboratory
  - Northern Illinois University
  - NREL
  - PNNL
  - Purdue University
  - SilLion
  - Solid Energy Systems

Approach – FY 20 Milestones

- Flow Chemistry Development:
  - Development of new continuous processes for electrolyte materials:
    - Lithium tricyanoimidazole (TCI) via diazotiation chemistry is **ongoing**.
    - Continuous flow process for 3,3,3-trifluoropropylene carbonate (TFPC) is **ongoing**.
- Scale-up Programs:
  - Scale-up of lithium bis(2-perfluoroethyl)dicyanoimidazole (Li-PDI) is **complete**.
  - Batch scale-up of 3,3,3-trifluoropropylene carbonate (TFPC) is **complete**.

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, evaluationat 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 for final approval.

- MERF evaluates emerging manufacturing technologies, conducts process R&D, develops and validates optimal process parameters for new material production.

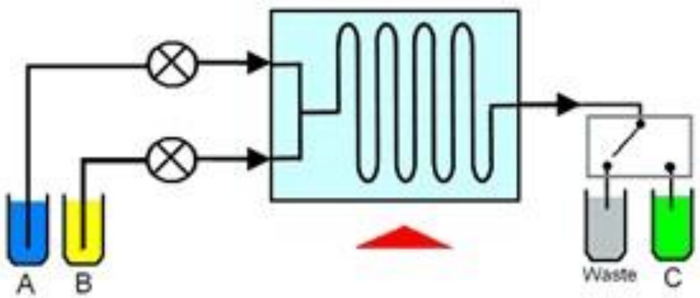
- Proof of concept in stages from milligrams to10g to 100g to kilograms.
  - Validate electrochemical performance.
  - Develop performance *vs.* purity and impurity profile relationship (material specification).

- 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

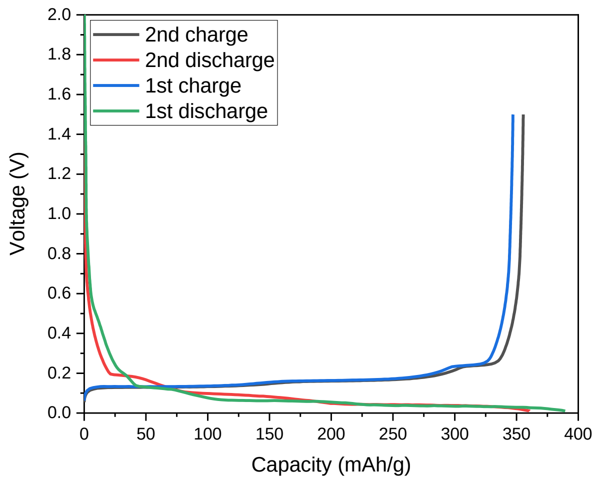
- In the quest for better, advanced electrolyte materials (solvents, salts, additives) scientists design, synthesize and evaluate more and more complex molecules.
- The complexity of the molecular structure is frequently translated into increased complexity and cost of the manufacturing processes.
- 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.**



Argonne NATIONAL LABORATORY

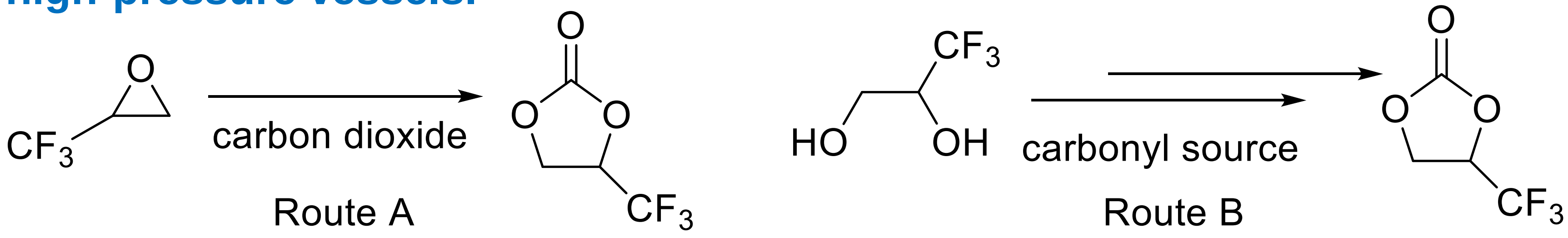
Technical Accomplishments

Trifluoropropylene carbonate (TFPC) Flow Chemistry – Background



A-12 Gr/Li TFPC/TTE 5:1 1.0M $LiPF_6$; 0.01-1.5 V, C/10 formation, C/3 cycling

- **Why TFPC?** Stable solvent to high voltage cell, stabilizes Si anode SEI.[1]
- Shows better temperature and voltage stability, less currant leakage.
- Forms a stable SEI layer without EC (data courtesy J. Zhang, ANL).
- Main issue to address for flow synthesis: suitable soluble conditions.
- Prior technologies (Route A) use high pressure, high temp steel autoclaves.
  - Various solvents, bases, catalysts, and reaction conditions (temperature, time, work-ups) have been reported. None are amenable to large-scale continuous processing due to problems with solids, extended time, pressure, etc.
  - Other routes (B) suffers from heavy suspensions limiting to batch processes.
- **Our new method allows continuous synthesis of the solvent without the use of bulky, expensive, and low-volume high-pressure vessels.**



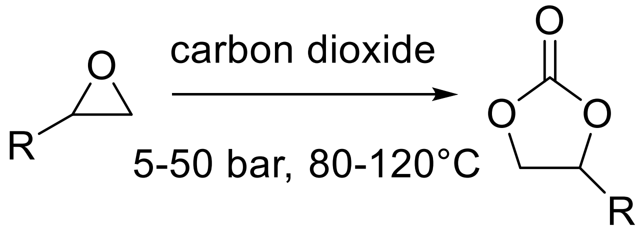
- [1]See: a) Adv. Funct. Mater. 2019, 29, 1906548. b) PCT Int. Appl. (2019), WO 2019113527. c) U.S. Pat. Appl. Publ. (2019), US 20190173124. d) Energy & Environmental Science (2019), 12(4), 1249-1254.

Argonne NATIONAL LABORATORY

Technical Accomplishments

Design of the TFPC Flow Process

- Route A prior technology requires high-pressure reactors.
  - Very expensive process to scale-up.
  - Real safety concerns on large scales.
- However, route A benefits from a shorter, better synthetic pathway.
  - One step from commercial materials.
  - Green Chemistry.[2] 100% atom efficient.
- Flow chemistry technology represents a new opportunity, but traditional glass microfluidic chip reactors are not well-suited for gases.



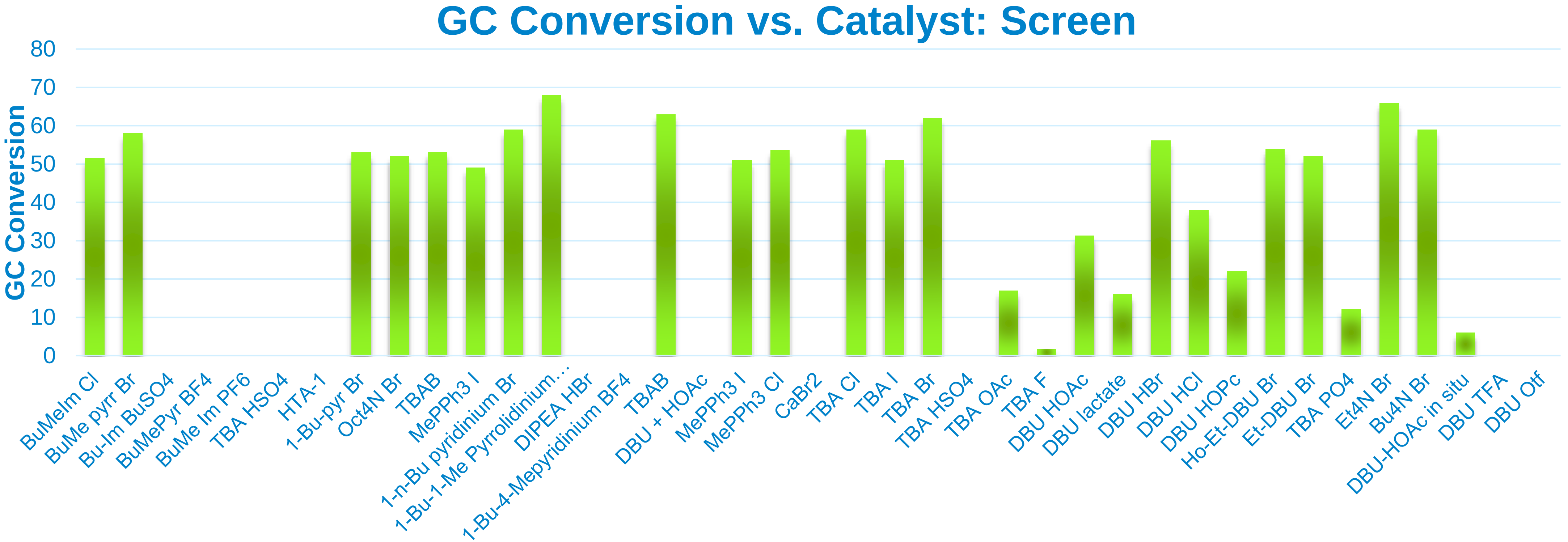
- **Flow chemistry enables scalable, safe high pressure continuous manufacturing using gases.**

- [2]Environmental Chemistry Letters 2019, 17, 501.

Technical Accomplishments

Catalyst Determination: Screening

- General conditions for epoxide/CO_2 cycloaddition use high pressure/ variety of catalysts.[3]
- Many procedures use heterogeneous catalysts unsuitable for flow reaction chemistry.
- **Screening needed to determine an effective *soluble* catalyst for this process.**
  - Conditions: 1 atm, 5 mol% catalyst, RT, 24h, MeCN. GC/MS analysis.
  - All available CO_2 is consumed at 50-60% conversion.

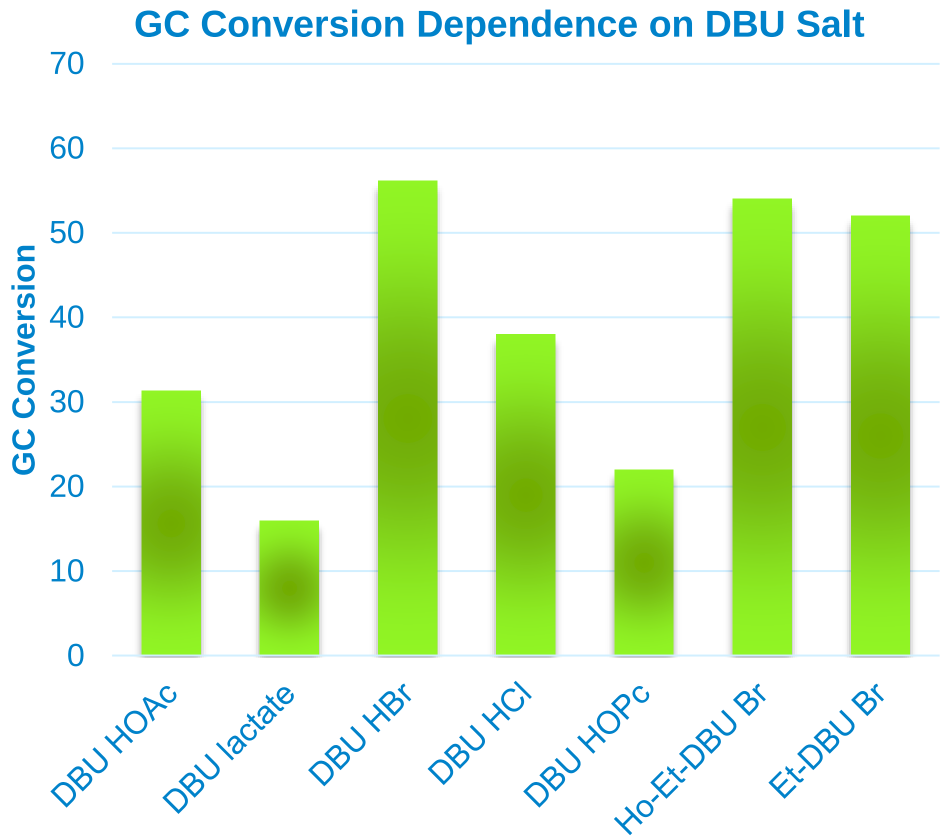


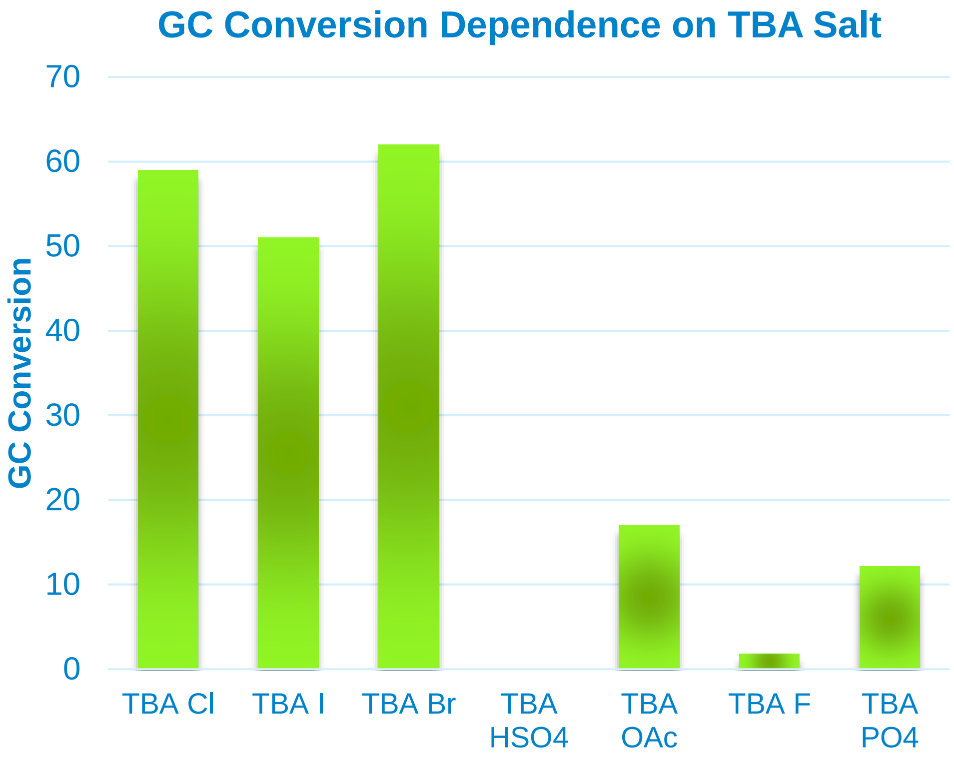
[3]See: a) New Journal of Chemistry, 43(6), 2583-2590, 2019. b)Environmental Chemistry Letters, 17(1), 501-508, 2019. c) J. Electrochem. Soc. 162(7), A1319, 2015.

Technical Accomplishments

Catalyst Determination: Anion Effect

- Different anions were investigated- with surprising results. The same cation shows dramatic variability.
- **Clearly halides are more efficient, regardless of cation.[4]** Non-nucleophilic anions show little reaction.
  - Conditions: 1 atm, 5 mol% catalyst, RT, 24h, MeCN. GC/MS analysis.
  - All available CO_2 is consumed at 50-60% conversion.



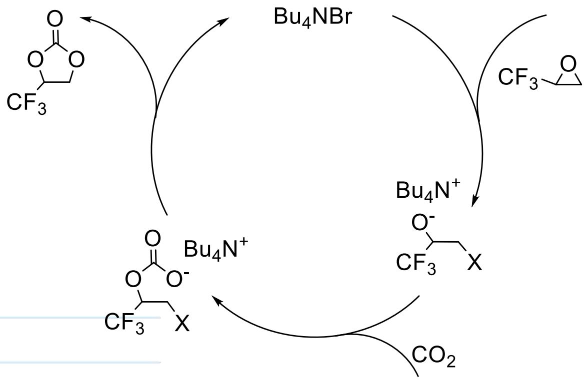


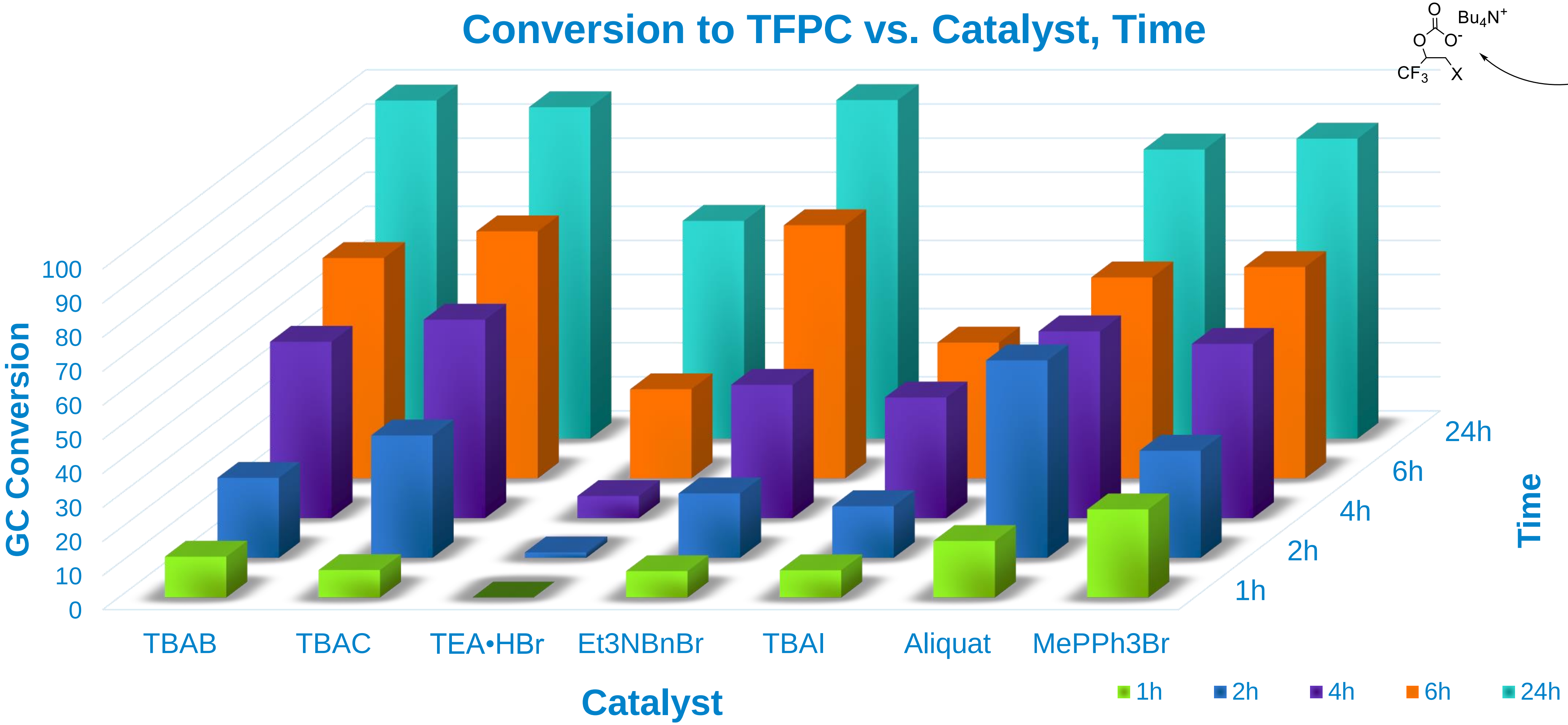
[4]In contrast see: Catalysis Communications 8 (2007) 167–172.

Argonne NATIONAL LABORATORY

Technical Accomplishments

Evaluation in Microfluidic Continuous Flow Reactor





- Full scale runs generally tracked the screening results. All catalysts showed enhanced activity.

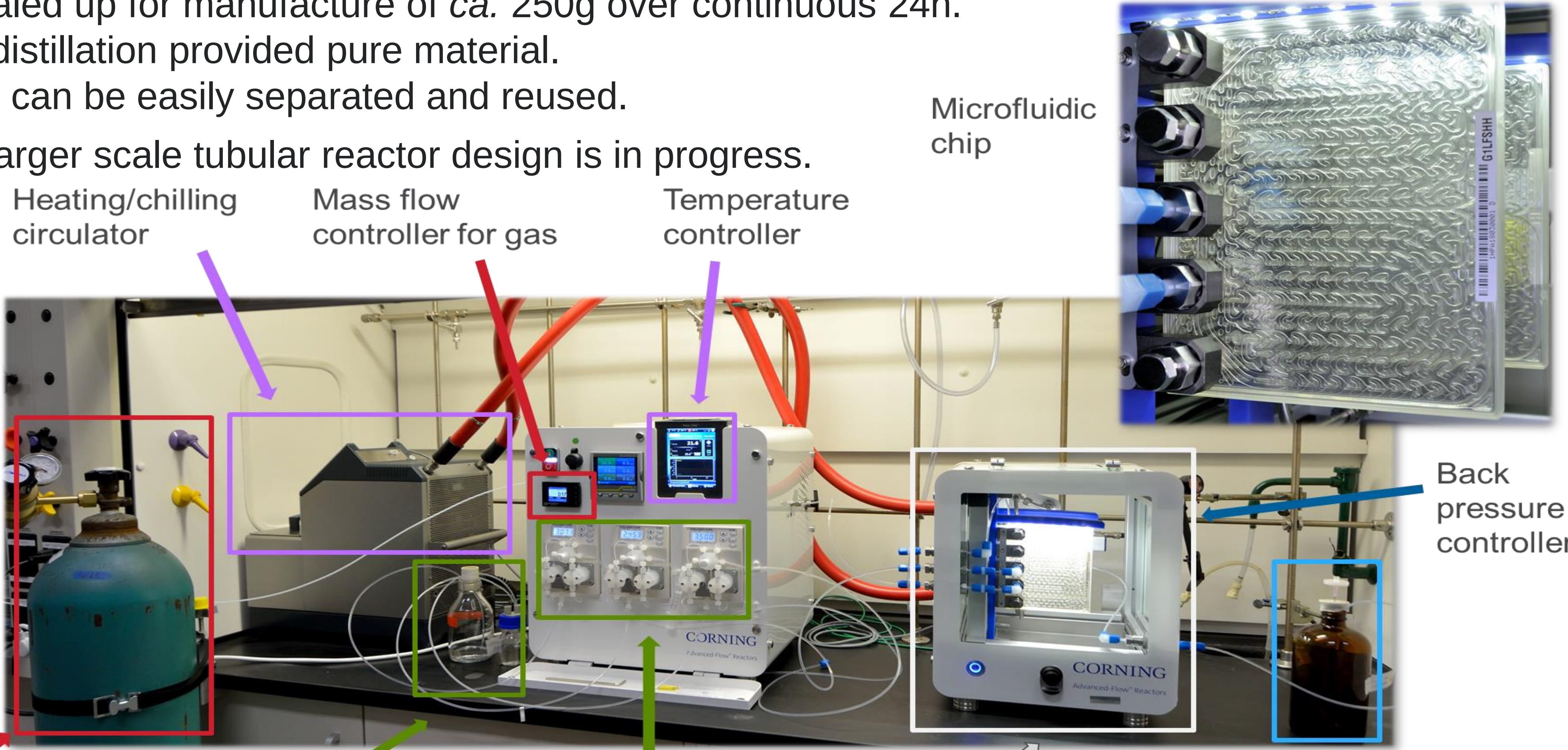
Conditions: 10mol% catalyst, CH_3CN, 75°C, 5ml/min solution, 10 ml/min CO_2, back-pressure set to 2.5 bar.

Argonne NATIONAL LABORATORY

Technical Accomplishments

Catalyst Determination: Flow Reactor

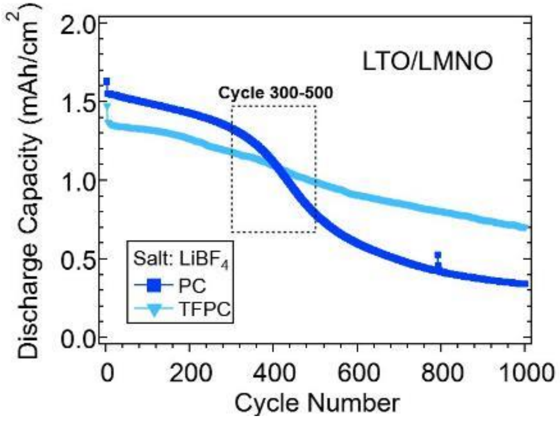
- **Final catalyst (Bu_4NBr) was selected for activity, cost, and easy of handling.**
- Process scaled up for manufacture of *ca.* 250g over continuous 24h.
  - Simple distillation provided pure material.
  - Catalyst can be easily separated and reused.
- Improved, larger scale tubular reactor design is in progress.



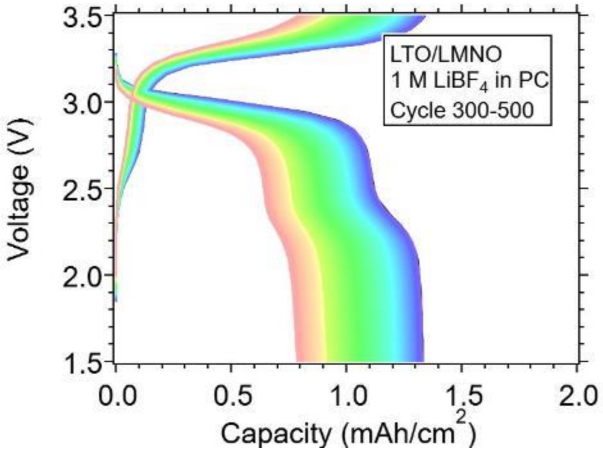
Technical Accomplishments: Feedback on TFPC

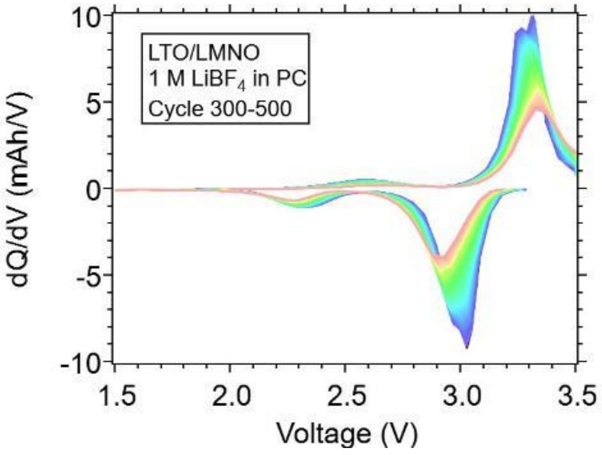
NREL Results with TFPC (Data Courtesy K. Park, NREL)

- Project goal: develop electrolyte systems for $Li_4Ti_5O_{12}$ (LTO) / $LiNi_{0.5}Mn_{1.5}O_4$ (LMNO) cell.
- 1M $LiBF_4$, TFPC or PC, 1.5-3.5V Anode: LTO (A-A014), Cathode: LMNO (A-C008), courtesy CAMP.
- Cycling @ 45°C, 6 h rest → 2x formation cycles at C/10 → 1000x aging cycles at 1C.
- **TFPC outperforms PC, which had rapid capacity fade in cycle 300- 500, seen in both the voltage profiles and dQ/dV plots.**
- Additional studies are in progress.

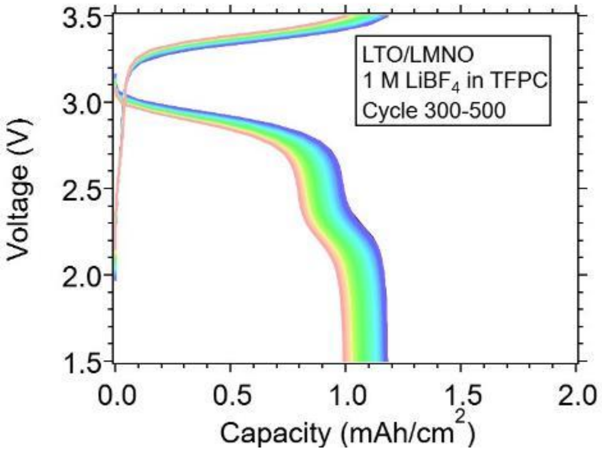


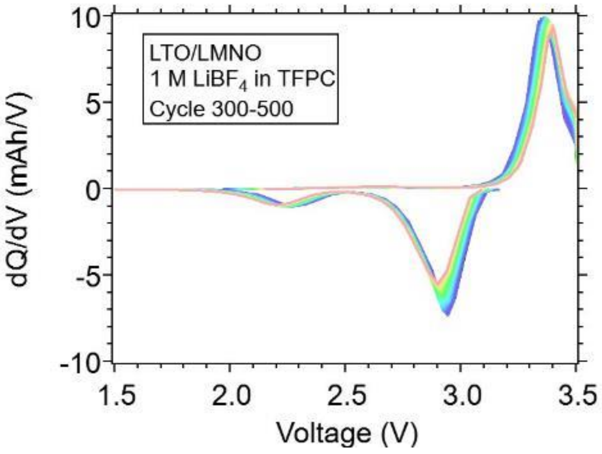
PC





TFPC

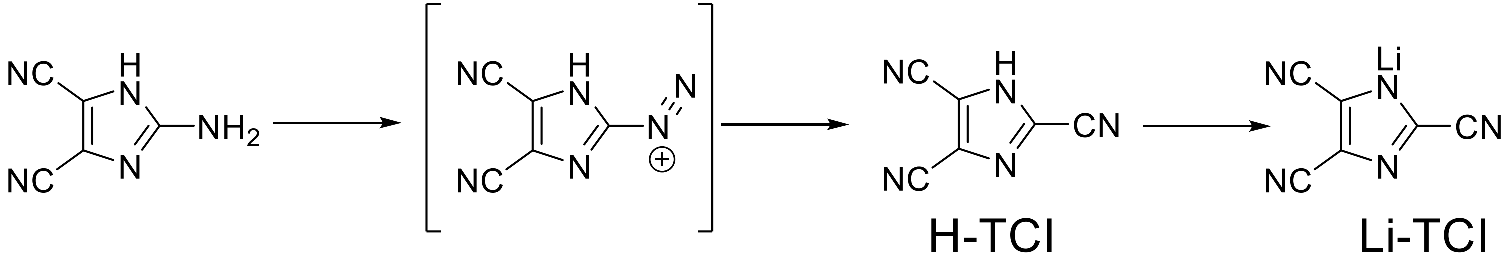




Technical Accomplishments

Diazotization Reactions in Flow Synthesis: Li-TCI

- Reported effect of Li-TDI in preventing anodic dissolution[5] prompted a search into other imidazole derivatives.
  - Possible targets include:
    - Tricyanoimidazole (TCI)[6]
    - Fluorodicyanoimidazole (F-DCI)
- Diazonium intermediates (TCI route) are particularly hazardous and ill-suited for large scale reactions, but suitable for flow reactions.
- Development required to adapt literature procedures to flow.

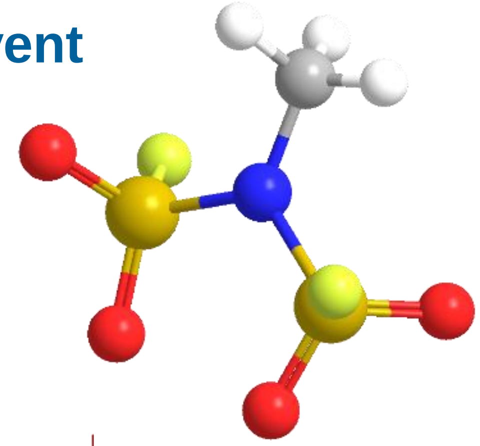


- Challenges: limited solubility of the starting amine in most solvents, diazonium intermediate also has limited solubility, smooth reaction with CuCN, KCN (water soluble).
- Able to run in DMF or other highly polar aprotic solvents.
- Several grams of Li-TCI was produced. Project is currently on hold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

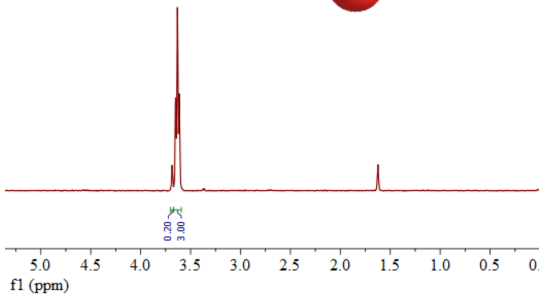
[5]See: a) Journal of Physical Chemistry Letters (2017), 8(15), 3678-3682. b) Journal of Physical Chemistry C (2016), 120(50), 28463-28471. c) LiTDI: An electrolyte additive for extended battery life and fast charging. Charged Magazine March 30, 2020.
[6]See: a) World Intellectual Property Organization,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

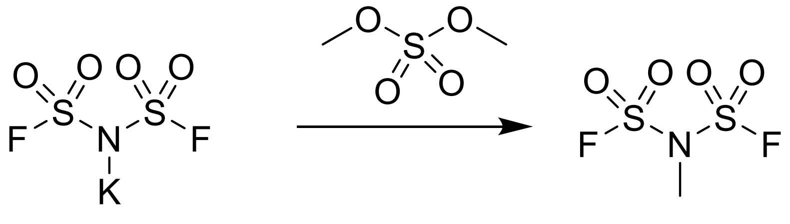
Technical Accomplishments

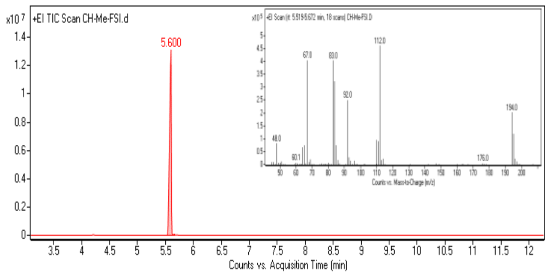
N-Methyl Bis(fluorosulfonyl)imide (Me-FSI): Unique electrolyte solvent



- Originally needed for salt-free synthesis of new Ionic Liquid (IL) by J. Zhang group (ANL).
- Non-flammable, improved viscosity and Li-ion conduction.
- One step synthesis: requires high purity materials.
- New use as an electrolyte solvent.
  - Initial coin cell results are promising.
- Additional amount of material will be produced to distribute samples fror electrochemical evaluation.

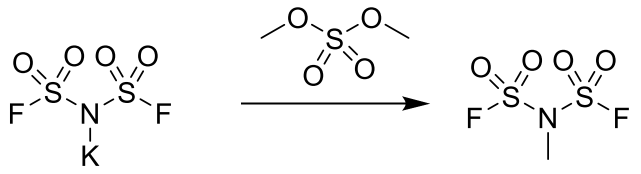






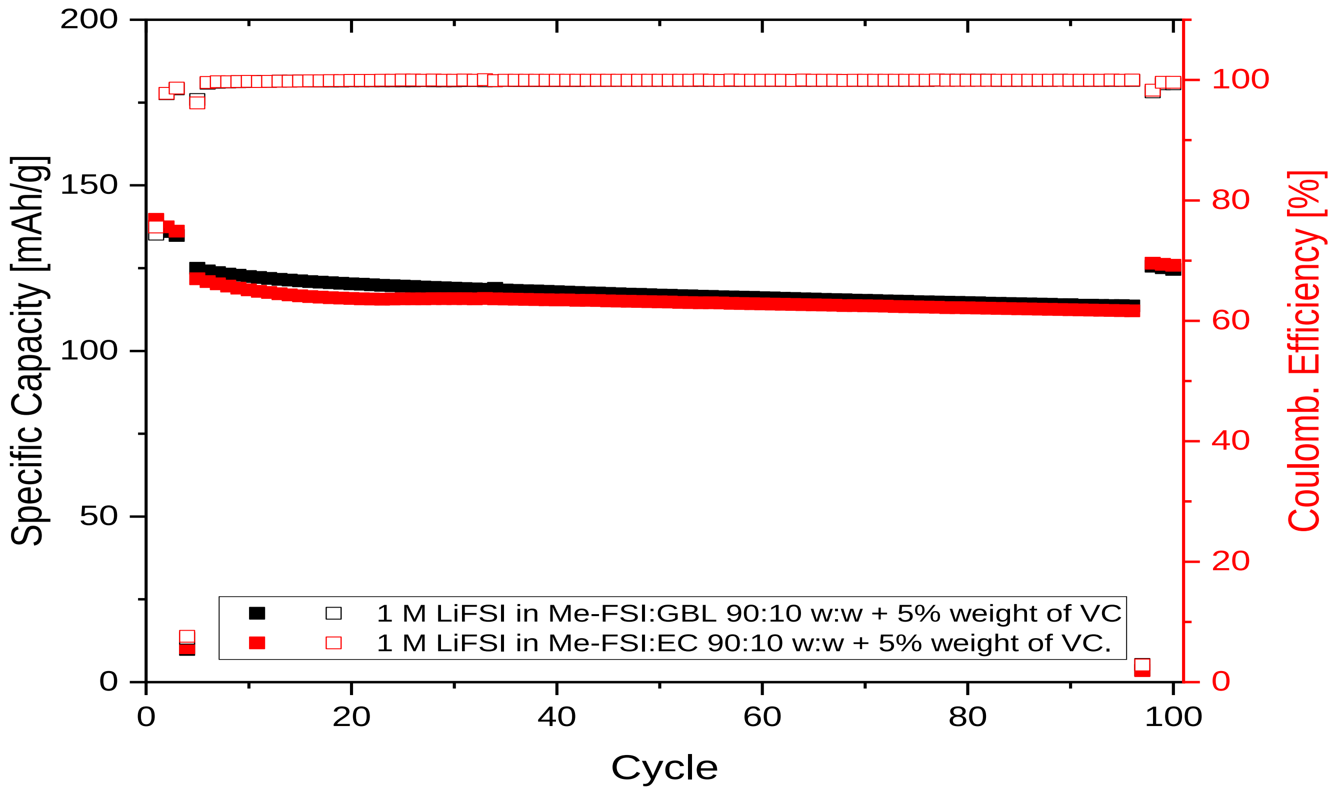
Technical Accomplishments

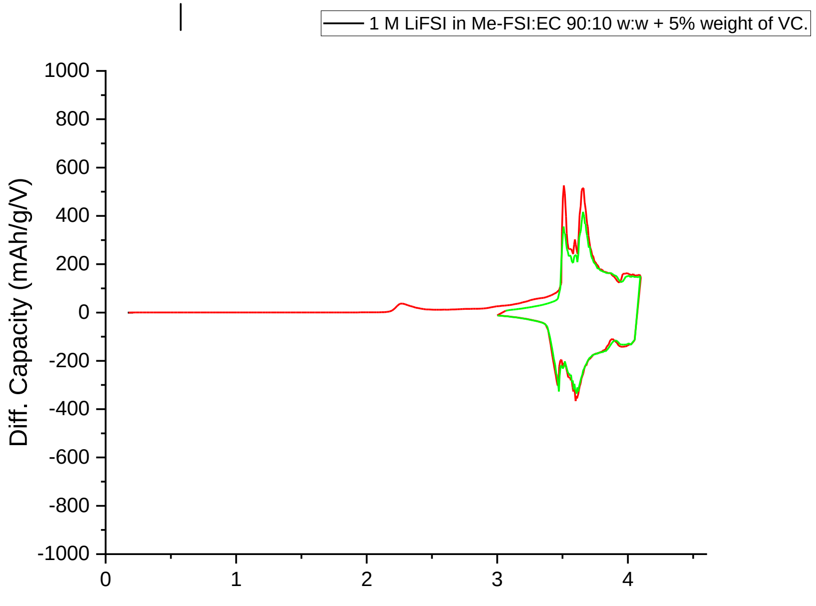
Me-FSI with GBL or EC + 5 % VC

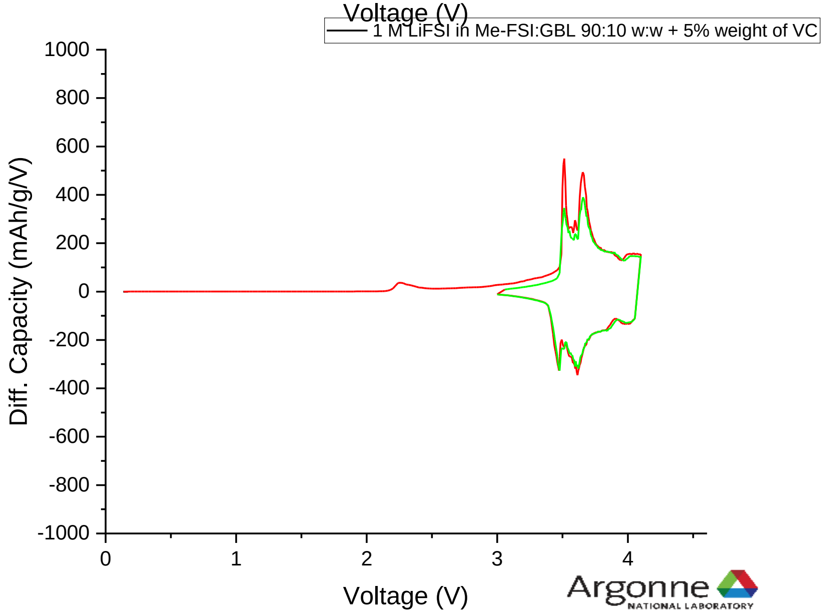


MeFSI

- Full cell analysis: NMC622 (C022)/Gr (A002B); 1C = 1.6 mA; 4.1-3.0 V.
  - Solvent: 1M LiFSI in Me-FSI:GBL or EC (90:10) + 5 wt% VC.
  - FEC in place of VC did not result in satisfactory performance in coin cells experiment.







Technical Accomplishments: Feedback

ADA evaluation of fluorinated solvents (Data Courtesy W. Xing and B. Almeida)

- Project goal: develop high voltage electrolyte systems for high-Ni NMC.
- ***Solvents provided by MERF were used to formulate proprietary electrolyte*** that out-performed 1M $LiPF_6$ in carbonate solvents.
- Cycling @ 2.5V-4.5V at less than C rate in Li/high-Ni NMC coin-type cells.
- Cells showed high specific capacity of 220mAh/g
- ADA high voltage electrolyte more stable: >96% capacity retention, baseline electrolyte <80% capacity retention after 30 cycles.
- ADA high voltage electrolyte cell showed higher CE (99.7%) than baseline (99.4%)

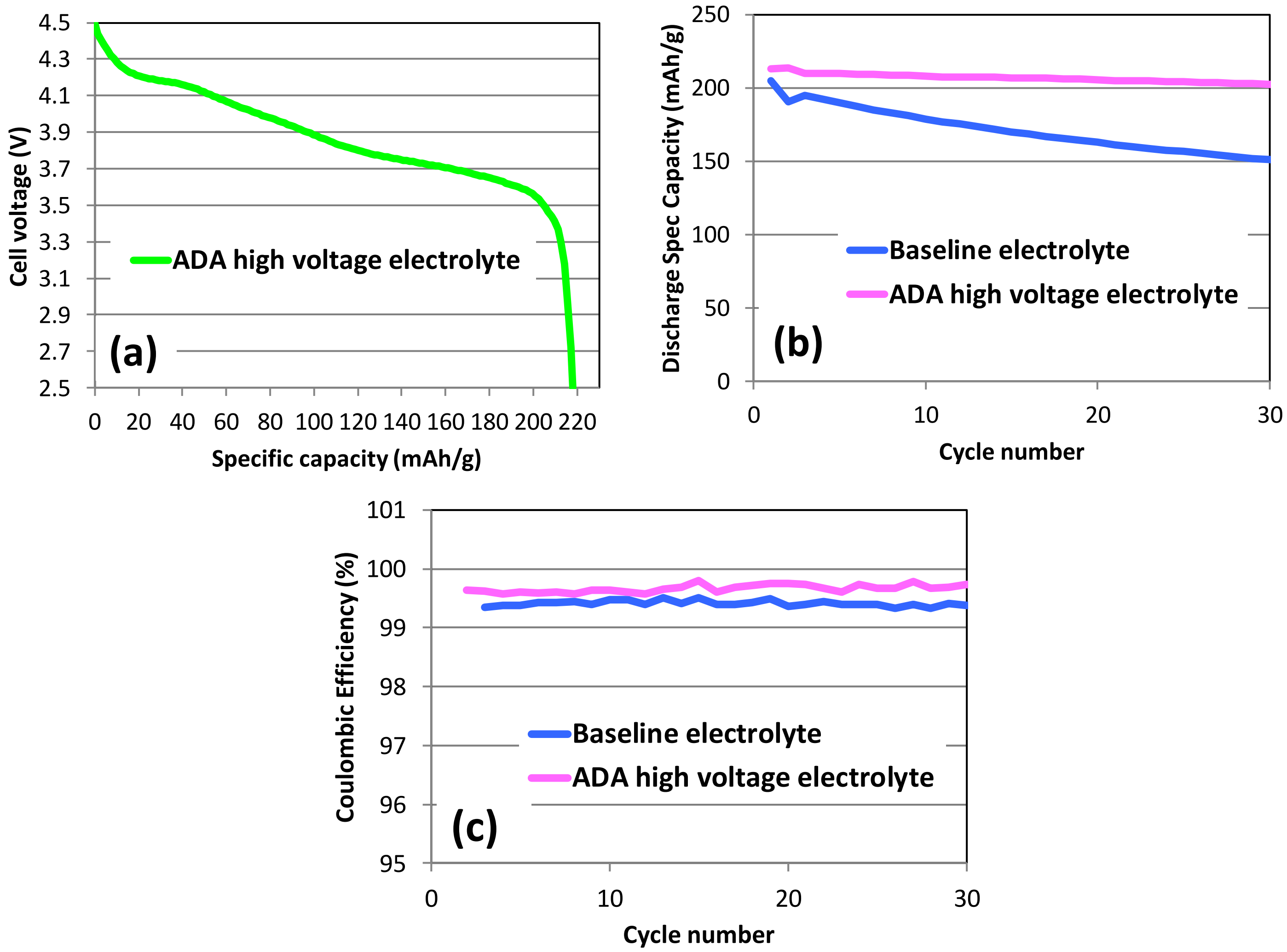


Figure 1. (a) Discharge voltage profile, (b) specific capacity and (c) CE vs. cycle number of Li/high-Ni NMC cells.

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 (John Zhang)

- **Material samples provided for further research:**
  - 24M Technologies
  - ADA Technologies
  - Army Research Laboratory
  - Northern Illinois University
  - NREL
  - PNNL
  - Purdue University
  - SilLion
  - Solid Energy Systems

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

Summary

- **Accomplishments**
  - We have scaled up both Li-PDI and TFPC.
  - Efficient continuous methods for other advanced electrolyte materials (TFPC, Li-TCI) are in development.
  - To date, hundreds of samples totaling over 20 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 have shown a 16% increase in capacity retention 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.**

Acknowledgements And Contributors

- Continuous support from David Howell and Peter Faguy of the U.S. Department of Energy's Office of Vehicle Technologies is gratefully acknowledged.

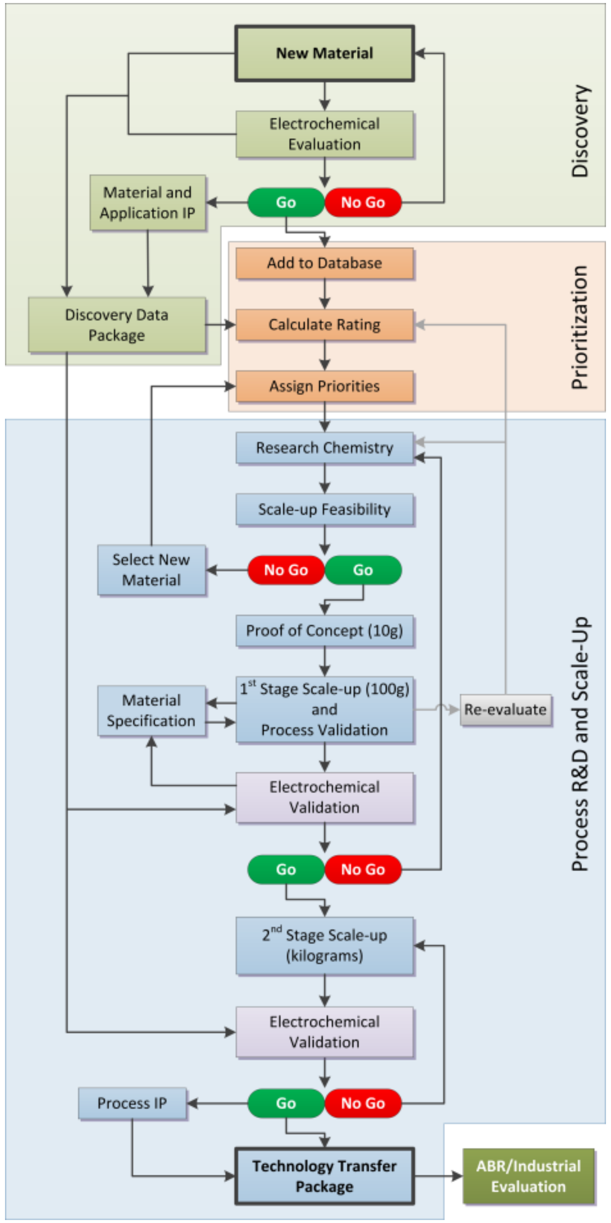
- MERF Team:
  - Kris Pupek
  - Trevor Dzwiniel
  - Chia-Wei Hsu
  - Gerald Jeka
  - Andrew Turczynski
  - Donghao Liu

- Argonne National Laboratory collaborators:
  - Bryant Polzin
  - Steven Trask
  - Allison Dunlop
  - Wenquan Lu
  - Qian Liu
  - Daniel Abraham
  - Christopher Johnson
  - Andrew Jansen
  - John Zhang

For samples and further information: Kris Pupek kpupek@anl.gov, www.anl.gov/merf

Technical Back-up Slides

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.

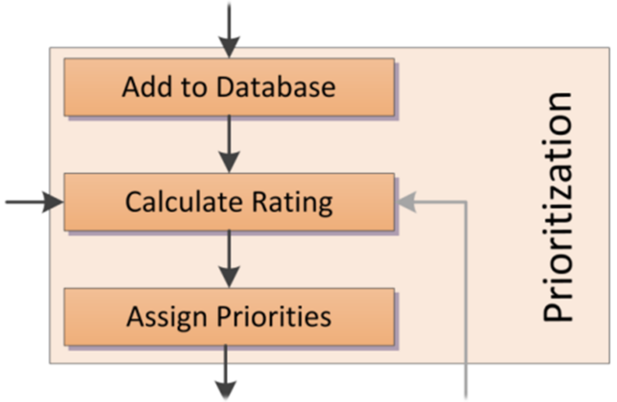
Provide feedback to discovery chemists, helping guide future research.

Technical Back-up Slides: Candidate Materials

Electrolyte Material	Chemical formula/ full name	Date added to spreadsheet	Organization	IP or patent #	Main Reference	Redox Potential (vs Li^+/Li)	Solubility in Electrolyte (1.2M LiPF6 EC/EMC (3/7 V/V)	Diffusion coefficent (cm^2 S^{-1})	100% Overcharge Cycling Stability	Side Effect Prior Overcharge	Chemical Stability	Ionic Conductivity (in Electrolyte System)	Viscosity (in Electrolyte System)	Applicable Chemistries
ANL-1NM2	$(CH_3)_3SiO(CH_2CH_2O)_3CH_3$	11/1/2010	Argonne National Laboratory	unknown	unknown	4.89	0.9	LiTFSI only	2.5	5	68	0.32	250	$LiMO_2$ (Co, Mn, Ni) $LiMn_2O_4$ $LiFePO_4$
ARL-HFiPP	tri(hexafluoro-iso-propyl)phosphate (C3HF6O)3PO	12/10/2011	Army Research Laboratory	unknown	Cresce & Xu, JES 158 A337 (2011)	unknown	<10%		unknown		Highly Moisture sensitive			LMNO 4.6 V
ARL-PFTBP	tris(perfluoro-tert-butyl)phosphate (C4F9O)3PO	1/12/2012	Army Research Laboratory	unknown	unpublished	unknown	~10%	unknown	unknown	unknown	Moisture sensitive	unknown	Unknown	Protects cathode surface at high potentials
ANL-RS2	2,5-di-tert-butyl-1,4-di-(2-methoxyethoxy)benzene (DBDMB)	11/1/2010	Argonne National Laboratory	ANL-IN-09-082 unpublished	US 2011/0294003	4.00V	0.5M	in progress	200 cycles for Li/$LiFePO_4$ 200 cycles for $Li_4Ti_5O_{12}$/$LiFePO_4$ 200 cycles for MCMB/$LiFePO_4$	Stable	Stable in air	Excellent	Medium	$LiFePO_4$
ANL-RS21	Confidential - Patent Pending	1/11/2012	Argonne National Laboratory	unknown	unknown	4V	> 0.4M	unknown	150 cycles	stable	stable in the air	excellent	Low	LiFePO4
FRION	Confidential - Patent Pending	2/1/2013	Case Western University	unknown	unknown	unknown	unknown	unknown	unknown	unknown	Moisture sensitive	Excellent	unknown	unknown

Electrolyte Material	Electrochemical Evaluation (Y/N) (attached if Y)	Industrial/Commercial Interest (1-10, best 10)	Material Performance (1-10, best 10)	Intellectual property clear (Y/N)	Scale previously achieved/ commercial (#g or unknown)	Number of Validations/ Syntheses (# or unknown)	Number of Synthetic Steps (# or unknown)	Product commercially available? (Y/N)	Cost (L/M/H)	Safety Hazard (L,M,H)	Raw Materials Readily Availability (Y/N)	OVERALL SCALE SCORE (best score 89)	Commercially available No/Yes (green/red)	Electrochemical Evaluation Yes/No (green/red)	Intellectuall Property Clear (Y/N)	Raw Materials Available (Y/N) (green/red)
ANL-1NM2	Y	8	5	Y	50	2	1	N	L	L	Y	61	No	Yes	Yes	Yes
ARL-HFiPP	Y	10	7	Y	500	5	1	N	L	M	Y	71	No	Yes	Yes	Yes
ARL-PFTBP	unknown	10	7	unknown	5	2	1	N	M	M	Y	57	No	unknown	unknown	Yes
ANL-RS2	Y	9	8	Y	1	5	2	N	L	L	Y	68	No	Yes	Yes	Yes
ANL-RS21	unknown	8	8	Unknown	5	3	1	N	L	M	Y	62	No	unknown	unknown	Yes
FRION	unknown	unknown	unknown	unknown	2	5	unknown	N	unknown	unknown	Y	53	No	unknown	unknown	Yes

- 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.



Argonne NATIONAL LABORATORY

Technical Back-up Slides: Available Samples

Abbreviation	Chemical Name	Uses	Sample Size (g)
ANL-1NM2	2,2-dimethyl-3,6,9-trioxa-2-siladecane	Low Flammability Solvent	100s
ANL-1NM3	2,2-dimethyl-3,6,9,12-tetraoxa-2-silatridecane	Low Flammability Solvent	0
ANL-1S1M3	2,2-dimethyl-4,7,10,13-tetraoxa-2-silatetradecane	Low Flammability Solvent	0
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
FEMC	Methyl (2,2,2-trifluoroethyl) carbonate	Fluorinated Solvent	100s
TFPC	3,3,3-Trifluoropropylene carbonate	Fluorinated Solvent	10s
ANL-RS2	1,4-di-tert-butyl-2,5-bis(2-methoxyethoxy)benzene	Flow Battery Catholyte/ Shuttle	0
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
ANL-RS21	6,7-dimethoxy-1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene	Flow Battery Catholyte/ Shuttle	100s
ANL-RS51	(2,5-dimethoxy-1,4-phenylene)bis(diethylphosphine oxide)	Flow Battery Catholyte/ Shuttle	1s

Abbreviation	Chemical Name	Uses	Sample Size (g)
Li-TDI	lithium 4,5-dicyano-2-(trifluoromethyl)imidazol-1-ide	Lithium Salt	10s
ARL-LiPFTB	Lithium perfluoro-tert-butoxide	Lithium Salt	100s
Li-PFPBO	lithium 2-fluoro-4,5-dioxo-2-(perfluorophenyl)-1,3,2-dioxaborolan-2-uide	Electrolyte Additive	100s
ARL-HFiPP	Tris (1,1,1,3,3,3-hexafluoro-2-propyl) phosphate	Electrolyte Additive	0
MGC	methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate	Electrolyte Additive	10s
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
CWU-FRION Li[B(DPC)(Ox)]	Lithium [(3,6-diethoxyphosphoryl)-1,2-catecholato][oxalato]borate	Electrolyte Additive	1s
MTMSMC	Methyl (trimethylsilylmethyl) carbonate	Low Flammability Solvent	10s
ETMSMC	Ethyl (trimethylsilylmethyl) carbonate	Low Flammability Solvent	10s
BTMSMC	Bis-(trimethylsilylmethyl) carbonate	Low Flammability Solvent	10s