Process Development and Scale Up of Advanced Electrolyte Materials

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Project ID: ES168

Overview

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2014
- Percent complete: on going

Budget

- Total project funding :
  - $1.0M in FY12
  - $1.2M in FY13
    ($720K received, $480K expected)

Barriers

- Cost: Reduce cost to manufacture materials
- Performance: Optimize for highest purity and maximum performance

Partners

- Argonne National Lab's
  - Applied R&D Group
  - Materials Screening Group
- US Army Research Lab
- Pacific Northwest National Lab
- Sandia National Lab

Objectives and Relevance of this Program

- The objective of this program is to develop scalable processes for manufacturing electrolyte materials of benefit to the ABR program, synthesize kilogram quantities of each material and provide for industrial evaluation and basic research.
  - Identify, rank and prioritize electrolyte materials of interest.
  - Resolve commercialization constraints by developing cost-effective and safe manufacturing processes.
  - Validate electrochemical performance of the scale-up materials.
  - Provide sufficient quantities for large format industrial evaluation.
  - Prepare process technology transfer packages.

- The relevance of this program to the DOE Vehicle Technologies Program is:
  - This program is a key missing link between discovery of advanced battery materials, market evaluation of these materials and high-volume manufacturing.
  - This program provides large quantities of materials with consistent quality for further validation in large format prototype cells.
    - Provides a standardized material for evaluation by several different groups.
    - Addresses the need for larger amounts of material for basic R&D purposes.
  - This program provides the basis for meeting broader industrial needs to reduce the risk associated with developing and maintaining a domestic commercially viable battery manufacturing capability.

Approach

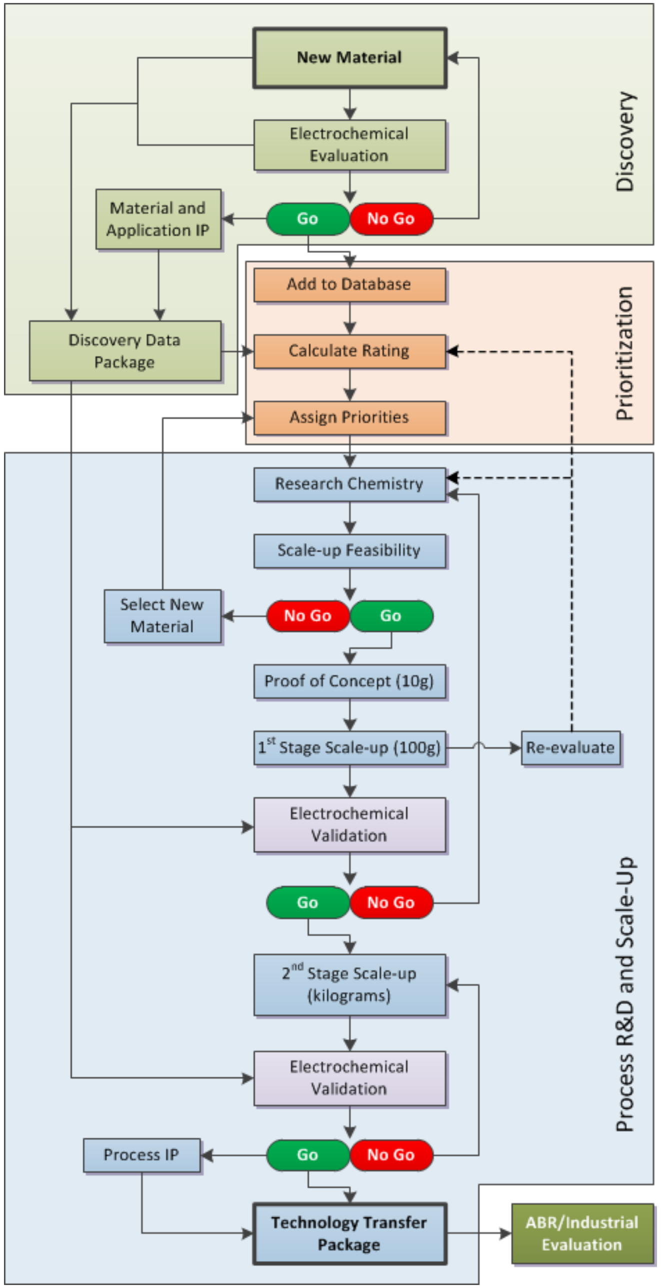
Header page	General Information					Performance								
Electrolyte Material	Chemical formula/ full name	Date added to spreadsheet	Organization	IP or patent #	Main Reference	Redox Potential (vs Li^+/Li)	Solubility in Electrolyte (1.2M LiPF6 EC/EMC (3/7 V/V))	Diffusion coefficent ($cm^2 S^{-1}$)	100% Overcharge Cycling Stability	Side Effect Prior Overcharge	Chemical Stability	Ionic Conductivity (in Electrolyte System)	Viscosity (in Electrolyte System)	Applicable Chemistries
ANL-1NM2	$(CH_3)_3SiO(CH_2CH_2O)_2CH_3$	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
INL-FM-2	Hexa-Alkoxy-phosphazene	10/25/2012	Idaho National Laboratory	unknown	unpublished	NA	NA	NA	NA	NA	intermediates water sensitive	N	Unknown	increase thermal stability
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 $Li_5Ti_{12}O_4/LiFePO_4$ 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

Header page	Readiness to Scale/Manufacturing Process Complexity											Scaling Calculation				
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
INL-FM-2	unknown	10	7	unknown	100	5	2	N	H	H	Y	52	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	16	No	unknown	unknown	Yes

- Identify candidate electrolyte materials of interest to ABR program participants
  - Electrolyte solvents
  - Redox shuttles
  - Passivation additives
  - Other materials
- Develop and maintain database of the materials
  - Source of the material
  - Chemical identity
  - Performance characteristics
- Develop rating criteria, rate and prioritize candidates for scale-up based on
  - Electrochemical performance
  - Manufacturing process complexity
  - Market needs

Approach

- Explore various chemical pathways and determine scale-up feasibility and best scalable route
- Proof-of-concept in a small-scale synthesis (10 g)
- First-stage scale-up and product quality verification, electrochemical performance validation (100 g)
- Second-stage scale-up and electrochemical performance validation (kilogram scale synthesis)
- Create Technology Transfer Package
- Make the material available for industrial evaluation and to support basic research with larger samples from a uniform standardized single batch

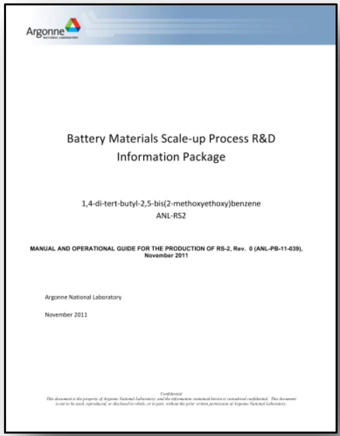


Approach - Milestones

- FY12
  - 2-4 electrolyte materials to be scaled
    - 3 materials completed
    - Completed relocation to Materials Engineering Research Facility (MERF)
- FY13
  - 4-6 electrolyte materials to be scaled
    - 3 materials completed (as of 3/15/13)
    - 2 materials scheduled for completion by end FY13
- FY14
  - 4-6 electrolyte materials to be scaled

MILESTONE	DATE	STATUS	COMMENTS
ANL-1NM2 Complete			
Assess scalability of disclosed process	7/20/12	Completed	
WP&C documentation approved	8/1/12	Completed	Approved under existing documentation
Develop and validate scalable process chemistry (10g scale)	8/20/12	Completed	
First process scale-up (100g bench scale)	9/17/12	Completed	
Second process scale-up (1000g pilot scale)	10/09/12	Completed	9,715g produced in 1 batch >99.9% purity
ANL- RS21 Complete			
Assess scalability of disclosed process	9/28/12	Completed	
WP&C documentation approved	9/28/12	Completed	
Develop and validate scalable process chemistry (10g scale)	10/30/12	Completed	
First process scale-up (100g bench scale)	11/30/12	Completed	
Second process scale-up (1000g pilot scale)	01/10/13	Completed	2,320 g produced in 1 batch, >99.9% purity
ARL-LiPFTB Complete			
WP&C documentation approved	9/28/12	Completed	Falls under existing documentation.
Develop and validate scalable process chemistry (10g scale)	12/21/12	Completed	
First process scale-up (100g bench scale)	1/31/13	Completed	
Second process scale-up (1000g pilot scale)	2/28/13	Completed 3/08/13	1,196g produced in 1 batch, >99%purity.
ANL- RS5			
Assess scalability of disclosed process	3/29/13	Completed 3/22/13	Original route is not safe or cost-effective for scale up. Other potential routes may be feasible.
WP&C documentation approved	3/29/13	Completed	Falls under existing documentation.
Develop and validate scalable process chemistry (10g scale)	5/31/13	In Process	
First process scale-up (100g bench scale)	6/28/13	Pending	
Second process scale-up (1000g pilot scale)	7/30/13	Pending	

Approach - Deliverables


Battery Materials Scale-up Process R&D
Information Package

1,4-di-tert-butyl-2,5-bis(2-methoxyethoxy)benzene
ANL-RS2

MANUAL AND OPERATIONAL GUIDE FOR THE PRODUCTION OF RS-2, Rev. 0 (ANL-PB-11-039), November 2011

Argonne National Laboratory

November 2011

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- For each electrolyte material selected we will:
  - Develop a scalable manufacturing process.
  - Develop analytical methods and quality control procedures.
  - Prepare a “technology transfer package” which will include:
    - Summary of the original process used by discovery researchers to synthesize the material.
    - Summary of the scalable (revised) process suitable for large scale manufacturing.
    - Detailed procedure of the revised process for material synthesis.
    - Analytical data/Certificate of Analysis for the material (chemical identity and purity).
    - The material impurity profile.
    - Electrochemical performance test data.
    - Preliminary estimates of production cost.
    - MSDS for the material.
  - Make kilogram quantities of the material available for industrial evaluation as well as for support of bench scale and basic research programs.
    - The material will be fully characterized chemically and electrochemically.

Technical Accomplishments and Progress Overview

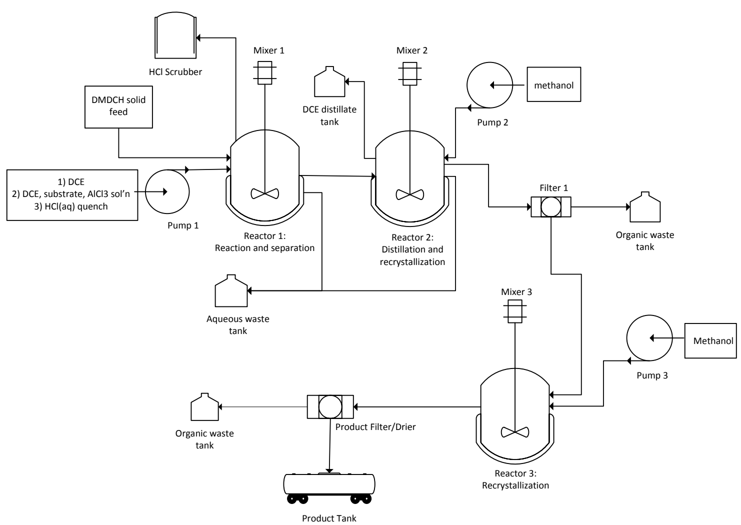
- Interim electrolyte process R&D and scale-up labs have been relocated to the MERF.
- Scalable processes were developed and kilogram quantities of materials were synthesized for 3 electrolyte materials.
  - ANL-1NM2 (electrolyte solvent) Chemical Name: 2,2-dimethyl-3,6,9-trioxa-2-siladecane
  - ANL-RS21 (redox shuttle) Chemical Name: (patent pending)
  - ARL-LiPFTB (electrolyte additive) Chemical Name: lithium perfluoro-*tert*-butoxide
- Other materials are in progress.
  - ARL-RS5 (redox shuttle) Chemical Name: (patent pending)
  - Case Western University FRION (electrolyte additive) pending electrochemical evaluation
- Technology transfer packages for all new materials were created.
- Materials were sampled for evaluation.
  - Since program start, 40+ material samples have been sent. A total amount of 6,700g of material has been sampled.
  - In FY12 alone, 25 sample requests (total amount 6,075g) were processed.

Technical Accomplishments and Progress
The Materials Engineering Research Facility (MERF)

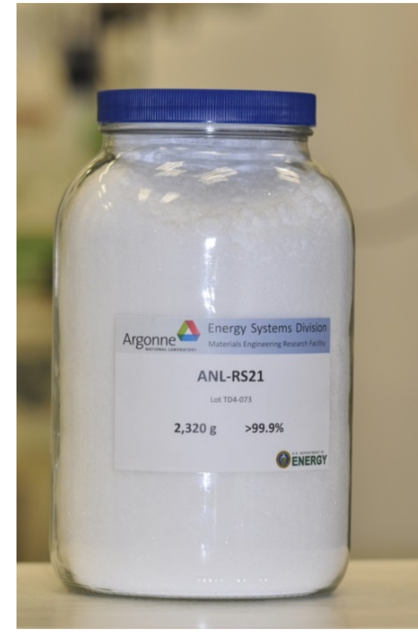
- Interim labs have been relocated
- Fully equipped electrolyte materials process R&D and scale-up labs
  - (12) 10ml parallel reactors
  - 2L and 5L jacketed glass reactors
  - 20L jacketed glass reactor
  - 40L jacketed glass lined steel reactor
  - 20L jacketed filter reactor
  - 20L hastalloy filter dryer
  - 20L Buchi rotovap
  - 5 port Nexus glovebox
- Full complement of analytical equipment
  - Agilent GC/MS/FID
  - Mettler reaction calorimeter
  - Grabner flash point analyzer
  - Buchi melting/boiling point analyzer
  - Agilent HPLC and UHPLC
  - Bruker FTIR
  - Biotage Isolera prep LC

Technical Accomplishments and Progress
Redox Shuttle ANL-RS21

- Structure confidential- patent pending.
- Several process improvements were made.
  - Simple crystallization replaced chromatography for purification.
  - The amount of waste generated was reduced by a factor of 10.
  - Overall throughput of the process was improved.
- The scaled-up material was electrochemically validated.
- A Technology Transfer Package was created for the process.
- More than 2 kilograms were produced and samples of the material were provided to scientist for further research and to industry for evaluation.



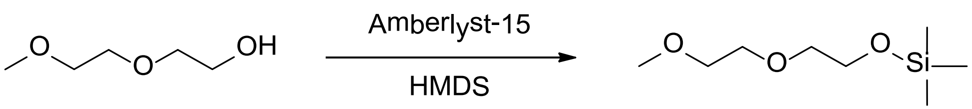
Process Flowchart for ANL-RS21 synthesis



2.3kg single-batch lot of ANL-RS21

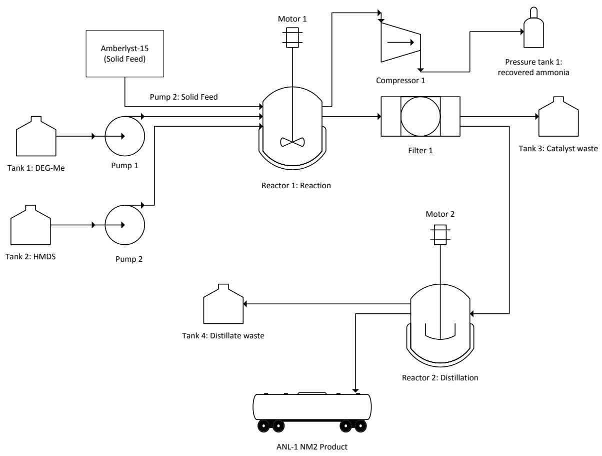
Analysis	Instrument/Method	Results	Analysis By:
HPLC	Agilent Eclipse Plus C18, 3.5 um, 4.6x100, UV 225, water/ACN gradient	>99.9% [2]	T. Dzwiniel
GC/FID	Agilent 7890A Agilent HP-5MS, 0.25 um, 30m x 0.250 mm, 40 to 300 °C, 30 °C /min	99.992% [1,2]	T. Dzwiniel
GC/MSD	Agilent 7890A/5975C Triple-Axis Agilent DB-5MS, 0.25 um, 30m x 0.250 mm, 40 to 300 deg, 30 deg/min	>99.9% [1,2]	T. Dzwiniel
Melting Point	Buchi M-565 Automatic, range method	76-77 °C	T. Dzwiniel
FTIR	Bruker Vertex 70 Attenuated Total Reflection	Consistent with Structure	G. Jeka
NMR	Bruker 500 MHz ^{1}H, ^{13}C observed in $CDCl_3$ solution	Consistent with Structure	T. Dzwiniel

Technical Accomplishments and Progress
Solvent ANL-1NM2



12L single-batch lot of ANL-1NM2

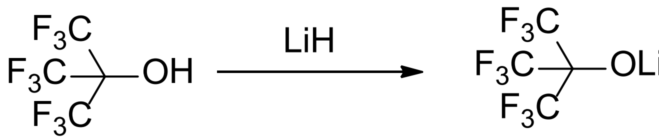
- A new process was developed:
  - Solvent free, significantly reducing waste by a factor of 10.
  - Utilizes a simple one-pass distillation.
  - Adding a catalyst allowed a lower temperature and faster reaction minimizing energy costs.
- The scaled-up material was electrochemically validated.
- A Technology Transfer Package was created.
- More than 12 liters were produced and samples were provided to researchers to support Li-air battery investigations.

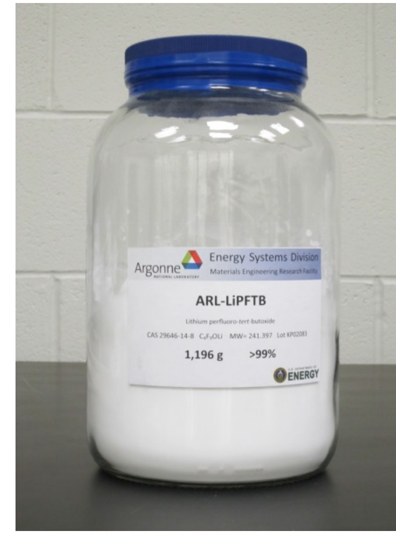


Process Flowchart for ANL-1NM2

Analysis	Instrument/Method	Results	Analysis By:
GC/FID	Agilent 7890A Agilent HP-5MS, 0.25 um, 30m x 0.250 mm, 40 to 300 °C, 30 °C /min	99.917% [1,2]	T. Dzwiniel
GC/MSD	Agilent 7890A/5975C Triple-Axis Agilent DB-5MS, 0.25 um, 30m x 0.250 mm, 40 to 300 deg, 30 deg/min	99.979% [1,2]	T. Dzwiniel
Boiling Point	Buchi M-565 Automatic, 0.6 Hz corrected to standard pressure	190-191 °C	T. Dzwiniel
KF Moisture Titration	KEM MCU-610 Coulometric, WaterMark 1612/1613	40ppm	K. Pupek
FTIR	Bruker Vertex 70 Attenuated Total Reflection	Consistent with Structure	G. Jeka
NMR	Bruker 500 MHz ^{1}H observed in $CDCl_3$ solution	Consistent with Structure	K. Pupek

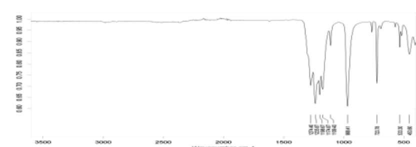
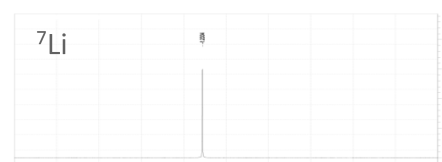
Technical Accomplishments and Progress
Electrolyte Additive ARL-LiPFTB



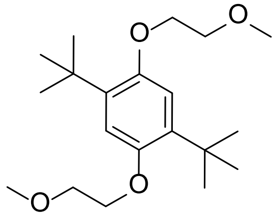


1.2kg single-batch lot of ARL-LiPFTB

- Reaction conditions were modified, providing:
  - Diethyl ether was replaced with less hazardous solvent.
  - Simple purification: heptane precipitation replaced multiple sublimations.
  - Higher recovery (85% compared to 30-50% in original procedure).
- A full analytical study (FT-IR, ^{19}F, ^{7}Li, ^{13}C NMR, GC/MS) confirmed the material (lithium perfluoro-*tert*-butoxide) matched the authentic sample.
- More than 1 kilogram was produced and is available for sampling.

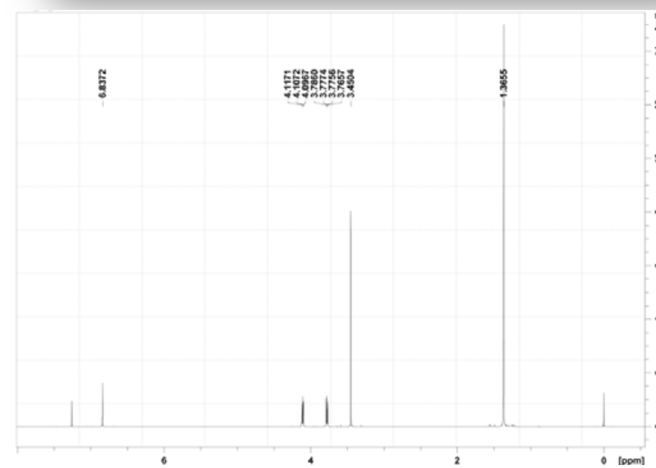
Analysis	Method	Results	Analysis By:
Melting Point	Automatic, range method (Buchi M-565)	143-144°C	K. Pupek
FTIR	Bruker Vertex 70, Attenuated Total Reflection		G. Jeka
NMR	Bruker 500 MHz, CD_3CN solution. ^{7}Li, ^{19}F, ^{13}C.		T. Dzwiniel

Technical Accomplishments and Progress
Redox Shuttle ANL-RS2- Update



1,4-di-tert-butyl-2,5-bis(2-methoxyethoxy)benzene

$C_{20}H_{34}O_4$ MW 338.48 CAS 1350770-63-6



- Scale-up process was reported at the 2012 AMR meeting.
- Process patent was filed.
- Numerous samples have been supplied to industry for evaluation and scientists for new research.
  - New areas of research in flow battery systems have been realized by the availability of this material.
    - An All-Organic Non-aqueous Lithium-Ion Redox Flow Battery *Fikile R. Brushett , John T. Vaughey , and Andrew N. Jansen* Adv. Energy Mater.* 2012, *2*, 1390–1396.
  - New safety analyses were enabled by accessibility of large amounts of the shuttle.
    - Thermal and overcharge abuse analysis of a redox shuttle for overcharge protection of $LiFePO_4$ *Joshua Lamb, Christopher J. Orendorff, Khalil Amine, Gregory Krumdick, Zhengcheng Zhang, Lu Zhang and Antoni S. Gozdz*: Submitted to Journal of Power Sources.
    - Overcharge Protection of Nanophosphate™ Li-Ion Cells With Two Redox Shuttles *Antoni S. Gozdz* A123 Systems, LLC 30TH International Battery Seminar & Exhibit, February 13, 2013.

Collaborations

- Electrolyte materials scaled
  - Argonne's Applied R&D Group (John Zhang)
  - US Army Research Laboratory (Kang Xu)
- Analysis and electrochemical validation of scaled materials
  - Argonne's Material Screening Group (Wenquan Lu)
- Materials used for further research
  - Pacific Northwest National Laboratory (Wu Xu)
  - Sandia National Laboratory (Joshua Lamb)
  - Argonne's Electrochemical Energy Storage, Applied R&D group (Andrew Jansen)
- In discussion for future scale-up
  - Case Western University (Daniel Scherson)
  - Idaho National Laboratory (Mason Harrup)

Activities for Next Fiscal Year

- Manage electrolyte materials database and populate with new candidates of electrolyte materials of interest to the ABR program.
  - Rank and prioritize the materials.
- Develop scalable process for 4-6 electrolyte materials and produce kilogram quantities for sampling.
  - Develop scalable process, analytical methods and quality control procedures.
  - Validate the manufacturing process, quality of the materials and their electrochemical properties.
  - Create Technology Transfer Packages.
  - Supply material samples to researchers, national laboratories, and industry for further evaluation.

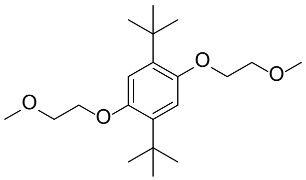
Summary

- This program has been developed to provide a systematic approach to process R&D and scale-up, and to provide sufficient quantities of advanced electrolyte materials for industrial evaluation.
- Argonne's process R&D program enables industry to carry out large-scale testing of new electrolyte materials and enable scientists to obtain next generation materials for further research.
- Integration of materials discovery with process R&D will expedite the time needed to commercial deployment.

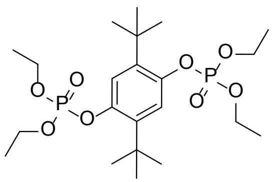
- **Over 40 samples have been presented to collaborating research entities**
- **Since the last AMR Meeting, processes for 3 additional electrolyte materials were successfully developed and materials were produced at the kilogram scale.**

Electrolyte Materials Scaled and Available

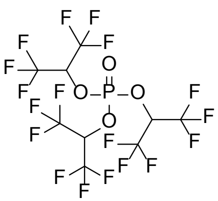
Redox shuttle ANL-RS2



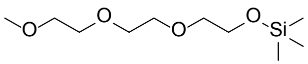
Redox shuttle ANL-RS6



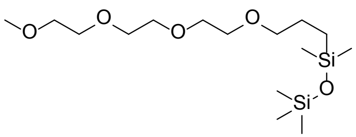
Electrolyte additive ARL-HFiPP



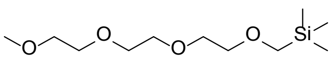
Solvent ANL-1NM3



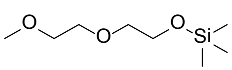
Solvent ANL-2SM3



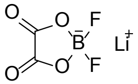
Solvent ANL-1S1MM3



Solvent ANL-1NM2



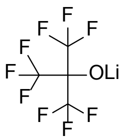
Electrolyte additive LiDFOB



Redox shuttle ANL-RS21

Patent Pending

Electrolyte additive ARL-LiPFTB



- 10 electrolyte materials have been scaled to date.
- Over 24,000 g of battery grade materials were produced.
- Since program start, 40+ material samples (over 6,700 g) have been sampled to scientists and industry.

Acknowledgements and Contributors

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

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  - Peng Du
  - Lu Zhang
  - Wei Weng

- US Army Research Laboratory
  - Kang Xu