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
- **Budget**
  - Funding received in FY11: $450K + internal funds
  - Funding received in FY12: $1.0M
- **Barriers**
  - Barriers addressed
    - Cost – Reduce cost to manufacture materials
    - Performance – Optimize process for highest purity for maximum performance
- **Partners**
  - Argonne's EES Applied R&D Group
  - Argonne's EES Materials Screening Group
  - US Army Research Laboratory
  - We are open to work with any ABR partner

Objectives and Relevance of this Program

- The objective of this program is to develop scalable processes for manufacturing electrolyte materials, synthesize kilogram quantities of each material and make them available for industrial evaluation:
  - 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 of these materials for evaluation by industry.
  - 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 will provide quantities of materials with consistent quality for further validation in large format prototype cells.
  - This program will provide the basis for meeting broader industrial needs to reduce the risk associated with developing and maintaining a domestic commercially viable battery manufacturing capability.

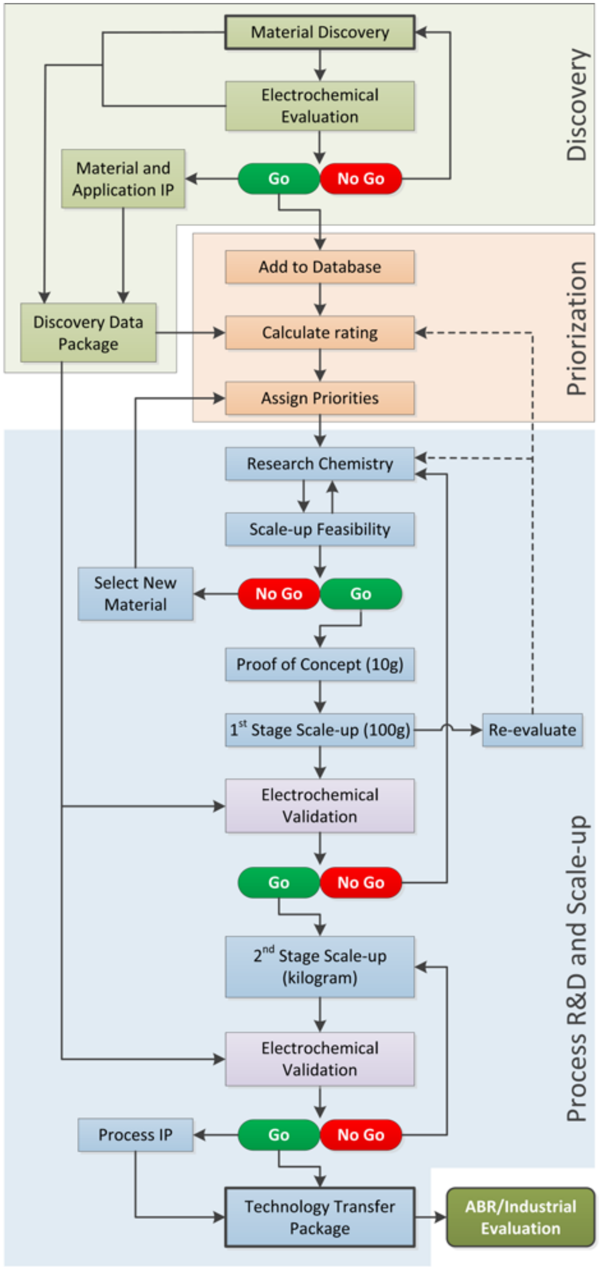
Approach

Shuttle Additives	Chemical formula/ full name	Date added to spreadsheet	Contact	Organization	IP or patent #	Reference	Redox Potential (vs Li^+/Li)	Solubility in Electrolyte (1.2M $LiPF_6$ EC/EMC (3/7 V/V))	Diffusion coefficient (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	Electrochemical Evaluation (Y/N) (attached if Y)	Scale previously achieved/ commercial (Kg or unknown)	Number of Validations/Trials (# or unknown)	Number of Synthesis Steps (# or unknown)	Commercially available? (Y/N)	Cost (L/M/H)	Safety Hazard (L,M,H)	Raw Material Availability (Y/N)	normalize cost (score 1-10, best 10)	normalize safety hazard (score 1-10, best 10)	normalize raw availability (score 1-10, best 10)	normalize scale (score 1-10, best 10)	normalize # trials (score 1-10, best 10)	Number of Synthesis Steps (# or unknown)	OVERALL SCALE SCORE (best score 59)	Commercially available No/Yes (green/red)	Electrochemical Evaluation Yes/No (green/red)		
ANL-RS2	2,5-di-tert-butyl-1,4-di(2-methoxyethoxy)benzene (DBDMB)	11/1/2010	Zhang, Zhengcheng <zzhang@anl.gov>	ANL	ANL-IN-09-032 unpublished	unknown	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	$LiFePO_4$	Y	1	1	2	N	L	L	Y	10	10	10	3	1	2		No	Yes		
ANL-RS6	Tetraethyl-2,5-di-tert-butyl-1,4-phenylene diphosphate (TEDBPDP)	11/1/2010	Zhang, Zhengcheng <zzhang@anl.gov>	ANL	ANL-IN-09-084 unpublished	unknown	4.80V	up to 0.5M	unknown	10 cycles in $Li/LiMn_2O_4$; 10 cycles in Li/[illegible]	Additive Required	Stable in air	Excellent	Low	High Voltage Cathode [illegible]	Y	1	1	2	N	M	L	Y	5	10	10	3	1	2		No	Yes		
ANL-RS4		11/1/2010	Zhang, Zhengcheng <zzhang@anl.gov>	ANL	ANL-IN-09-086	J. Power. Sources (2010) in press	4.17V	up to 1.0M	1.70x10[illegible]	20 cycles in $LTO/LiFePO_4$ (C/5); 42 cycles in $LTO/LiFePO_4$ (C/10)	Stable	Stable in air	Excellent	Medium	$LiFePO_4$	unknown	1	1	1	N	L	M	Y	10	5	10	3	1	1		No	unknown		
ANL-RS3		11/1/2010	Zhang, Zhengcheng <zzhang@anl.gov>	ANL	ANL-IN-09-086	J. Power. Sources (2010) in press	4.12V	up to 1.0M	1.40x10[illegible]	3 cycles in $LTO/LiFePO_4$ (C/5); 3 cycles in $MCMB/LiFePO_4$ (C/5)	Stable	Stable in air	Excellent	Low	$LiFePO_4$	unknown	1	1	1	N	L	L	Y	10	10	10	3	1	1		No	unknown		
ANL-RS0		11/1/2010	Zhang, Zhengcheng <zzhang@anl.gov>	ANL	unknown	J. Power Sources 195 (2010) 4957	4.30V	up to 1.0M	1.60x10[illegible]	11 cycles for $Li/LiFePO_4$ (C/10); 20 cycles for $MCMB/LiFePO_4$ (C/10)	Stable	Stable in air	N/A	unknown	$LiFePO_4$	unknown	1	1	2	N	L	M	Y	10	5	10	3	1	2		No	unknown		
ANL-RS5		11/1/2010	Zhang, Zhengcheng <zzhang@anl.gov>	ANL	ANL-IN-10-076 unpublished	unknown	4.55V	up to 1.0M	unknown	40 cycles in $MCMB/LiMn_2O_4$ (C/10); 40 cycles in MCMB/[illegible] (C/10)	Additive Required	Stable in air	Excellent	Low	$LiCoO_2$; [illegible]	unknown	2	2	2	N	H	M	Y	1	5	10	3	1	2		No	unknown		
ANL-RS1		11/1/2010	Zhang, Zhengcheng <zzhang@anl.gov>	ANL	unknown	J. Power Sources (2001) 566 (ANL) Electrochem. Comm. 9 (2007) 703	4.43V	0.57M or 3wt%	1.40x10[illegible]	170 cycles for MCMB/NMC (C/10) (C/10 and C/5 mixed rates and mixed temperatures)	Stable	Unstable (Hydrolysis)	N/A	unknown	[illegible]	unknown	1	1	5	N	H	M	N	1	5	1	3	1	5		No	unknown		
ANL-RS7		11/4/2011	Zhang, Zhengcheng <zzhang@anl.gov>	ANL	unknown	unknown	4.10V	>0.3M	unknown	> 70 cycles LiFePO4/LTO cell	stable	stable in air	Excellent	Low	LiFePO4 cathode	unknown	unknown	1	1	N	H	L	N	1	10	1	unknown	1	1		No	unknown		
ANL-RS-8		11/4/2011	Zhang, Zhengcheng <zzhang@anl.gov>	ANL	unknown	unknown	4.05V	> 0.3M	unknown	in progress	Stable	stable in air	Excellent	Low	LiFePO4 cathode	unknown	unknown	unknown	1	N	H	L	N	1	10	1	unknown	unknown	1		No	unknown		
ANL-RS2b		1/11/2012	Zhang, Zhengcheng <zzhang@anl.gov>	ANL	unknown	unknown	4V	> 0.4M	unknown	150 cycles	stable	stable in the air	excellent	Low	LiFePO4	unknown	unknown	unknown	2	N	M	H	Y	5	1	10	unknown	unknown	2		No	unknown		

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

Approach

- Develop experimental work planning and control (EWPC) procedure
- Explore various chemical pathways and determine scale-up feasibility
- 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
- Project reporting



Approach - Milestones

- FY11
  - 2-4 scale-up processes to be developed
    - 4 materials completed
    - 1 material considered not suitable for scale-up
- FY12
  - 2-4 scale-up processed to be developed
    - 3 materials completed (as of 3/22/12)
  - Decommission interim laboratory, relocate to the Materials Engineering Research Facility (MERF)
- FY13
  - 4-6 scale-up processes to be developed

MILESTONE	DATE	STATUS	COMMENTS
Establish electrolyte scale-up lab	9/30/2010	Completed	
ANL-RS2 – Scale up work completed			Kilogram quantities available
Select CSE material to scale	10/1/2010	Completed	
Assess scalability of CSE process	10/18/2010	Completed	
WP&C documentation approved	11/1/2010	Completed	
Develop and validate scalable process chemistry (10g bench scale)	12/1/2010	Completed	
First process scale-up (100g bench scale)	12/23/2010	Completed	
Second process scale-up (1000g pilot scale)	03/04/2011	Completed 02/21/2011	1,576 g produced in a single batch, purity > 99.9%.
1NM3 – Scale up work completed			Kilogram quantities available
Select CSE material to scale	11/01/2010	Completed	
Assess scalability of CSE process	11/15/2010	Completed	
WP&C documentation approved	12/23/2010	Completed	
Develop and validate scalable process chemistry (10g bench scale)	02/18/2011	Completed	
First process scale-up (100g bench scale)	03/11/2011	Completed 03/09/2011	130 g produced in a single batch, purity >99.9%. Single fractional distillation delivered high purity product.
Second process scale-up (1000g pilot scale)	05/13/2011	Completed 05/17/2011	3.36 kg, produced in a single batch, purity >99.95%
2SM3			Kilogram quantities available
Select CSE material to scale	01/07/2011	Completed	
Assess scalability of CSE process	01/14/2011	Completed	
WP&C documentation approved	03/07/2011	Completed	
Develop and validate scalable process chemistry (10g bench scale)	04/28/2011	Completed	Requires double fractional distillation to achieve purity >99.5%. Difficult to handle in a small scale.
First process scale-up (100g bench scale)	05/20/2011	Completed 05/26/2011	Single fractional distillation yield material with purity 99.7 %. The reaction in 250 g (total reagents) scale exhibited very strong exothermic effect not observed on 10 g scale. The process needs to be re-designed.
Develop and validate scalable process chemistry (10g bench scale)	06/03/2011	Completed	A modified procedure has been developed that allows full control of thermal effect of the reaction. The new procedure was validated in 25g scale reaction.
Second process scale-up (1000g pilot scale)	06/24/2011	Completed 06/24/2011	1,477 g of material was made in a single batch. The purity of the material is > 99.9%.
ANL-RS6			Kilogram quantities available
Select CSE material to scale	01/07/2011	Completed	
Assess scalability of CSE process	01/14/2011	Completed	
WP&C documentation approved	03/14/2011	Completed	
Develop and validate scalable process chemistry (10g bench scale)	05/06/2011	Completed	Requires multiple crystallizations to achieve purity greater than 99%. We are still working to simplify/optimize the process.
First process scale-up (100g bench scale)	06/03/2011	Completed 05/26/2011	
Second process scale-up (1000g pilot scale)		Completed 07/25/2011	1,815 g was produced in a single batch. The purity of the material is > 99%.

Approach – Deliverables


Battery Materials Scale-up Process R&D
Information Package

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

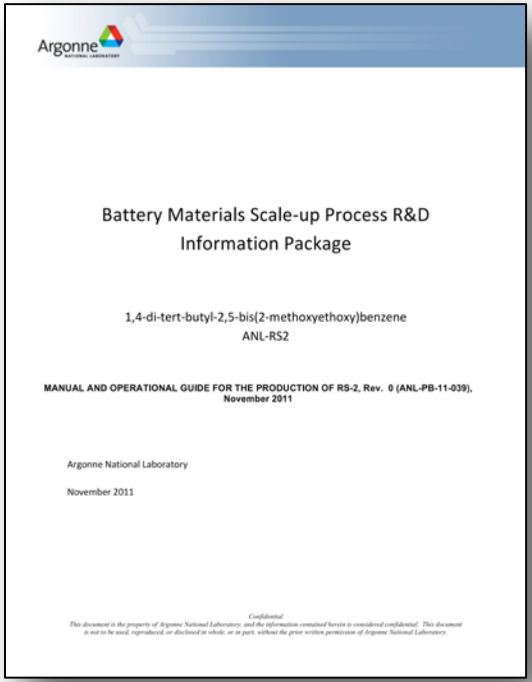
- For each electrolyte material selected we will:
  - Develop a scalable manufacturing process.
  - Develop analytical methods and quality control procedures.
  - Prepare a “technology transfer package” which will include:
    - Summary of the original process used by discovery researchers to synthesize 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.
    - The material will be fully characterized chemically and electrochemically

Technical Accomplishments and Progress Overview

- Scalable processes were developed and kilogram quantities of materials were synthesized for 5 electrolyte materials.
  - ANL-1NM3
  - ANL-2SM3
  - ANL-1S1M3
  - ARL-HFiPP
  - ANL-RS6
- Technology transfer packages were created.
- Materials were sampled for evaluation.

Technical Accomplishments and Progress
Redox Shuttle ANL-RS2

- Scale-up process developed and reported at previous AMR meeting.
- Technology Transfer Package was created.
- Process technology patent filing is in progress.
- Samples of the material were supplied for evaluation to researchers and industry.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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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Technical Accomplishments and Progress
Redox Shuttle ANL-RS6

- New chemistry was developed for the process.
- Multi-step synthesis was simplified to a single reaction.
- The reaction is carried out using “green” solvents.
- The material is purified to the required grade by simple crystallization.
- The amount of waste generated was reduced.
- Overall yield of the process was improved.

- The scaled-up material was validated and matched the electrochemical properties of the original material from discovery.

- Technology Transfer Package was created for the process.

- Sample of the material was provided to scientist for further research and to industry for evaluation.


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Battery Materials Scale-up Process R&D
Information Package

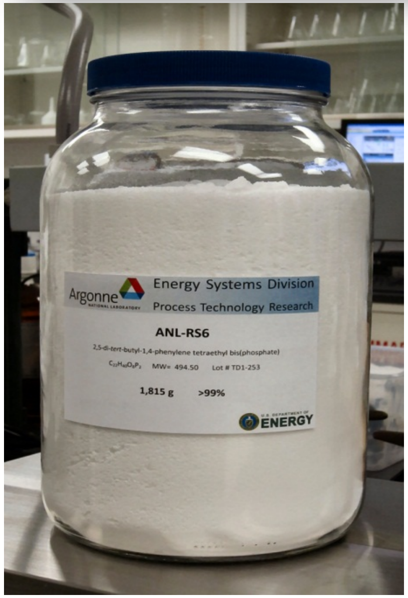
2,5-di-tert-butyl-1,4-phenylene tetraethyl bis(phosphate)

ANL-RS6

MANUAL AND OPERATIONAL GUIDE FOR THE PRODUCTION OF RS-6, Rev. 0 (ANL-PB-11-105), January 2012

Argonne National Laboratory

January 2012



Technical Accomplishments and Progress
Solvent ANL-1NM3

- All solvents were eliminated from the process (solvent-free process).
- The amount of waste generated was minimized.
- Used of a catalyst allowed lower temperature and shorter reaction time (lower cost and use of energy).
- Overall yield and purity of the material was improved.

- The scaled-up material was validated and matched the electrochemical properties of the original material from discovery lab.

- Technology Transfer Package was created for the process.

- Sample of the material was provided to scientist for further research and to industry for evaluation.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Battery Materials Scale-up Process R&D
Information Package

2,2-dimethyl-3,6,9,12-tetraoxa-2-silatridecane
ANL-1NM3

MANUAL AND OPERATIONAL GUIDE FOR THE PRODUCTION OF 1NM3, Rev. 0 (ANL-PB-******),
March 2012

Argonne National Laboratory

July 2011

Technical Accomplishments and Progress
Solvent ANL-2SM3

- The developed process is solvent-free.
- Used of an advanced catalyst allowed better utilization of feedstock and minimized by-product formation.
- The catalyst is fully recoverable and recyclable.
- The amount of waste generated was minimized.
- Overall yield of the process was improved.

- Validation of the electrochemical performance of the material is in progress.

- Technology Transfer Package was created for the process.

- Sample of the material was provided to scientist for further research.


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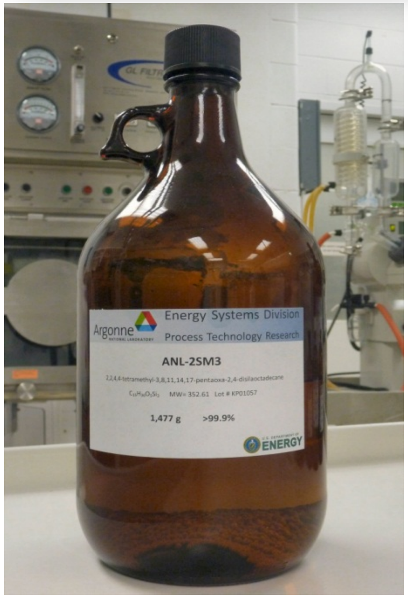
Battery Materials Scale-up Process R&D
Information Package

2,2,4,4-tetramethyl-3,8,11,14,17-pentaoxa-2,4-disilaoctadecane
ANL-2SM3

MANUAL AND OPERATIONAL GUIDE FOR THE PRODUCTION OF 2SM3, Rev. 0 (ANL-PB-******).
March 2012

Argonne National Laboratory

March 2012



Technical Accomplishments and Progress
Solvent ANL-1S1M3

- Complex process (four subsequent chemical transformations).
- Chlorinated solvents were eliminated from the process.
- Highly flammable ethers were replaced with less hazardous solvents.
- Pyrophoric butyllithium was eliminated from the process.
- Purification of intermediate materials were eliminated.
- The amount of waste generated was reduces.

- Validation of the electrochemical performance of the material is in progress.

- Technology Transfer Package compilation is in progress.

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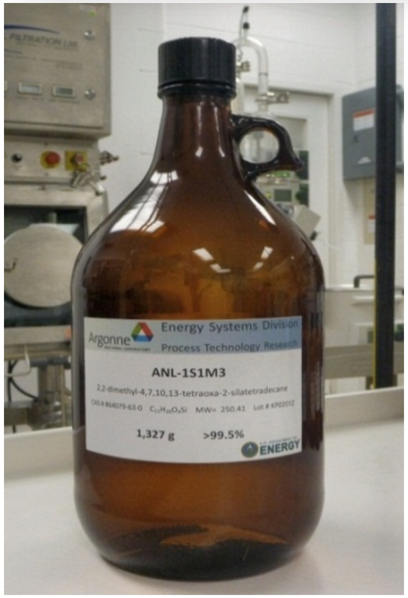
Battery Materials Scale-up Process R&D
Information Package

2,2-dimethyl-4,7,10,13-tetraoxa-2-silatetradecane
ANL-1SM3

MANUAL AND OPERATIONAL GUIDE FOR THE PRODUCTION OF 1S1M3, Rev. 0 (ANL-PB-******),
March 2012

Argonne National Laboratory

March 2012



Technical Accomplishments and Progress
Passivation Additive ARL-HFiPP

- Scale-up process developed in cooperation with ARL
- Optimizing the reagents ratio and reaction condition resulted in improved yield and quality of the product.
- The material is purified to the required grade by simple, one-step distillation (originally double distillation followed vacuum sublimation).
- Hazardous diethyl ether was replaced with a less flammable solvent.
- Overall yield of the process was improved.

- Validation of the electrochemical performance of the material is in progress.

- Technology Transfer Package was created for the process.

- Sample of the material was provided to scientist for further research.

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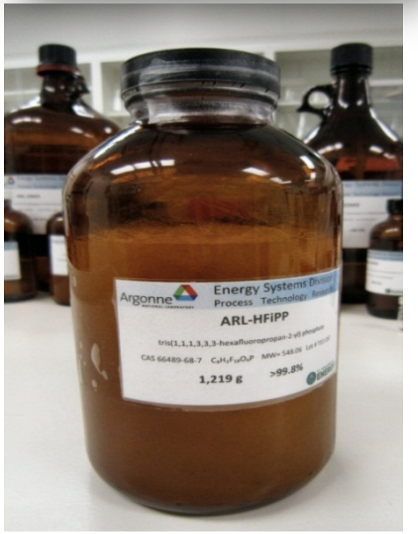
Battery Materials Scale-up Process R&D
Information Package

tri(1,1,1,3,3,3-hexafluoro-2-propyl)phosphate
ARL-HFIPP

MANUAL AND OPERATIONAL GUIDE FOR THE PRODUCTION OF HFIPP, Rev. 0 (ARL-PB-11-039), March 2012

Argonne National Laboratory

March 2012



Collaborations

- Argonne’s Electrochemical Energy Storage, Applied R&D group
  - Electrolyte solvents and redox shuttle were scaled
- US Army Research Laboratory
  - Passivation additive was scaled
- Argonne’s Electrochemical Energy Storage, Material Screening group
  - Conducted electrochemical validation of scaled materials
- **We invite all ABR program participants to submit new candidates to our advanced electrolyte materials process R&D program.**

Activities for Next Fiscal Year

- Manage electrolyte materials database and populate with new candidates from other institutions in the ABR program.
  - Rank and prioritize the materials.
- Develop scalable process for manufacturing 4-6 electrolyte materials from discovery to bulk quantities.
  - Develop scalable process, analytical methods and quality control procedures.
  - Validate the manufacturing process, quality of the materials and their electrochemical properties.
  - Create Technology Transfer Package.
  - Supply material samples to researchers and industry for further evaluation.

Activities for Next Fiscal Year
The Materials Engineering Research Facility (MERF)

- 10,000 sq. ft. facility consists of "Group-H occupancy" pilot labs and high bay spaces.
- All interim labs will be relocated to the MERF, starting in April.
- 50% DOE – 50% DoD funded

Analytical Lab

Pilot Labs (benchtop)

Pilot Labs (walk-in)

High Bay Spaces

Summary

- The procedures used to make small, research sample of materials are not suitable for large scale production. Manufacturing processes for the newly discovered advanced materials must be scalable to facilitate the transition from basic research to commercial application.
- 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.
- Integration of materials discovery with process R&D will expedite the time needed to commercial deployment.
- Processes for 5 electrolyte materials were successfully developed. The materials were manufactured at the kilogram scale.
- Samples of the material were provided to various entities for industrial evaluation.

Acknowledgements and Contributors

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