Integrated Laboratory and Industry Research Project Overview – 2

Application of stabilized lithium metal powder in lithium ion batteries

Participant organizations: Lawrence Berkeley National Laboratory; Argonne National Laboratory, FMC Co. & Saft USA

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Industrial point of contacts: Marina Yakovleva (FMC), Bridget Deveney (Saft)

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Project ID: ES156

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Overview

Timeline
Project started: FY 2011
Project end date: FY 2014
Percent complete: 35%

Budget
Total project funding
-DOE share: $1,000K/yr., 100%
FY11 funding: $500K LBNL, $300K ANL
FY12 funding: $500K LBNL, $300K ANL
FY13 funding requested: $1,000K (LBNL&ANL)

Barriers Addressed
Performance: High first cycle irreversible capacity, low coulombic efficiency, and poor cycle life
Life: Poor calendar life
Cost: High manufacture cost
(Research in high energy system)

Partners
LBNL
ANL
FMC-Lithium
Saft USA

Relevance – Project Objective

Applications of Stabilized Lithium Metal Powder (SLMP) in Lithium-ion Batteries to achieve *lower cost* and *higher energy density*

This project is designed to address two main issues in regard to the current lithium ion technology - the high cost associated with **formation process**, which accounts for over 20% of the production cost of lithium-ion battery; and **first cycle loss of capacity** (10-30%) depending on the chemistry.

Lawrence Berkeley National Laboratory (LBNL) and Argonne National Laboratory (ANL) are teaming with FMC-Lithium and Saft USA to work on problems that impede or prevent the Stabilized Lithium Metal Powder (SLMP®) from being used as a performance enhancing additive in the electrode in commercial rechargeable batteries. If successful, this will lead to commercialization of batteries with simplified formation process, lower irreversible capacity losses (leading to higher energy densities) and allow for a wider range of cathode materials to be utilized for transportation applications.

Tasks

Participants: LBNL, ANL, FMC-Lithium and Saft USA

Task 1. Enable SLMP in the slurry-based process

Task 2. Investigate SEI formation and stability on graphite and other high capacity materials

Task 3. SLMP activation process

Motivation: SLMP provides a bridging step between the current Lithium ion chemistry and the future Lithium metal battery.

The milestones are designed around the three tasks

Milestones

FY 2011, LBNL milestones

1. Identify SLMP stable solvents with the guidance of FMC-Lithium and study the compatibility of the current binder materials (accomplished)
2. Investigate SEI formation on graphite electrode using different amount of SLMP doping (accomplished)
3. Analyze the morphology, conductivities, and mechanical properties of the Li_2CO_3 coating layer (accomplished)

FY 2011, ANL milestones

1. Develop SLMP stable slurry systems based on new solvent and binder with the guidance of FMC-Lithium (accomplished)
2. Investigate the physical and chemical properties of the coating materials on the surface of SLMP (accomplished)
3. Develop new activation process to activate the SLMP coated graphite anode (accomplished)

Milestones

FY 2012 LBNL milestones

Binder development project

1.Use material design and synthesize to optimize the SBR/CGP-G8 graphite interface to achieve similar power performance at C/2 rate as a controlled PVDF electrode (on schedule)
2.Demonstrate the interface optimization on high-first-cycle-loss hard carbon materials (on schedule)
3.Incorporate SLMP into the slurry mixing, coating and drying process (on schedule)

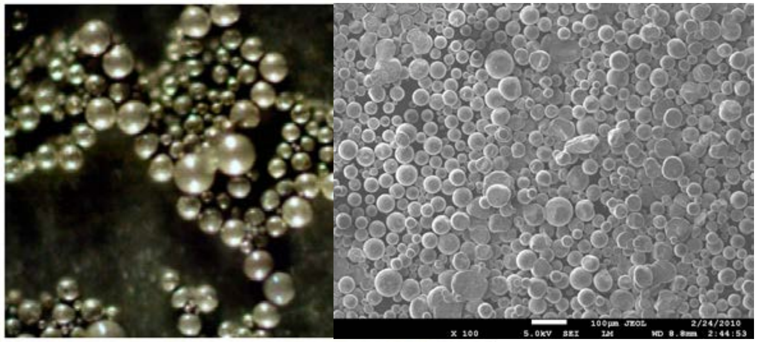
Formation and activation project

1.Demonstrate technology transfer of presently accepted activation processes as developed by FMC and study the formation effect of the electrode (on schedule)
2.Demonstrate a more industry acceptable activation process (on schedule)

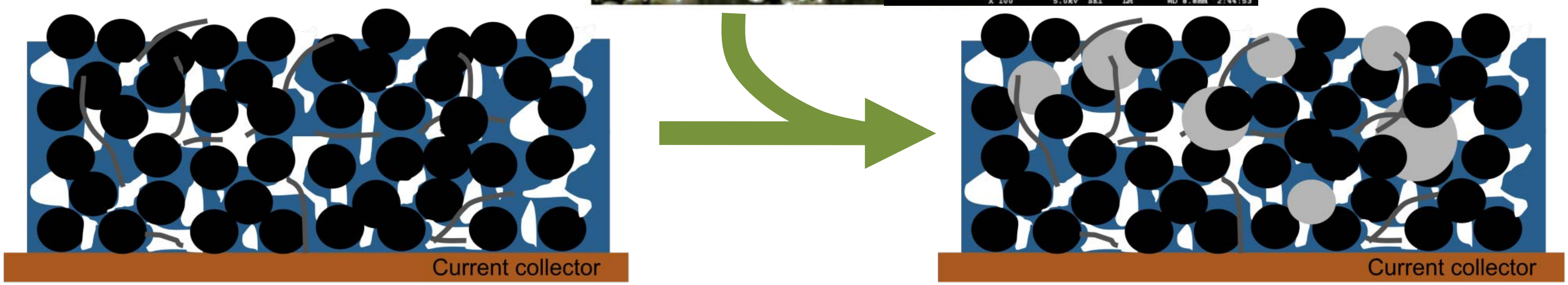
FY 2012 ANL milestones

1.Characterization of various surface coatings of SLMP synthesized by FMC using different methods (on schedule)
2.Continue the development of SLMP surface coating technique to enable it in lithium ion battery (on schedule)
3.Evaluate the physical and electrochemical performance of the SLMP-containing electrode made by the discovered solvent/binder couple (on schedule)
4.Continue the exploration of new solvent/polymer binder combinations to enable the SLMP application in lithium ion battery (on schedule)
5.Demonstrate the new SLMP activation process through electrolyte additive approach (on schedule)

Approach - Application of Stabilized Lithium Metal Powder (SLMP) to prelithiate electrodes



SLMP optical & SEM image



Regular electrode

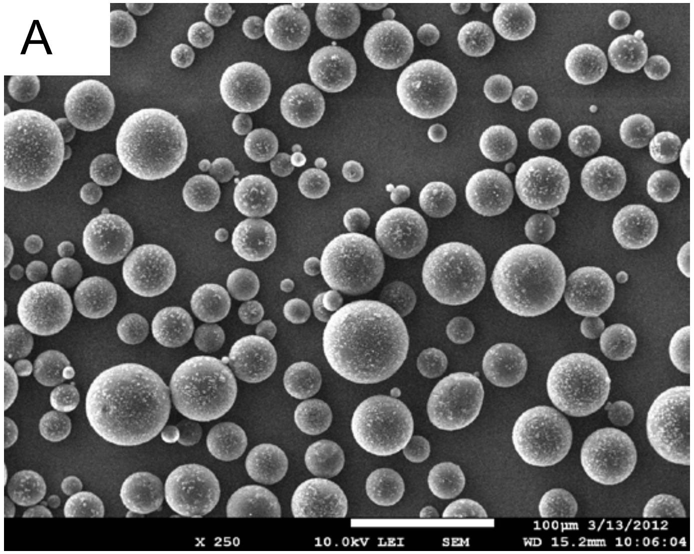
Electrode doped with SLMP

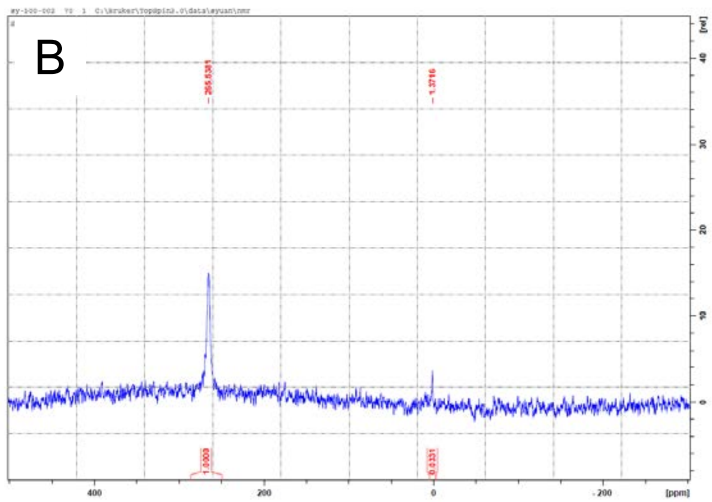
- Graphite
- SLMP
- Binder and conductive additive
- Carbon fiber

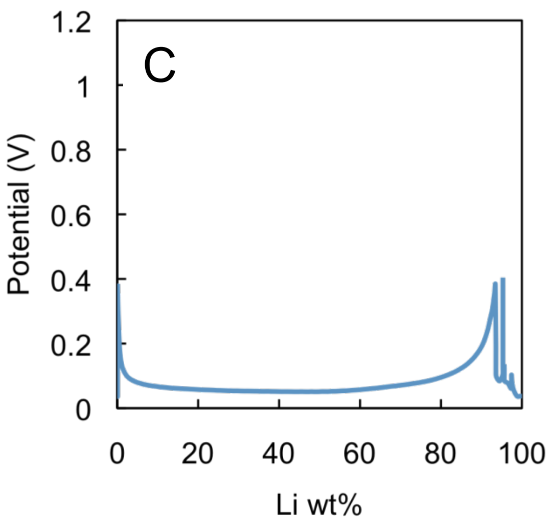
To develop enabling technology:
Simple and fast formation; decrease first cycle loss, utilize none-lithium containing cathodes

Start with lithium metal, but cycle lithium-ion

Accomplishments - Characterize SLMP material's morphology and chemical compositions







A: SEM image of SLMP
B: ^{7}Li-NMR spectrum of SLMP*
C: *Available Li is around 90% measured by lithium plating*

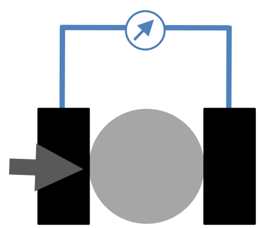
NMR analysis identified the coating on SLMP is Li_2CO_3. (Major peak is from the bulky Li at 265.5ppm and the small peak at 1.37ppm indicates Li_2CO_3 species.)

Accomplishments - Characterize SLMP material's mechanical properties and conductivity with in situ TEM – Andrew Minor, NCEM, LBNL

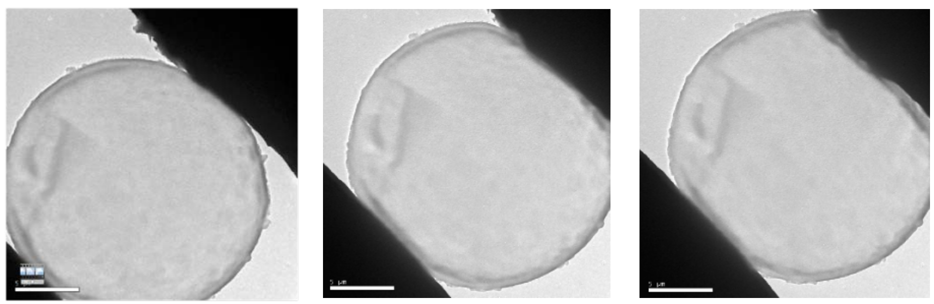
Schematics

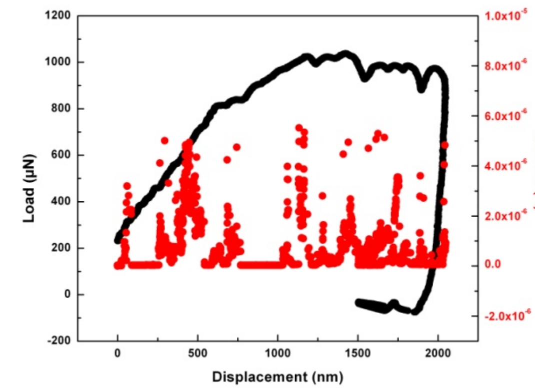
In situ TEM

Load and electric conduction



Compression

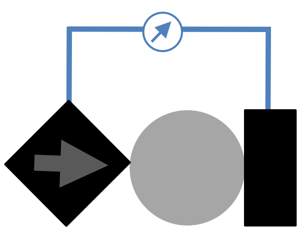




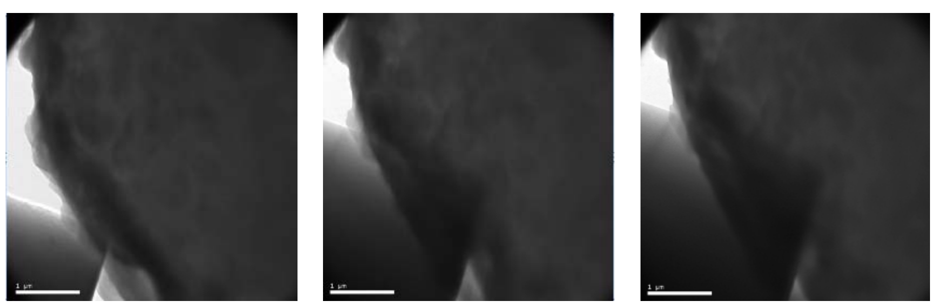
Compression without exposing lithium metal does not change conductivity

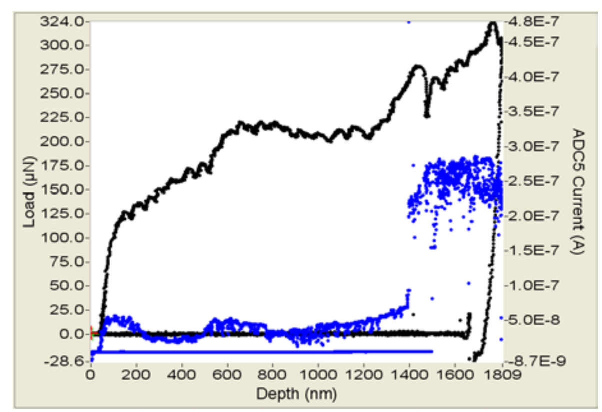
Force direction

Increasing displacement



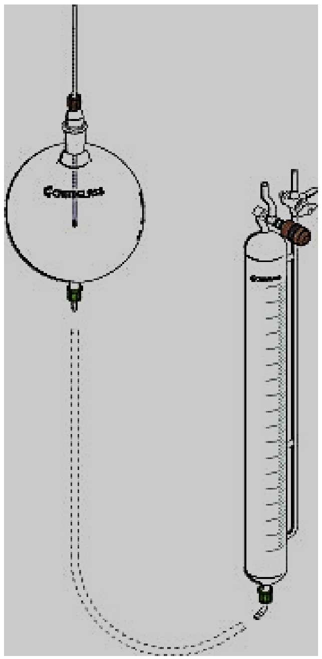
Penetration





Penetration leading to contact of lithium metal improves conductivity

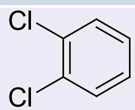
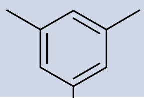
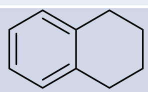
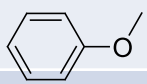
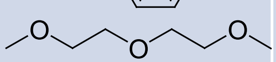
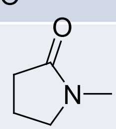
Accomplishments - Quantify solvent stability with standard CO_2 coated SLMP powder



Solvent	None	Tetrahydro-naphthalene	Anisole	Dichloro-benzene	Dichloro-benzene	NMP
SLMP Added (mg)	18.3	21.2	20.6	21.0	21.4	21.6
Test Condition*	N/A	mix with solvent for 72h	mix with solvent for 72h	mix with solvent for 72h	mix with solvent and stir for 30h	mix and stir with solvent for 24h
H_2 generated (mL) upon adding H_2O	27.2	32.2	31.7	32.5	28.3	1.5 (before adding H_2O)+1.2
Theoretical H_2 (mL, assuming Li 97% content)	28.4	32.9	31.9	32.6	33.2	33.5
Actual Li% based on test	92.9	94.9	96.2	96.7	82.6	7.8

- ❑ All mixing and stirring processes are performed in the Ar glove box.
- ❑ *NMP and water are not compatible with SLMP, while tetrahydronaphthalene, anisole and dichlorobenzene are the mostly compatible solvents with SLMP.*

Accomplishments - Quantify solvents and binder compatibilities

Solvent	PPO	Polysiloxane	Polyfluorene	PVdF (KF9130)
Chlorobenzene	10.2wt%	soluble	2.5wt%	--
O-Dichloro-benzene 	10.4wt%	soluble	2.0wt%	Doesn’t dissolve
Mesitylene 	slight	soluble	--	Doesn’t dissolve
Tetrahydra-naphthalene	5.1wt% (40^{o}C)	soluble	1.7wt% (40^{o}C)	Doesn’t dissolve
Anisole 	5.2wt% (40^{o}C)	soluble	slight	Doesn’t dissolve
Diglyme 	Swells	--	--	--
Triglyme 	Swells	--	--	--
NMP 	--	--	--	Dissolves

Accomplishments - Stable solvents and binder systems identified based on this and previous studies

1. Styrene-butadiene rubber binder and toluene solvent - Existing binder with new process

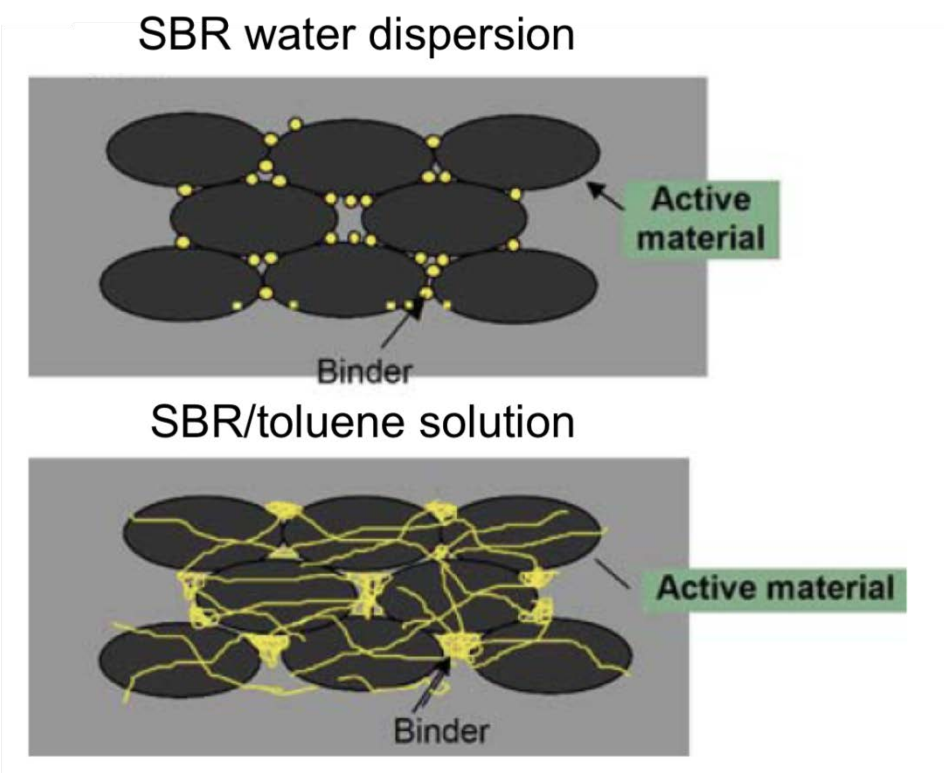
Advantage: Binder stability in the lithium-ion chemistry is well studied and understood
Disadvantage: Need to develop new process

2. PPO binder and anisole solvent - New binder with existing process

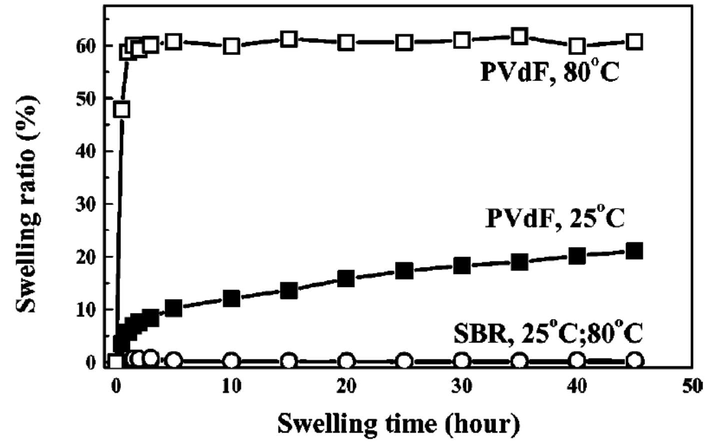
Advantage: Use existing process
Disadvantage: Need to understand binder compatibility in lithium ion chemistry

Accomplishments - SBR in toluene results in different coating morphology on active material

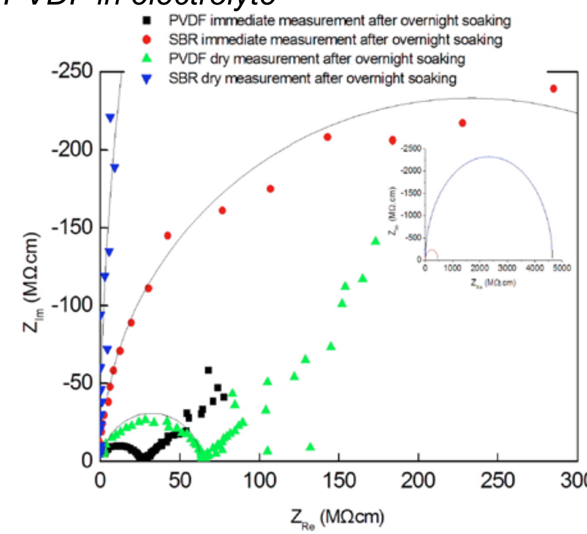
Conceptual illustration of binding between binder and active materials



SBR does not swell much in electrolyte

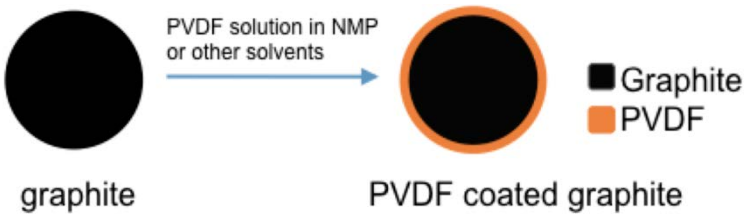


SBR member has much higher impedance than that of PVDF in electrolyte

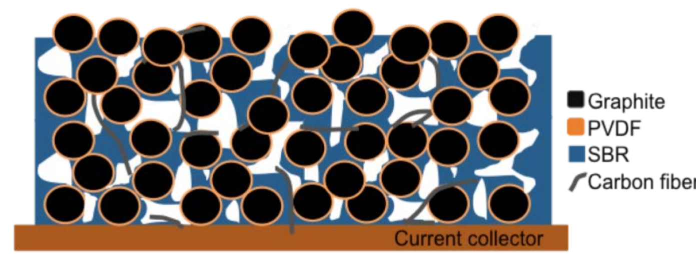


Accomplishments - PVDF coating on graphite surface creates lithium-ion channels

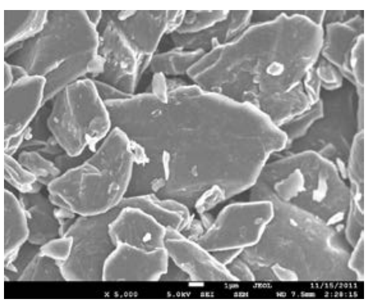
Material modification



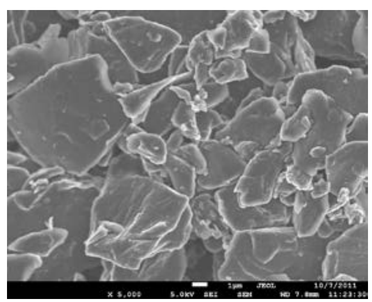
Electrode



No surface coating

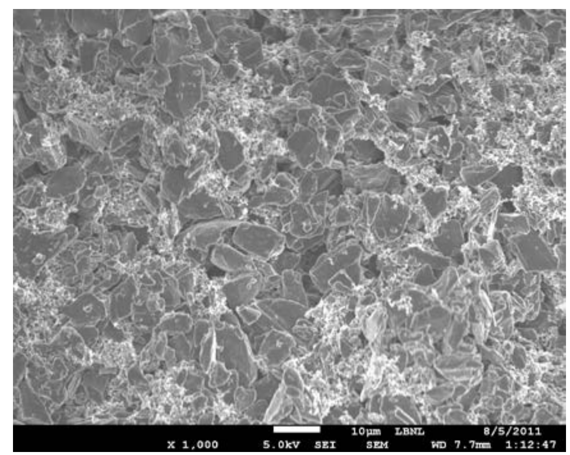


2% PVDF coated



No visible difference between PVDF coated and none coated particles

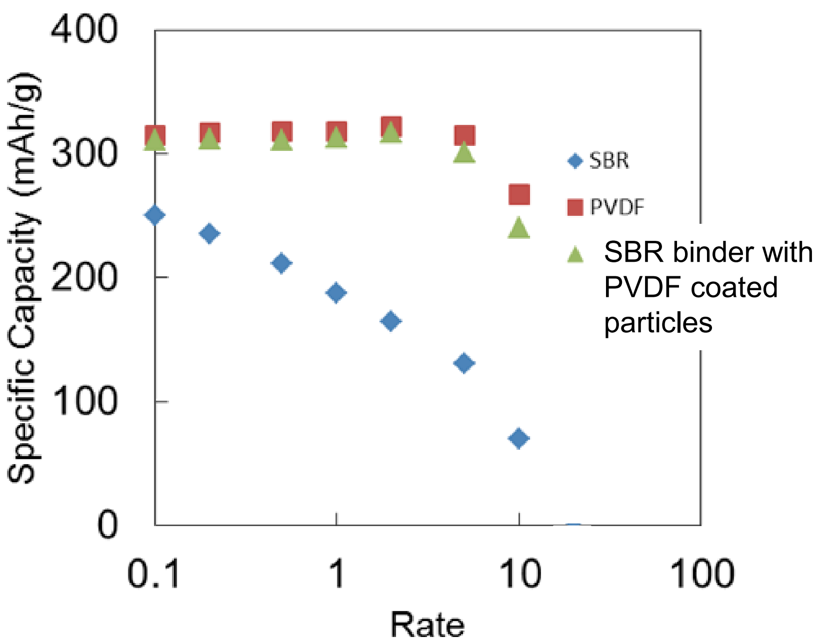
Electrode made with PVDF coated graphite and SBR binder



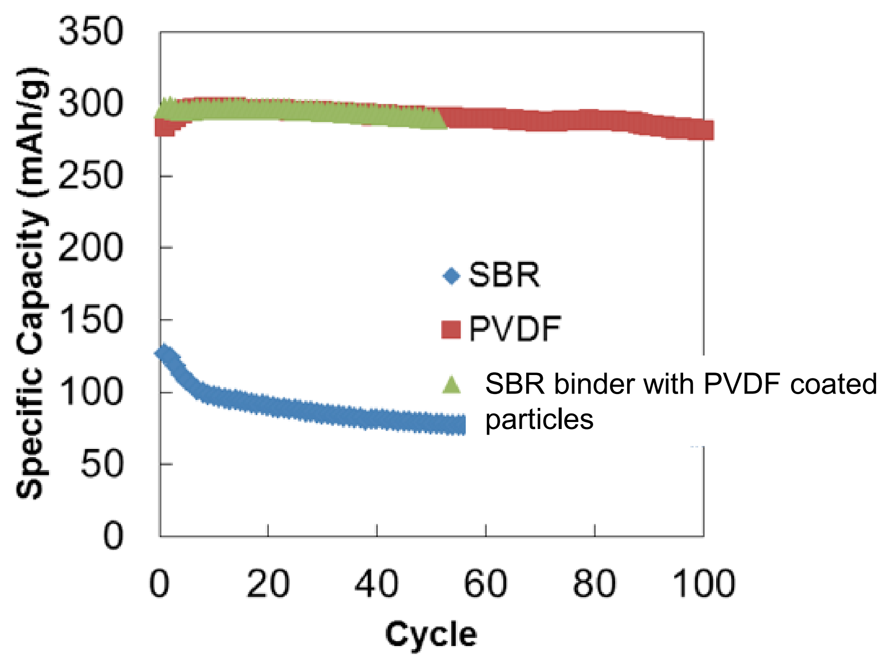
Similar morphology as PVDF binder based graphite electrode

Accomplishments - Graphite electrodes achieve similar performance with PVDF/NMP process and with SBR/toluene process

Rate performance

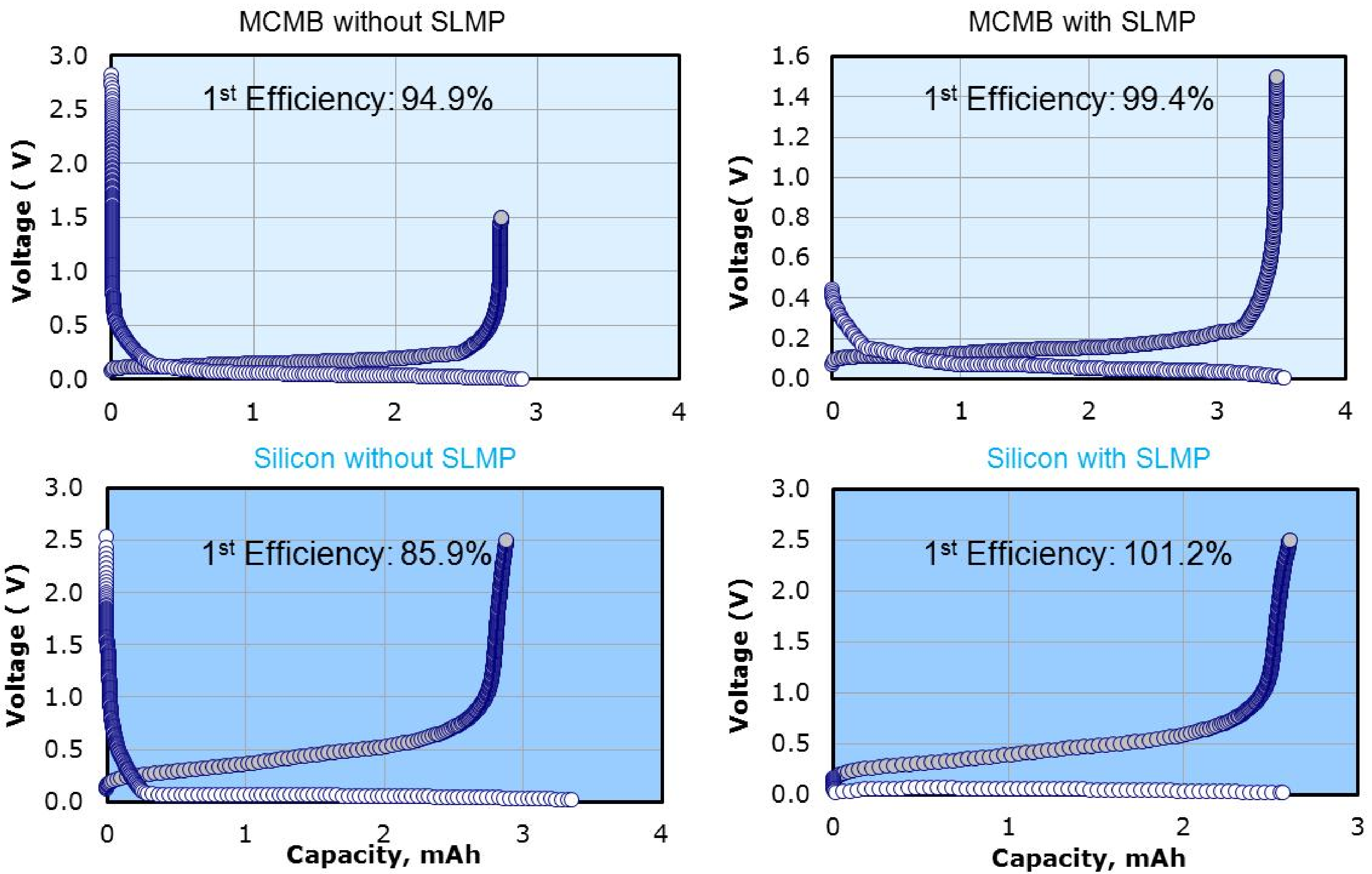


Cycling performance



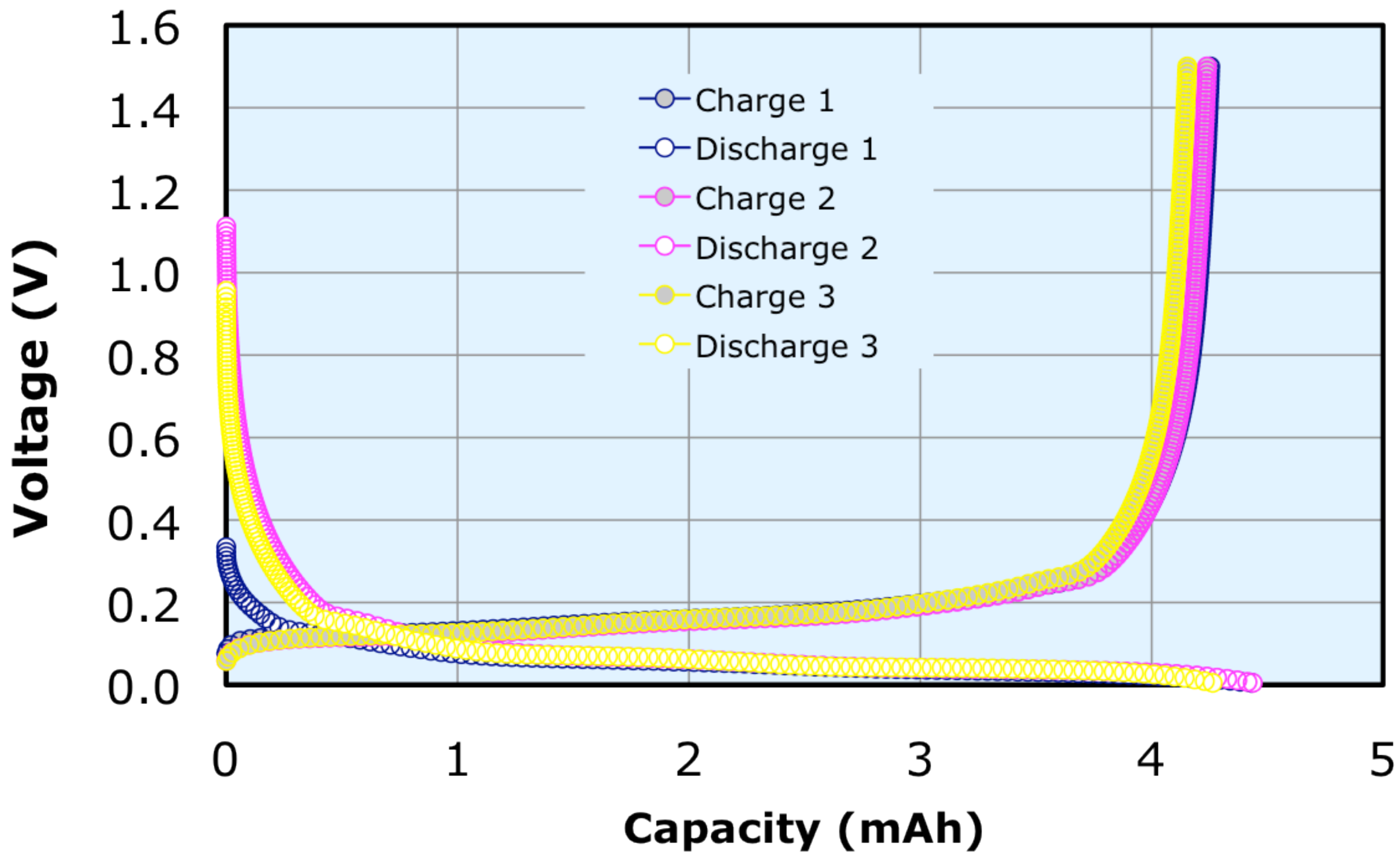
Both rate and cycling performance are not compromised at initial testing using SBR/toluene process when the graphite is coated with 2% of PVDF.

Accomplishments - SLMP coating on the surface of anode electrodes followed by compression activation process leads to lower first cycle irreversible capacity losses



Accomplishments – Incorporate SLMP into slurry process of the anode

PPO/anisole binder solvent system



- *SLMP is incorporated during slurry preparation process using PPO/anisole combination*
- *Half cell testing demonstrated that the irreversible capacity is removed due to the SLMP*

Collaborations - Team functions

Lawrence Berkeley Lab
•Existing binder with new process
•SLMP electrochemical activation
•Electron microscopy based diagnostic

Argonne National Lab
•New binder with existing process
•Chemical activation
•NMR diagnostics

FMC-Lithium provides different grade of SLMP and knowledge base for compatible materials and processes, as well as industry feedback

Saft USA provides commercial cells for formation study with the technology developed in the program

Proposed Future Work

1. The team are on schedule to accomplish the milestones defined in the remaining FY2012.

2. For the FY 2013, we propose to investigate in the following areas. The detailed milestones will be developed based on the on-going investigation, AMR review comments and discussions between the collaborators.

    a. In collaboration with Saft USA to study the formation effect of the SLMP doped anode electrode
    b. In collaboration with FMC-Lithium to develop scalable and controllable process to incorporate SLMP into the electrode
    c. Develop SLMP activate processes that are suitable for large scale and low cost electrode production

Summary

1. Acquired a comprehensive understanding of the SLMP material of its morphology, chemical composition, mechanical and electrical properties.
2. Developed a list of solvent responses to the SLMP materials, and concluded two binder/solvent combinations for formulating electrode slurry.
3. Developed a scalable process to use SBR/toluene to formulate electrode with equivalent rate and cycling performance of PVDF/NMP based process.
4. Developed a new PPO/anisole combination for electrode formulation
5. Investigated the pressure based SLMP activation process on the surface and in the electrode
6. Investigated the pro and con of SLMP prelithiation with SLMP applied either on the surface of pre-fabricated electrode or mixed in the electrode slurry