2011 DOE Vehicle Technologies Program Review

Stabilized Lithium Metal Powder, Enabling Material and Revolutionary Technology For High Energy Li-ion Batteries

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Project ID # ES011

FMC Lithium

Life begins with Li

Overview

Timeline

- Project start date: May 1st, 2009
- Project end date: April 30th, 2012
- 65% complete:

Budget

- Total project funding
  - DOE share: $2,999,424
  - FMC share: $2,999,425
- Funding received in FY10
  - $ 1,003,053
- Funding for FY11
  - $1.2 M

Barriers

- Barriers addressed
  - Develop technologies to reduce the production cost of a PHEV battery with a 40 mile all-electric range from the present $1,000/kWh to $300/kWh by 2014 enabling cost competitive market entry of PHEVs
  - Substantial petroleum displacement
  - Improved air quality

Partners

- FMC does not have partners on this project
- FMC has numerous ongoing collaborations outside this project to support development and enable advanced electrode materials

Relevance

- Lithium chemistry provides the best chance for the highest energy density batteries
- Recent developments in Li-ion battery technology have advanced its application into the area of large format batteries, for example HEV/PHEV/EV automotive markets
- This, in turn, has heightened the need not only for research on higher capacity, safer and less expensive battery materials but also for the development of improved scalable manufacturing processes for the production of battery materials and components to support high volume production of Li-ion batteries

Relevance

- In the current lithium-ion battery design, the lithium, which is the one that carries the energy, comes in the form of lithium metal oxide in cathode, hence limiting the choice of electrode active materials and the energy density that is possible with lithium chemistry. It has long been desired for lithium to come in the elemental form especially in the powder form to prelithiate the Li-ion anode host material for the most efficient utilization and fastest diffusion, but it was not possible because of lithium's high reactivity until the advancement of technology brought the stabilized lithium metal powder (SLMP®) to light.

- Achieving the DOE technical and cost targets for the PHEV/EV batteries will require development and use of new electrode materials. SLMP Technology provides an independent source of lithium for Li-ion systems, breaks the current limitation that all lithium has to come from the cathode and, thus, allows the use of non-lithium providing cathode materials with potentially larger capacities. These new cathode materials are expected to be more overcharge tolerant and could be used with high capacity advanced anodes having high irreversible capacities.

Objectives

FY09-FY12

The objective of this project is to expedite the development of cost-effective manufacturing processes for SLMP to support high volume production of Li-ion batteries and to make available commercial quantities of SLMP, the independent source of lithium that will enable higher energy, safer, environmentally friendlier and lower cost lithium batteries

Objective 1: Develop a process and prototype unit for the commercial production of dry stabilized lithium metal powder (SLMP)

Objective 2: Develop a process and design a commercial unit to scale-up the production of SLMP dispersion

Objective 3: Explore the use of alternative pilot scale unit to produce dry SLMP powder directly from battery-quality lithium metal (cost reduction)

Objective 4: Integrate SLMP Technology into the Li-ion cell for PHEV application

Year 2 Objectives
FY10-FY11

Objective 2

Develop a process and design a commercial unit to scale-up the production of SLMP dispersion

Objective 4/2

Integrate SLMP Technology into the Hard Carbon/$LiMn_2O_4$ system

Milestones: Commercial Unit to Scale-up Production of SLMP Dispersion

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Month/Year	Milestone
8/09	Equipment designed and vendor selected
8/09	AFE written and approved
11/09	Customized design approved
3/10	Location for installation prepared
4/10	Vendor delivered unit
5/10	Safety review of planned Installation completed
6/10	Unit installed and Pre-Start-up Safety review completed
7/10	Trial runs completed
11/10	Initial Designed Experiment completed
3/11	Experimental runs completed
3/11	Data analyzed and final report written

Milestones: Integrate SLMP Technology into the Hard Carbon/$LiMn_2O_4$ system

Month/Year	Milestone
3/10	Procured electrode materials and conducted half cell evaluation
6/10	Conducted full cell evaluation
9/10	Evaluated effect of multiple parameters on the SLMP utilization
12/10	Evaluated effect of different cycling protocols on cycleability
12/10	Evaluated effect of SLMP loading
3/11	Studied impedance and rate capability for the SLMP incorporated cells
5/11	Summarized and presented results at the ECS meeting

The Gaston Gazette, by John Clark, 3/7/2010

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Approach/Strategy

- Currently, there is not one cathode/anode system that can satisfy safety, cost and performance requirements for the EV application
- As the initial step in SLMP Technology introduction, industry can use commercially available $LiMn_2O_4$ or $LiFePO_4$, for example, that are the proven safer and cheaper lithium providing cathodes vs. $LiCoO_2$ or $LiNiO_2$. Currently, systems using these cathodes do not take full advantage of the SLMP Technology
- Unfortunately, these cathodes alone are inferior to the energy density of conventional $LiCoO_2$ cathodes and, when paired with advanced anode materials, such as silicon composite material, the resulting cell will still not meet the energy density requirements, unless SLMP® Technology is used to compensate for the irreversible capacity in the anode and thus improve efficiency of the cathode utilization

Approach/Strategy

The proposed battery system works by adding lithium to the anode of a cell in the form of SLMP. If the anode material is carbon, lithium will intercalate into the carbon to form LiC_6 on addition of the electrolyte just as in a standard lithium ion cell. The system is therefore still a Li-ion system. However, the cathode no longer needs to contain lithium and using non-lithiated cathode materials based on vanadium oxides, manganese oxides or metal fluorides now becomes feasible.

Performance & Cost

- Lower cost through the use of more efficient and less costly cathode materials and the elimination of cobalt from the system
- Greater performance through the ability to compensate for inefficiencies in, hitherto, unsuitable anode materials with high irreversible capacity
- Longer calendar life: SLMP serves as a “getter” of moisture and acidic species

Safety

- Improved safety on overcharge. Since the lithium is introduced into the anode, the cell is charged when it is manufactured. This system, that has non-lithium providing cathode, cannot be overcharged. Safety issues are transferred from the end-user to the factory where they can be fully controlled.
- Non-lithiated cathode materials are inherently more stable than the $LiCoO_2$ used in the majority of Li-ion cells today
- The cell is a Li-ion cell. There is no metallic lithium in the cell after the electrolyte is added during cell assembly and the cell has completed its formation cycle, thereby avoiding the risks associated with ‘conventional’ lithium metal cells.

Technical Accomplishments and Progress (1)

All tasks are completed to meet Objective 2 technical targets. The major challenge was to mitigate the 3 month delay in equipment fabrication

- Selected a vendor who has demonstrated the capability of fabricating equipment that meets technical and safety requirements*
- Standard Equipment Design was carefully reviewed and key modifications applied
- Factory Acceptance Testing revealed no significant items that required correction
- Unit was delivered on April 20th, 2010
- A P&ID (piping and instrumentation drawing) was created to assist with installation
- Site was prepared for the installation and all safety reviews completed
- Trial runs were completed and the procedure was modified to improve performance
- A 2^3 designed experiment was planned and implemented
- Commercial-scale dispersion system consistently makes better quality SLMP than does the pilot-scale dispersion unit – SUCCESSFUL SCALE-UP!
- Equipment modifications were made to improve process control and data collection

Technical Accomplishments and Progress (2)

All tasks are completed to meet Objective 4/2 technical targets.

- A major challenge was to procure electrode materials for this study
- Material from Kureha Corporation was selected and was used as an anode material for all electrochemical testing with the spinel material from Toda Corporation
- First cycle coulombic efficiency was improved from 61% to 92%

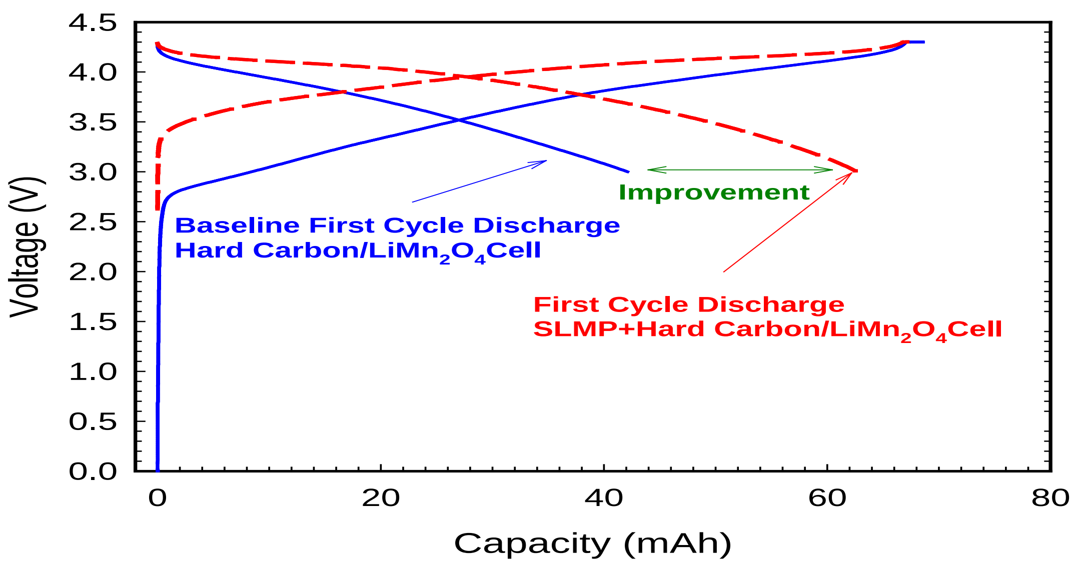

FIGURE . Effect of SLMP on delivered capacity for hard carbon/$LiMn_2O_4$ system

The cell test protocol : constant current charge at 0.25 mA/cm^2 to 4.3 V followed by 7 hours constant voltage charge at 4.3 V and constant current discharge at 0.25 mA/cm^2 to 3.0 V.

Cathode formulation: $LiMn_2O_4$ (90%) + Super P carbon black (5%) + Kynar 761 PVdF (5%). Anode formulation: Carbotron P S(F) (90%) + carbon black (3%) + PVdF (7%). We used Ferro 1M $LiPF_6$ /EC+DEC (1:1) electrolyte.

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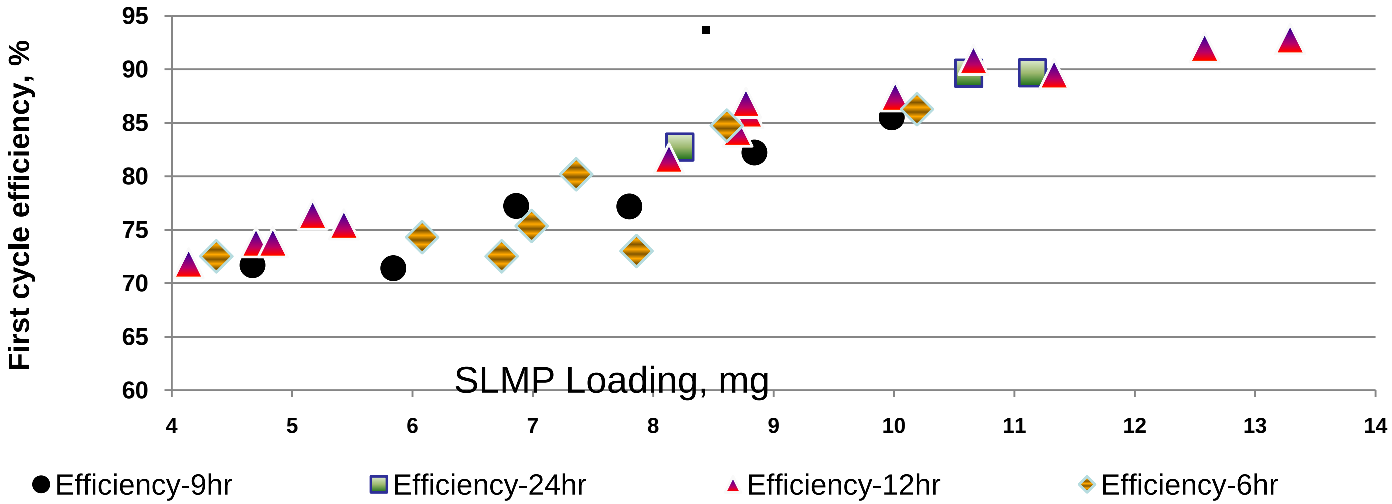
Technical Accomplishments and Progress (3)

Effect of formation time and SLMP loading on the 1st cycle efficiency of hard carbon/$LiMn_2O_4$ system



- 1st cycle efficiency for the baseline cells was about 60%
- Higher SLMP loading for the same conditions yields higher 1st cycle efficiency
- The R-squared statistics indicates that the linear regression as fitted explains 87 % of the variability in the 1st cycle efficiency measured. The highest scatter in data is observed for the 6-hour experimental set (R-squared=64%) and if removed, results in improvement in the R-squared statistics to 93%.

Technical Accomplishments and Progress (4)

Effect of cycling protocol on cycling performance of hard carbon/$LiMn_2O_4$ system

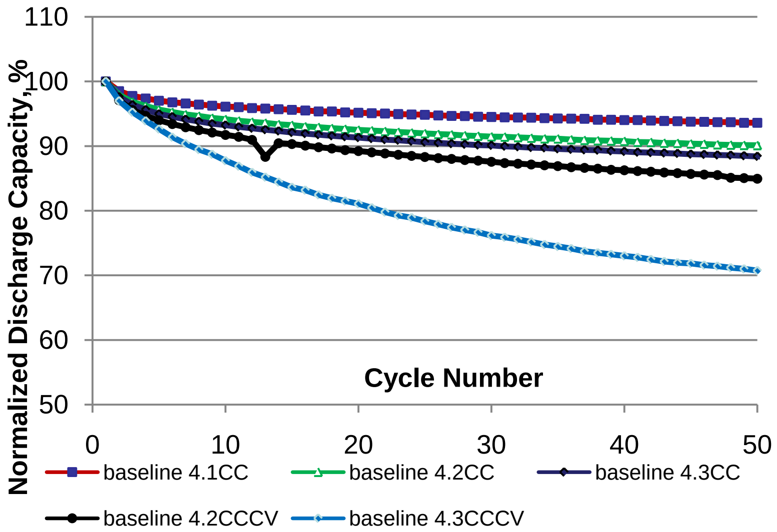


Figure Effect of cycling procedure on the cycling performance of hard carbon /$LiMn_2O_4$ pouch cells

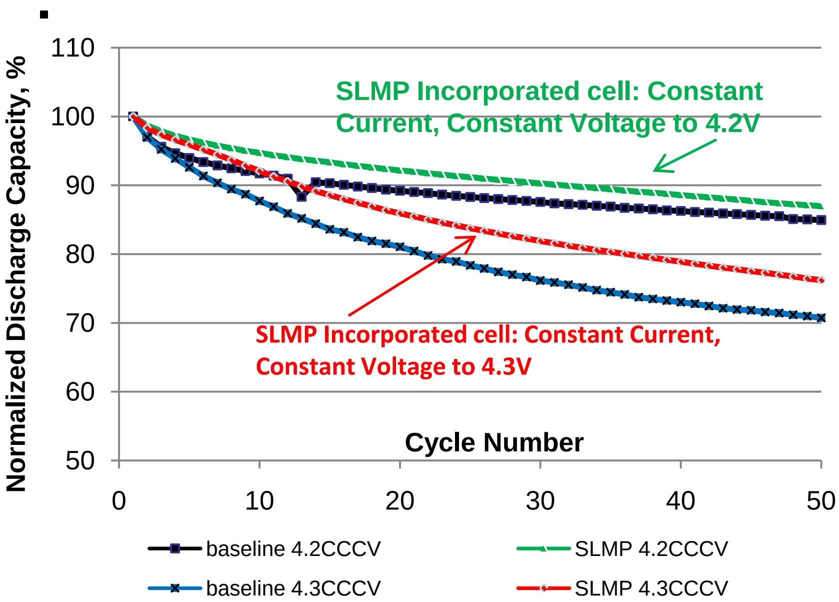


Figure Comparison of the cycling performance of carbon /$LiMn_2O_4$ pouch cells and SLMP-incorporated cells

Technical Accomplishments and Progress (5)

SLMP Lithiation vs. Electrochemical Lithiation

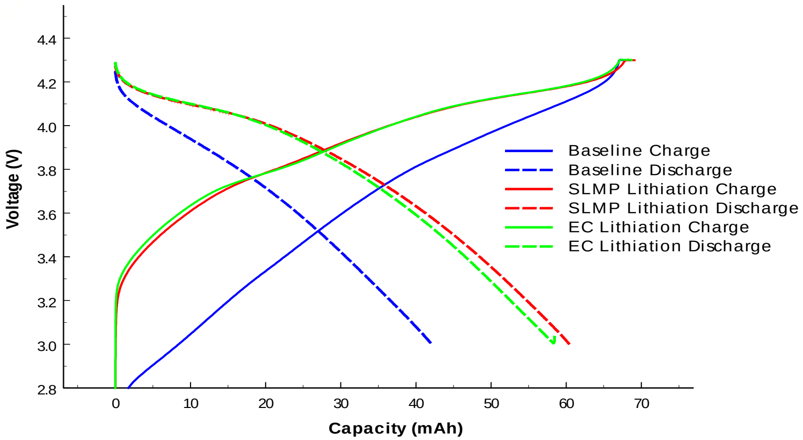


Figure. The capacity-voltage profiles of the 1st cycle for the baseline, SLMP lithiated, and electrochemically lithiated cells.

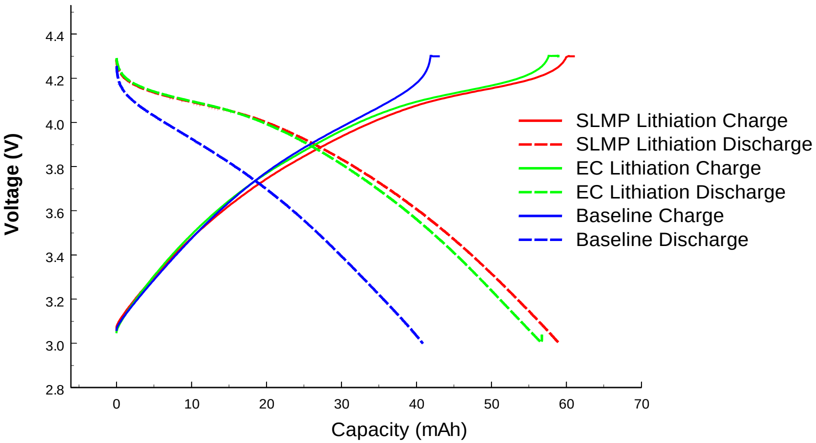


Figure. The capacity-voltage profiles of the 2nd cycle for the baseline, SLMP lithiated, and electrochemically lithiated cells

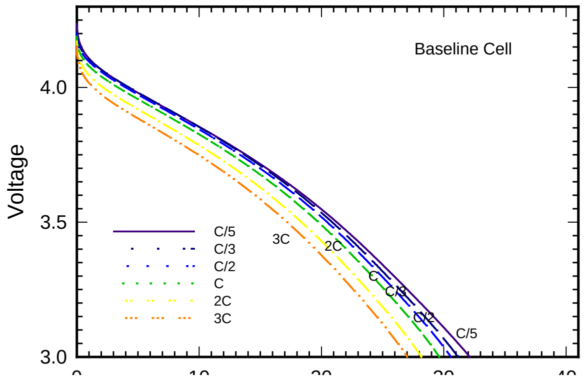
Procedure to construct an electrochemically lithiated cell:

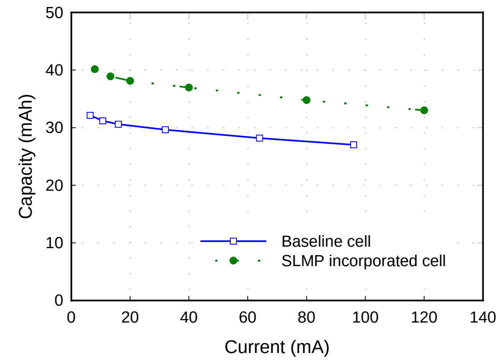
1. Assemble baseline hard carbon / $LiMn_2O_4$ pouch cells with no SLMP added
2. Charge cells to 30 mAh and disassemble to recover the partially charged hard carbon anode (assumption: 3000 mAh/g capacity for SLMP)
3. Assemble new pouch cell using partially lithiated anode and spinel cathode

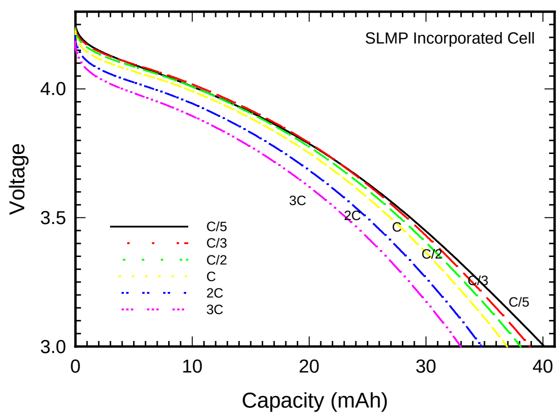
Cycle cells using the following protocol: constant current charge at 0.25 mA/cm^2 to 4.3 V, and then constant voltage charge at 4.3 V; the whole charge process proceeded for about 10 hours followed by a constant current discharge at 0.25 mA/cm^2 to 3.0 V.

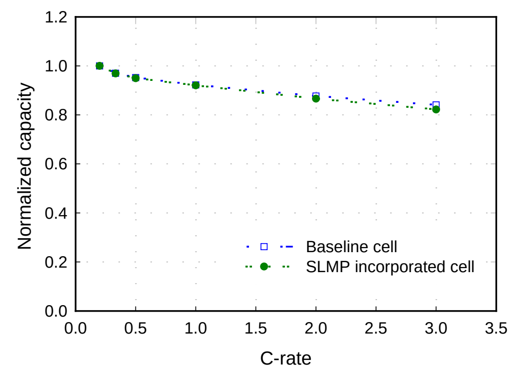
Technical Accomplishments and Progress (6)

Discharge Rate Capability for Hard Carbon/$LiMn_2O_4$ system









rate	C/5	C/3	C/2	C	2C	3C
Baseline cell (mA)	6.4	10.67	16	32	64	96
SLMP cell (mA)	8	13.3	20	40	80	120

Collaboration and Coordination with Other Institutions

- The objective of this project is to expedite development of cost-effective manufacturing processes for SLMP to support high volume production of Li-ion Batteries. This Program is covered under Special Protected Data Statutes (10 CFR 600), provision entitled Rights in Data
- FMC has extensive program outside of this project focused on
  - Educating industry in safe handling of SLMP (http://fmclithium.com)
  - Collaborating with major research institutes and universities
    - Development of non-lithium providing cathodes
    - Enabling advanced anode materials, such as Si/Sn composites and hard carbons
    - Development of the application technologies
  - Engaging in joint development agreements with major Li-ion battery manufacturers
  - Providing technical support, including on-site support
  - Engaging with advanced battery equipment manufacturers: requirements for SLMP application technology development are in line with the advanced manufacturing technologies targeting increase in line yield

Proposed Future Work

Activities for the Year 3 of this Program will be focused on executing all the tasks as described for Objectives #3 and #4/3 in our Program

- Objective 3: Explore the use of pilot scale alternative unit to produce dry SLMP powder directly from battery quality lithium metal. This unit will produce dry SLMP in a continuous manner but as purchased the unit can only run for short durations (3 – 15 minutes). If this “batch” operation is successful, the unit will be redesigned to allow continuous feed of lithium metal and continuous take-off of SLMP. The continuous production process will offer significant cost saving over the current SLMP process.

- Objective 4/3: Integrate SLMP Technology into the Li-ion cell using SiO/$LiCoO_2$ system.

Summary

- We have designed, purchased, installed and commissioned a commercial-scale unit for the production of SLMP dispersion. The experimental program for making SLMP dispersions in the new commercial-scale unit is successfully completed and the optimum dispersion conditions determined.
- The benefits of the SLMP Technology have been demonstrated on the hard carbon/ $LiMn_2O_4$ electrochemical system.
- We have developed procedure using micro-gravure method to uniformly apply SLMP.

Acknowledgement

Key Technical Contributors:

- Scott Petit
- Terry Arnold
- Yangxing Li
- Brian Fitch
- Mike Barr
- Prakash Palepu
- Chris Woltermann

Technical Back-up Slides

(Note: please include this “separator” slide between those to be presented and the “Supplemental” slides.)

Technical Accomplishments and Progress (7)

Cycling Performance of Carbotron PS(F) vs. Li

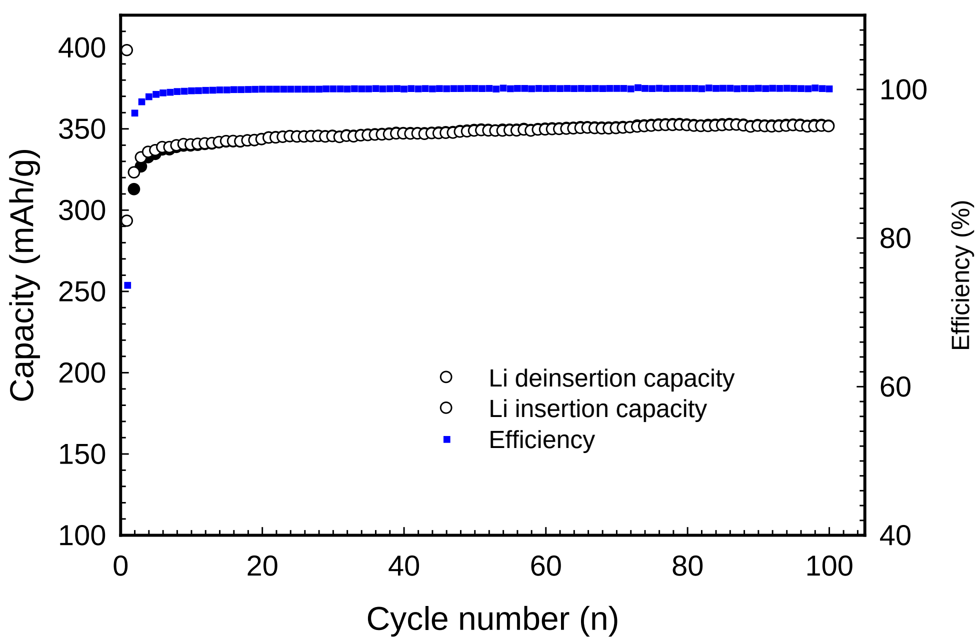


Figure. Cycling performance of hard carbon vs. Li

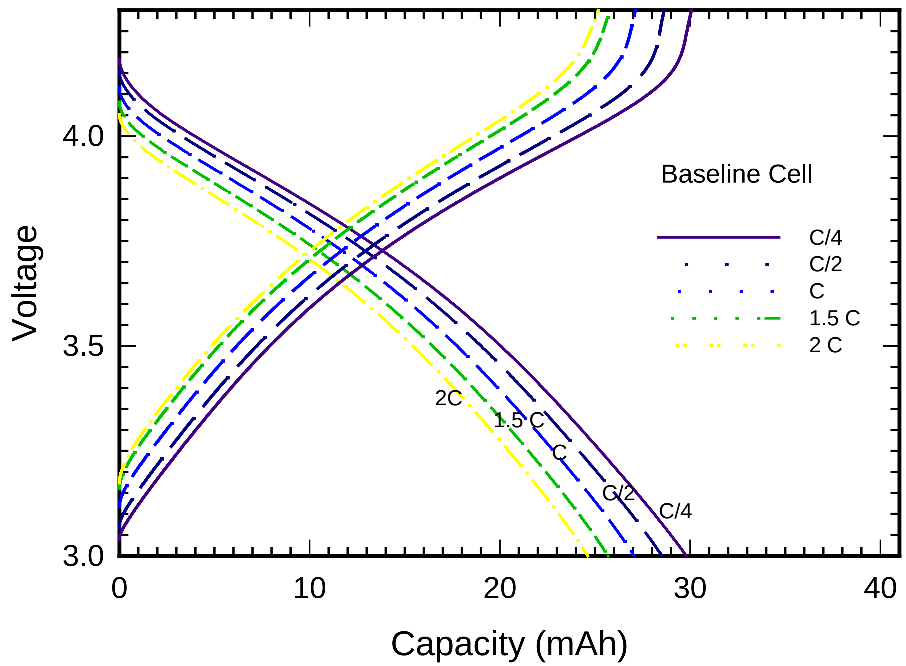
The irreversible capacity for this material was calculated to be ~28%, average charge capacity 291.5 mAh/g, average discharge capacity 403.2 mAh/g

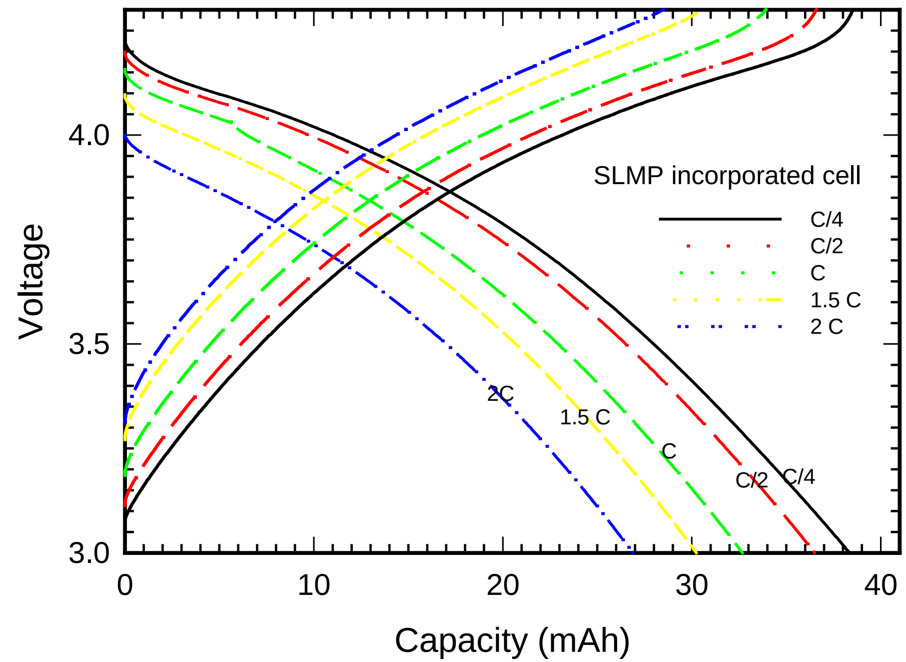
- Carbotron PS(F) was selected as a baseline anode for the demonstration of the SLMP Technology
- Electrode has the following formulation: 90% Carbotron PS(F),, 5% PVdF, 5% Conductive Carbon (Super P)
- The half cell testing protocol:
  - - constant current discharge (lithium insertion) at 0.5 mA/cm^2 to 5 mV,
  - - constant voltage discharge at 5 mV, the CC and CV discharge (total time is 10 hours)
  - - constant current charge (lithium desertion) at 0.5 mA /cm^2 to 2.0 V

Table: Physical/Chemical profile for Carbotron PS(F)

Average particle size	9 µm
True density	1.52 g/cm^3
Specific surface area	5 m^2/g
XRD	d_{002}=0.38 nm
	$L_{c(002)}$=1.1 nm
Ash	Fe< 100 ppm
	Zn< 50 ppm
	Cu< 50 ppm
	Cl< 0.50%

Charge-Discharge Rate Capability

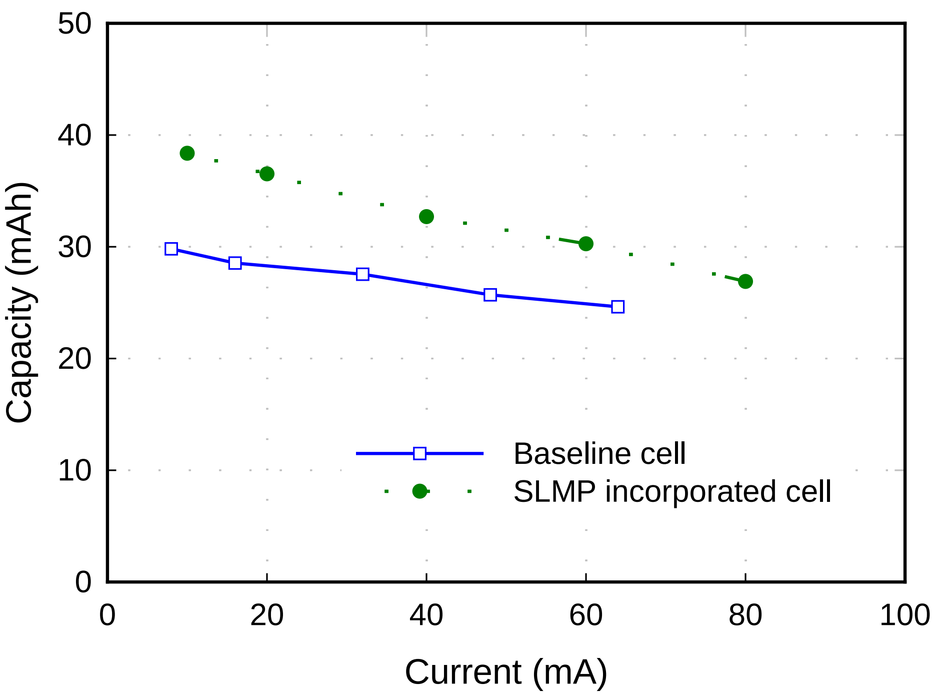


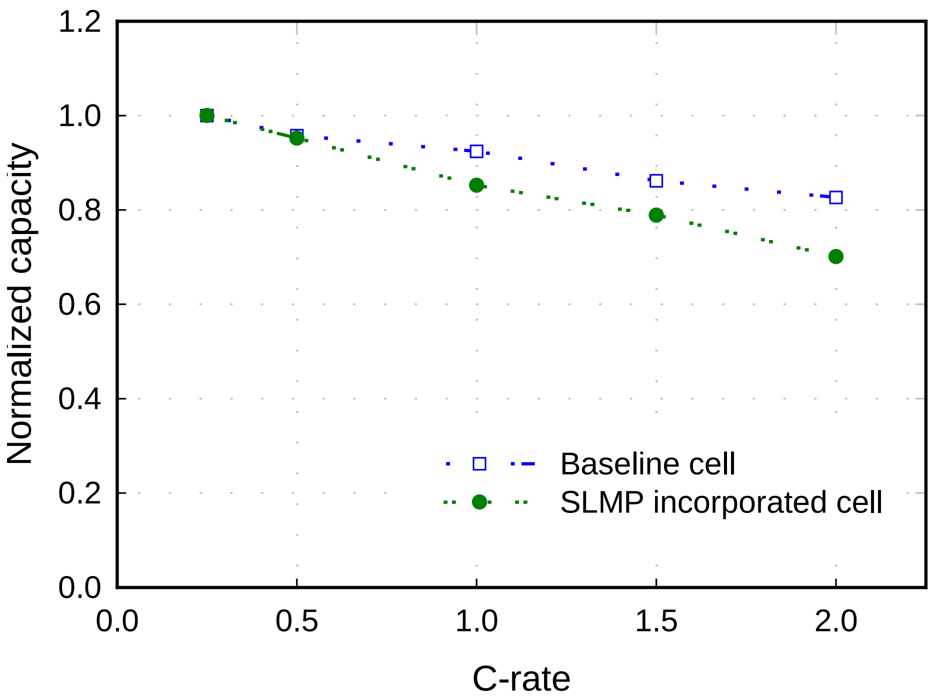


rate	C/4	C/2	C	1.5 C	2C
Baseline cell (mA)	8	16	32	48	64
SLMP cell (mA)	10	20	40	60	80

Charge-Discharge Rate Capability (2)

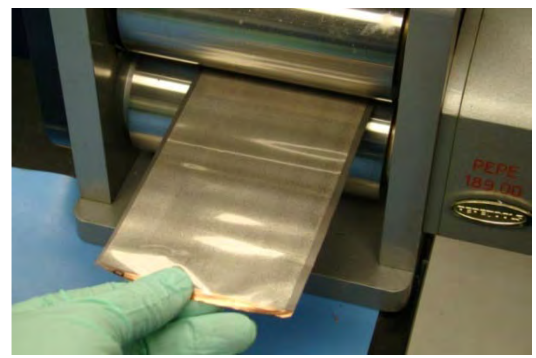
C-rate	C/4	C/2	C	1.5 C	2C
Baseline cell (mA)	8	16	32	48	64
SLMP cell (mA)	10	20	40	60	80





New Way to Incorporate SLMP

Micro Gravure coating method



SLMP can be directly coated onto the pre-fabricated electrode or transferred to electrode surface through a carrier film