2010 DOE Vehicle Technologies Program Review

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

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FMC

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Project ID # ES011

This presentation does not contain any proprietary, confidential, or otherwise restricted information

FMC Lithium

Life begins with Li

Overview

Timeline

- Project start date: May 1st, 2009
- Project end date: April 30th, 2012
- 35% complete:

Budget

- Total project funding
  - DOE share: $2,999,424
  - FMC share: $2,999,425
- Funding received in FY09
  - $470,018
- Funding for FY10
  - $1.4M

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 1 Objectives

FY09-FY10

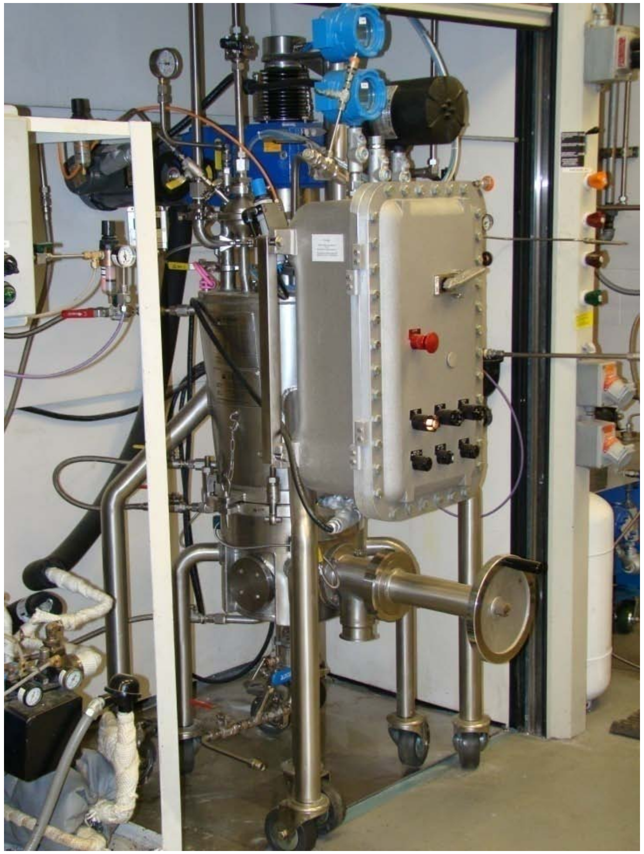
Objective 1

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

Objective 4/1

Integrate SLMP Technology into the MCMB/$LiMn_2O_4$ system

Milestones: Commercial Production of the Dry SLMP



Month/Year	Milestone
5/09	Equipment designed and vendor selected
5/09	AFE written and approved
7/09	Customized design approved
11/09	Location for installation selected and prepared
12/09	Vendor delivered unit
12/09	Safety review of planned Installation completed
1/10	Unit installed and Pre-Start-up Safety review completed
2/10	Trial runs completed
4/10	Experimental runs completed
4/10	Data analyzed/report written

Milestones: Integrate SLMP Technology into the $MCMB/LiMn_2O_4$ system

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

Month/Year	Milestone
3/09	Procured electrode materials
6/09	Conducted half cell evaluation
7/09	Selected vendors
10/09	Evaluated selected materials in the full pouch cell design
11/09	Developed specifications for the matched cathode/anode pair
12/09	Received and evaluated the electrodes from the vendor
3/10	Built baseline pouch cells
3/10	Built SLMP-incorporated pouch cells
4/10	Summarized and presented results at the ECS meeting

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 the possibility of using non-lithiated cathode materials based on vanadium oxides, manganese oxides or metal fluorides now becomes feasible.

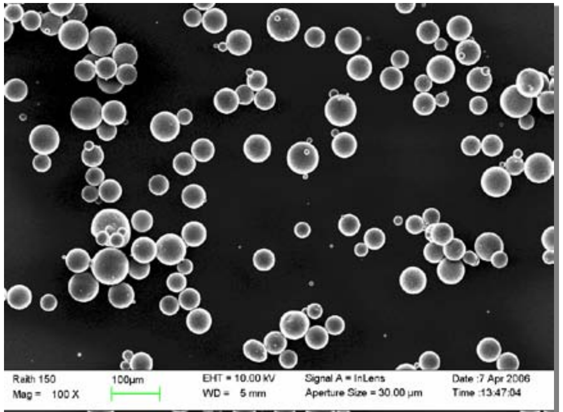
Performance & Cost

- 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

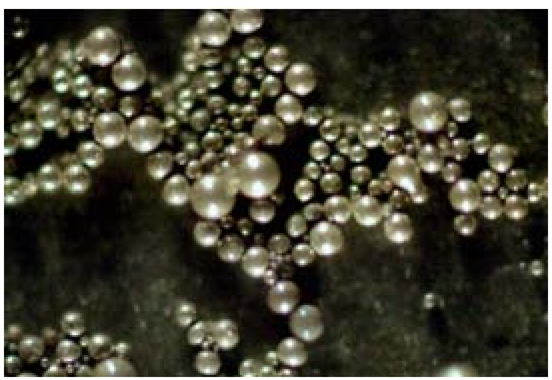
Safety

- 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.

Approach/Strategy



SEM Image of SLMP



Optical Microscope Image of SLMP sprayed on the electrode

- FMC has pioneered a way to use SLMP in Li-ion batteries
  - Developed and patented the route to manufacture
  - Applies coating that significantly reduces the reactivity but still allows Li to react in a controlled manner in the battery system
- Normal lithium powder
  - Can only be handled in an argon filled glove box
  - Not commercially available as powder
- Stabilized Lithium Metal Powder (SLMP ®)
  - Safe to handle in a dry room
  - Can be transported by air or sea
  - Metallic Li content is at least 98%

Technical Accomplishments and Progress (1)

All tasks are completed to meet Objective 1 technical targets. The major challenge was to mitigate 2 months delay in equipment fabrication

- Significant effort was made to identify and select vendors capable of fabricating equipment that meets technical and safety requirements*
- Design and drawings were carefully reviewed and key modifications applied
- Factory Acceptance Testing revealed few items that required correction
- Unit was delivered on December 11th, 2009
- A P&ID (piping and instrumentation drawing) was created to assist the mechanical installation
- Site was prepared for the installation and all safety reviews completed
- A custom vessel to collect the dry SLMP powder as it is discharged from this unit has been designed
- Upon successful completion of the trial runs, full study was initiated and implemented
- Results are reported in the 1Q10 Progress report

*Lithium metal is a flammable solid that reacts violently with moisture to create flammable hydrogen and corrosive lithium hydroxides. Molten metal is especially reactive and given that the auto ignition point is essentially the same as the melting point, can spontaneously ignite in air. The reactivity of lithium increases with temperature and surface area. Therefore, molten metals or dispersions require special care in handling.

Technical Accomplishments and Progress (2)

All tasks are completed to meet Objective 4/1 technical targets.

- The major challenge was to procure electrode materials for this study
- Material from Supplier T was selected and will be used as a cathode material for all electrochemical testing
- Results for half cells are presented below

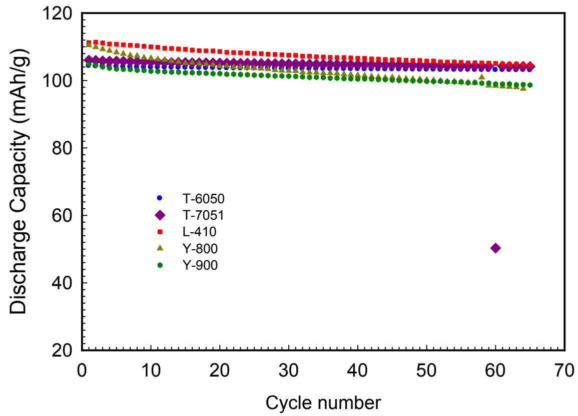


FIGURE 1. Comparison of the cycleability tests results for the $LiMn_2O_4$ materials at room temperature

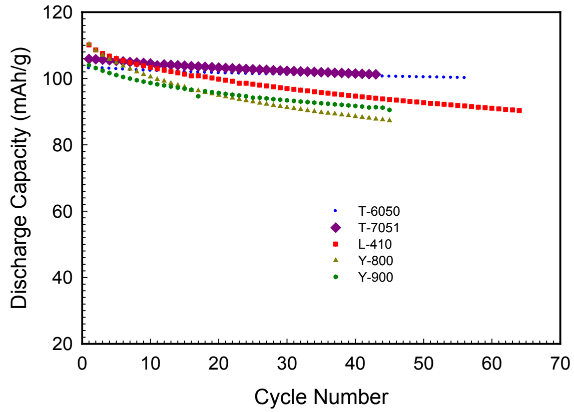


FIGURE 2. Comparison of the cycleability test results for the $LiMn_2O_4$ materials at 60°C

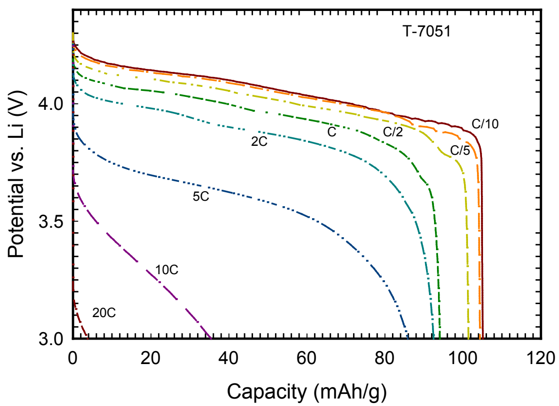


FIGURE 3. Rate capability of $LiMn_2O_4$ from supplier T

The cell test protocol : constant current charge at 0.5 mA/cm^2 to 4.3 V followed by 4 hours constant voltage charge at 4.3 V and constant current discharge at 0.5 mA/cm^2 to 3.0 V.

Electrode composition: $LiMn_2O_4$ (90%) + Super P carbon black (5%) + Kynar 761 PVdF (5%). We used Ferro 1M $LiPF_6$ /EC+DEC (1:1) electrolyte.

Technical Accomplishments and Progress (3)

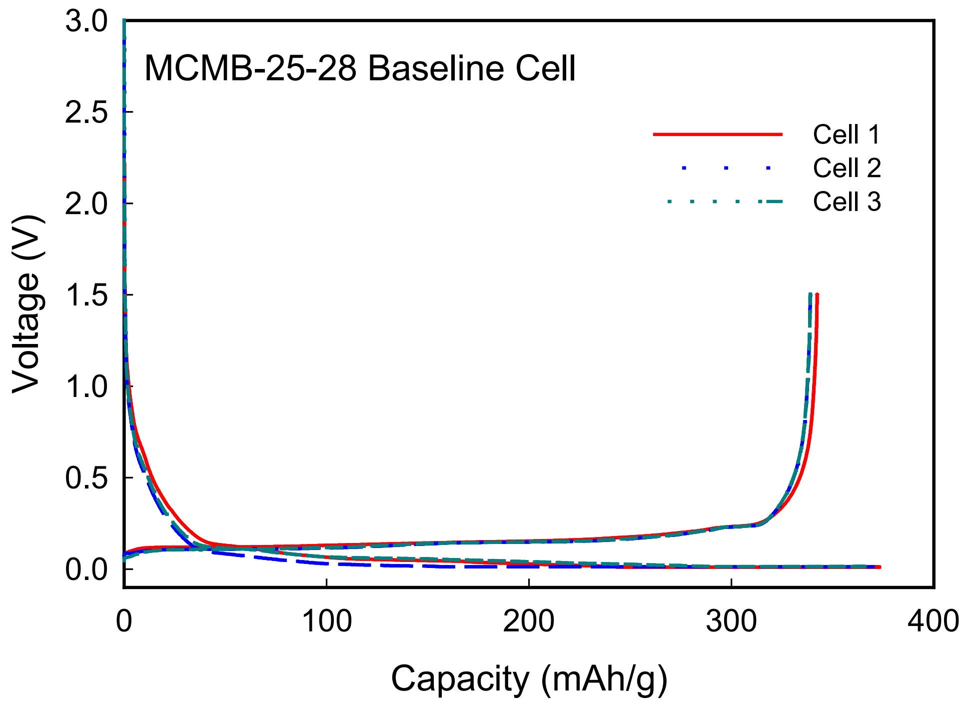


Figure. Voltage profiles for Li/MCMB 25-28 baseline cells

- MCMB 25-28 was selected as a baseline anode for the demonstration of the SLMP Technology
- The slurry containing MCMB has the following formulation: 90% MCMB, 5% PVdF, 5% Conductive Carbon (Super P)
- The cell testing protocol:
  - Discharge: constant current at 0.1 mA/cm^2 to 0.01 V, constant voltage at 0.01 V until the current reaches 0.01 mA/cm^2
  - Charge: constant current at 0.1 mA/cm^2 to 1.5 V

The irreversible capacity for this material was calculated to be ~9%

Technical Accomplishments and Progress (4)

Examples of the performance improvements using full pouch cell design and in-house produced electrodes

- 1st cycle efficiency improved from 82% to 91%
- After 50 cycles, the cell with SLMP incorporated has lost 2% of the initial capacity vs. 15% for the baseline cell
- During the discharge process, the SLMP treated cell shows more capacity delivered at higher voltage than baseline cell, which brings more energy for the battery system. The cell over-potential seems to decrease with the addition of SLMP.
- Cell testing protocol: constant current charge at 0.25 mA/cm^2 to 4.3 V, constant voltage charge at 4.3 V for 7 hours; constant current discharge at 0.25 mA/cm^2 to 3.0 V, 1M $LiPF_6$ /EC+DEC (1:1) from Ferro

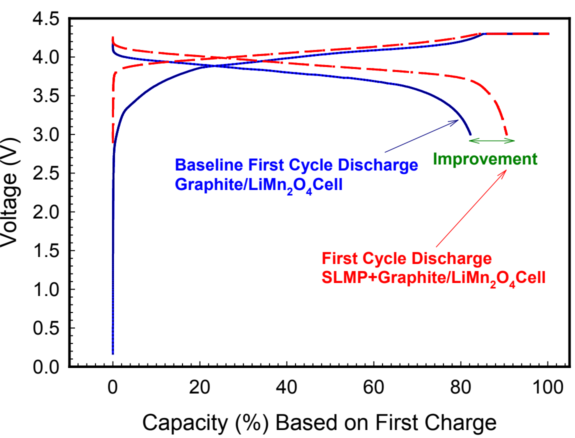


Figure 1. Effect of SLMP on energy increase

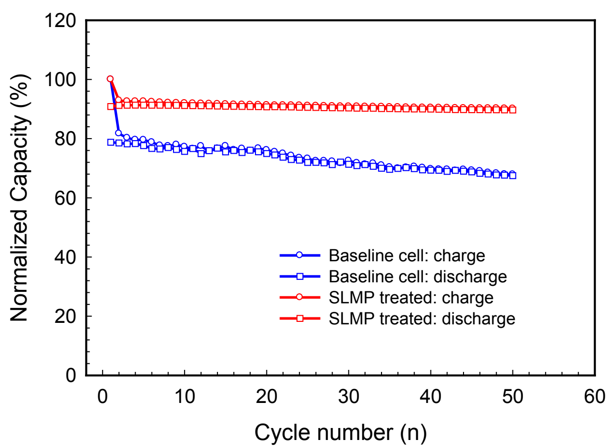


Figure 2. Effect of SLMP on the cycle performance improvement.

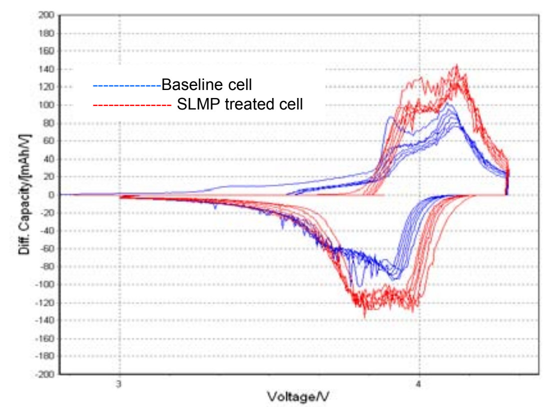


Figure 3. Differential capacity vs. voltage for MCMB/$LiMn_2O_4$ and (SLMP+MCMB)/$LiMn_2O_4$ pouch cells, the plot shows 1st, 10th, 20th, 30th, 40th, 50th cycle's results.

Technical Accomplishments and Progress (5)

Examples of the performance improvements using full pouch cell design and contractor-produced electrodes

- The average delivered discharge capacity has been improved from 66 mAh to 83 mAh, which is 25% increase
- 1st cycle efficiency improved from 75% to 93%
- The results are very consistent

Table 1. The baseline pouch cell results for the 1st cycle.

Cell ID	1st charge capacity (mAh)	1st discharge capacity (mAh)	Columbic efficiency
120309-B1	85.77	64.19	74.84%
120309-B2	85.05	61.95	72.84%
120309-B3	85.40	65.01	76.13%
120309-B4	86.17	66.41	77.07%
120309-B5	86.45	63.47	73.43%
120909-B1	90.42	68.54	75.80%
120909-B2	90.67	66.33	73.15%
120909-B4	89.67	70.58	78.71%
Average	**87.45**	**65.81**	**75.25%**
Standard deviation	2.38	2.79	2.07%
Standard deviation%	2.72%	4.24%	2.75%

Table 2. The SLMP-incorporated pouch cell results for the 1st cycle.

Cell ID	1st charge capacity (mAh)	1st discharge capacity (mAh)	Columbic efficiency
120909-S1	88.56	83.35	94.11%
120909-S2	88.78	79.71	89.78%
120909-S3	89.73	84.07	93.69%
120909-S4	90.01	84.45	93.82%
120909-S5	88.55	82.76	93.46%
Average	**89.13**	**82.87**	**92.97%**
Standard deviation	0.69	1.88	1.80%
Standard deviation%	0.78%	2.27%	1.94%

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

Limited examples of such activities are presented in the supplemental slides

Proposed Future Work

Activities for the Year 2 of this Program will be focused on executing all the tasks as described for the Objectives #2 and #4/2 in our Program and procuring the equipment to support Objective #3 technical targets

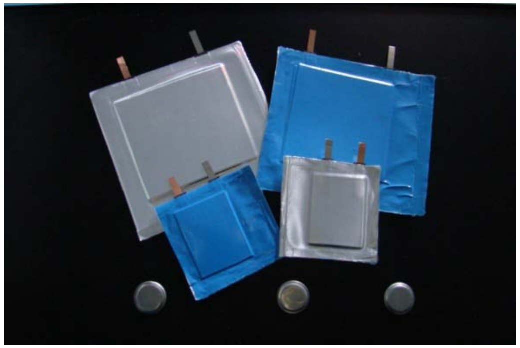
- Objective 2: Develop a process and design commercial unit to scale-up the production of SLMP dispersion in mineral oil. To accomplish this objective we will use our pilot expertise and conduct full factorial design of experiment to establish the operating parameters that will allow us to produce stabilized lithium metal dispersion meeting the requirements of the battery customers.

- Objective 3: Explore the use of pilot scale alternative unit to produce dry SLMP powder directly from battery quality lithium metal. If successful, this will allow streamlining the production process and offering significant cost benefits.

- Objective 4/2: Integrate SLMP Technology into the Li-ion cell using Hard carbon/$LiMn_2O_4$ system. Procure and screen electrode materials to support Objective 4/3.

Summary

- Prototype unit for the commercial production of dry stabilized lithium metal powder was designed, fabricated, tested and used to conduct a design of experiments to determine the process parameters
- In spite of the significant delay in the equipment delivery schedule resulting from the fact that the equipment manufacturers were overwhelmed with orders related to the Prime and sub-recipients of Recovery Act awards, all tasks were completed on time
- Full pouch cell capability was developed
- The benefits of the SLMP Technology have been demonstrated on the electrochemical system MCMB/ $LiMn_2O_4$



Acknowledgement

Key Technical Contributors:

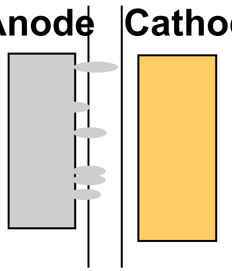
- Brian Fitch
- Yangxing Li
- Terry Arnold
- Scott Petit
- Mike Barr
- Prakash Palepu
- Chris Woltermann

SLMP Technology Background

The Concept

Li metal cell in the 1980s

Anode | Cathode



Metallic Li | MoS_2 or TiS_2

- Li provided by Li foil anode.
- MoS_2 and TiS_2 are abundant materials.
- Simple design.

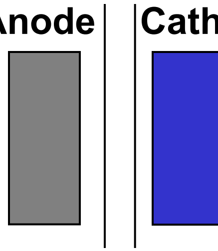
Safety issues with the design:
- Dendrites developed on the Li anode after repeated recharges → internal short-circuit and spontaneous thermal runaway!
- Safer Li-ion technology emerged, and replaced this design

- Li provided by $LiCoO_2$ cathode
- Li stays in graphite when fully charged. No dendrite formation on recharge because it is energetically favorable for Li to stay inside of graphite (host material) than on surface.

Issues
- Current technology reaches maturity.
- Cobalt expensive and price volatile.
- High safety management required (redundant overcharge protection): additional Li coming out of $Li_{0.4}CoO_2$ makes CoO_2 unstable and Li metal plating on graphite – both unsafe conditions.
- Choice of cathode limited.

Li-ion cell

Anode | Cathode



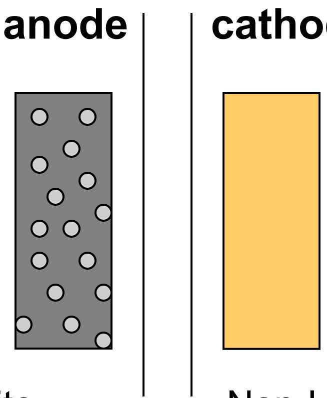
Graphite | $LiCoO_2$

Graphite + $LiCoO_2$ totally discharged.
LiC_6 + $Li_{0.4}CoO_2$ totally charged.

Technology based on SLMP ®

SLMP™ (stabilized lithium metal powder) provides an independent source of lithium into the Li-ion system, enabling many possibilities for energy and performance enhancement.

anode | cathode

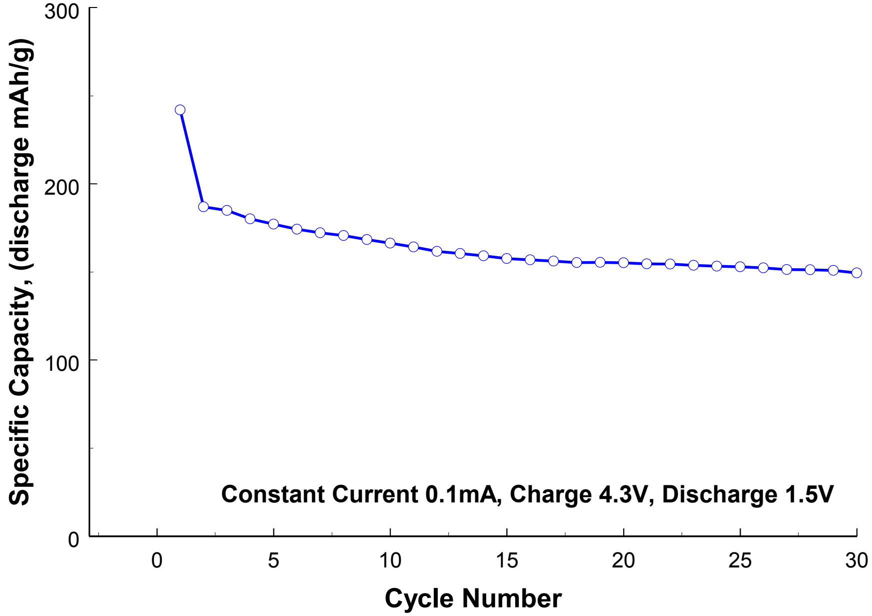


Graphite containing **SLMP** | Non-Li providing compound

Combining the benefits of the past two systems

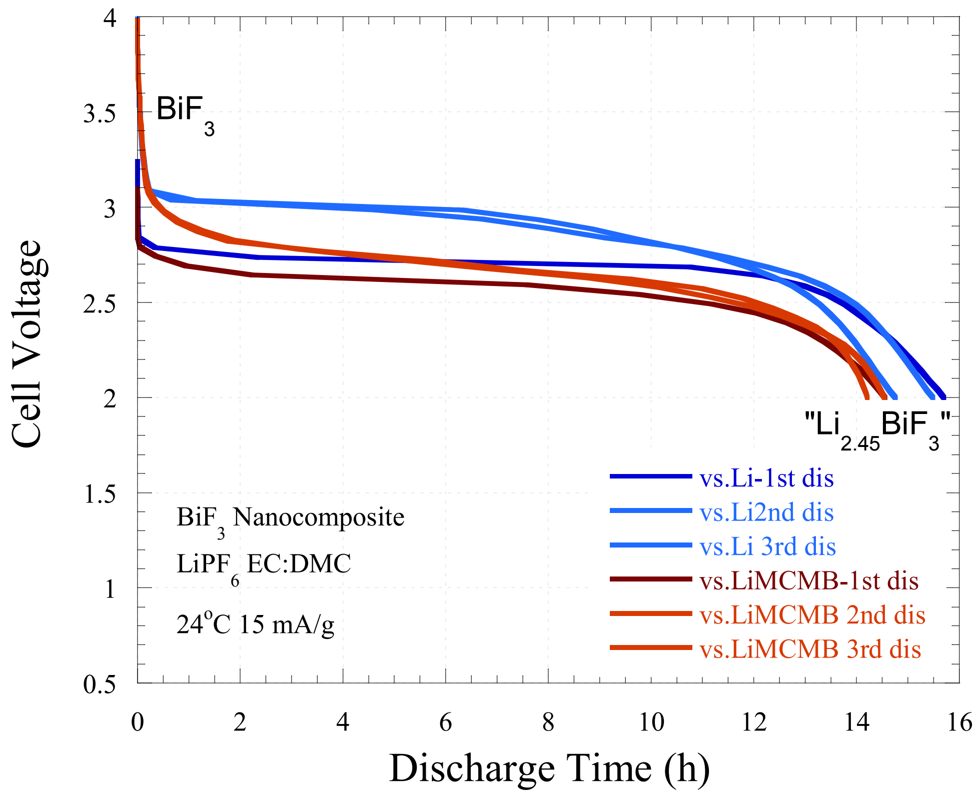
A non-lithium providing cathode is now possible e.g., MnO_2 – lower cost and safer

A Li-ion cell: (Graphite+SLMP) /EMD™



A Cathode Example, BiF_3

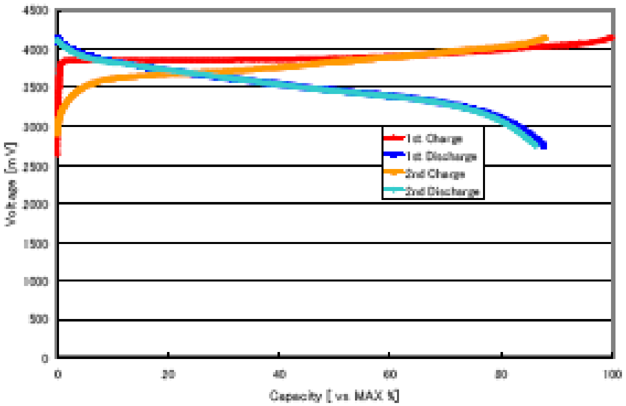
Li-ion cell: (Graphite+SLMP)/ BiF_3 Nanocomposite[TM]



(Data courtesy of Rutgers University)

High capacity anode is now possible

Improvement of 1st efficiency with SLMP™



Anode

Si composite

+ SLMP™ 0.0007g

(Approximate to the equivalent?)

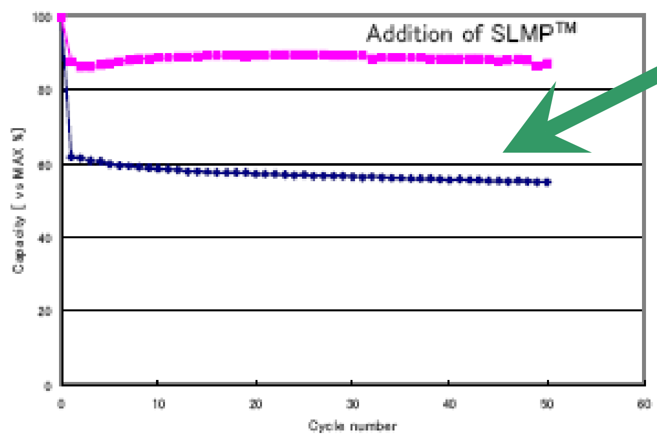
SLMP™ 0.0007g

Charge 0.6mA(4150mV)

Discharge 0.6mA(2750mV)

Electrolyte

$LiPF_6$/EC+DEC

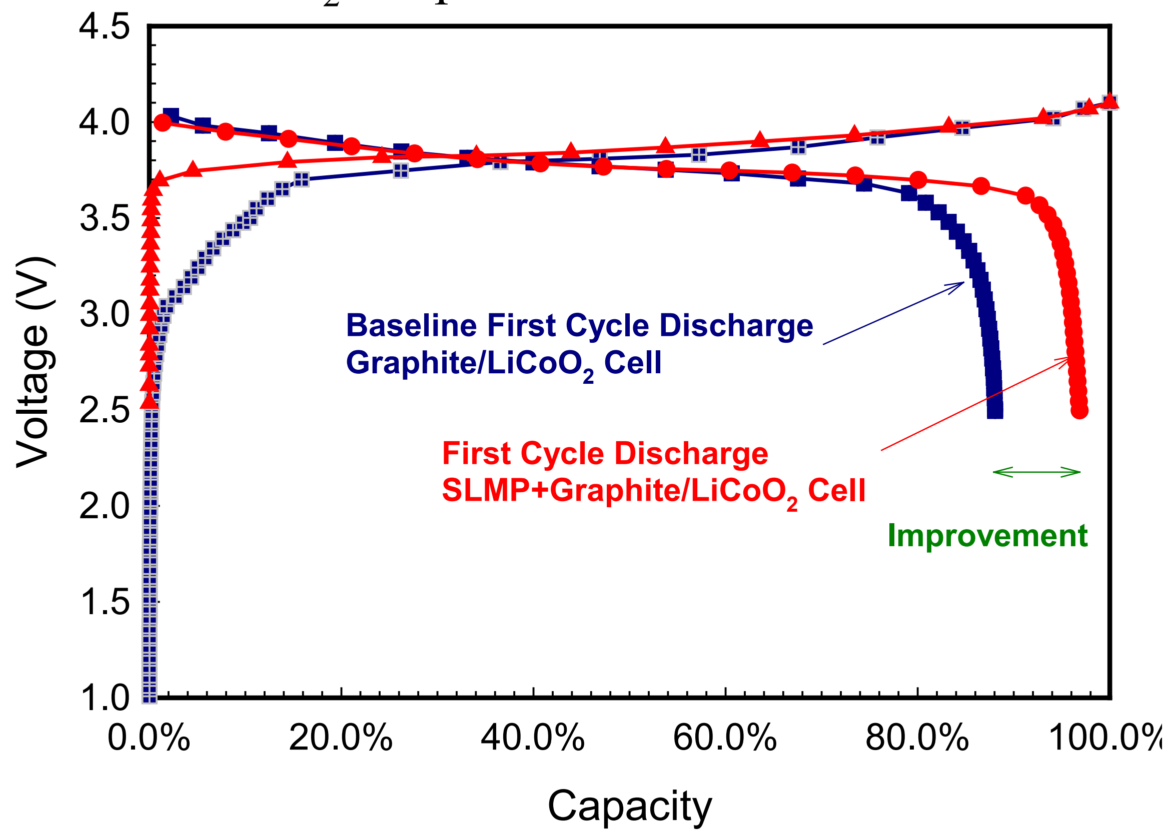


SLMP value

* Data courtesy of Shin Etsu

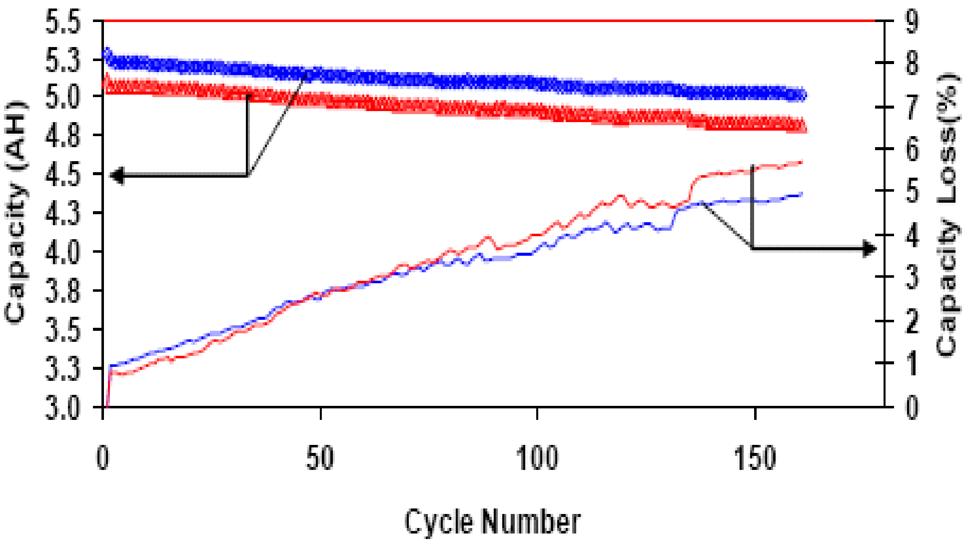
Cell examples

Li-ion cell: $LiCoO_2$/Graphite+SLMP



First Cycle Efficiency Improvement in $LiCoO_2$/Graphite System Using SLMP
(Data courtesy of MaxPower Corporation)

Calendar Life Improvements



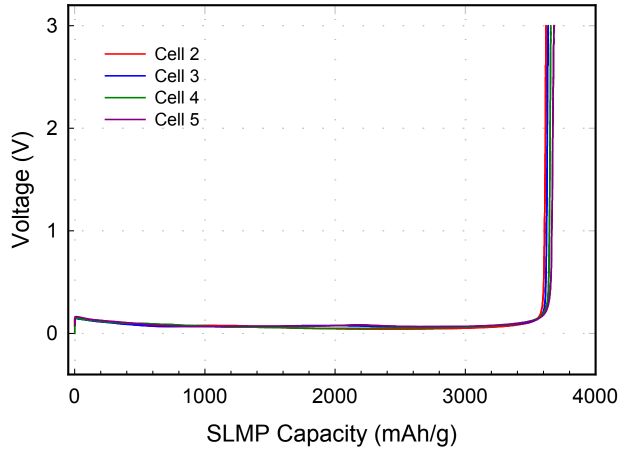
Cycling Performance of the 5Ah cells (a) baseline cell (red line), (b) electrode treated with SLMP (blue line) with the loading of 1.2% of the MCMB weight, C/2 rate, 3-4.2V range.

Important for long calendar life: SLMP serves as a "getter" of moisture and acidic species

(Data courtesy of SKC PowerTech Corporation)

- Method developed to measure reproducibly the active capacity of SLMP – important for battery designers.

- Improved stability of SLMP comes from surface passivation of lithium metal powder.
- Method developed to measure practical capacity of SLMP independently.
- 3625mAh/g can be extracted from SLMP, compared to the theoretical capacity of 3827mAh/g for pure elemental Li. This is 99.8% of what is expected (97% Li metal content).



- Voltage profile for the Li/electrolyte/SLMP + Cu cells

SLMP applied onto Cu foil

After cell test

Lithiation with thin Li foils – a very slow process

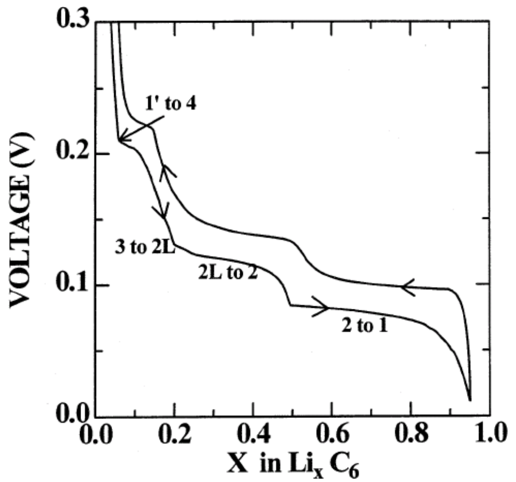
Rolled Li thin foil (<30 micron): micro view

prior to electrolyte addition

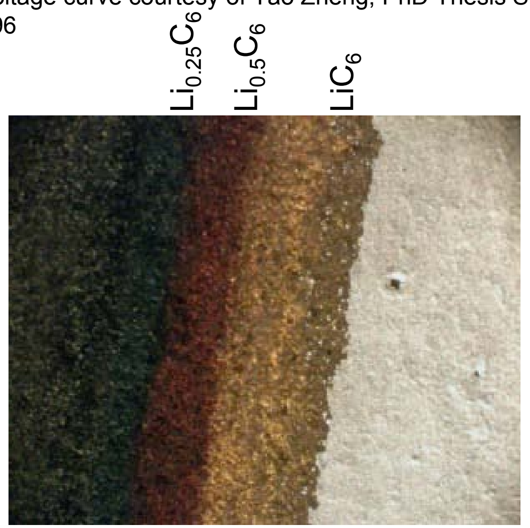
after electrolyte addition, time=1hr

time=1 day

time=7 days



Li/Graphite Voltage curve courtesy of Tao Zheng, PhD Thesis Simon Fraser University 1996



Optical observation of Li staging in graphite. The color bands indicate different Li concentration phases, as Li ions move from the foil attached into the graphite electrode

- The Li concentration inside of the graphite electrode near the foil remains high due to slow Li diffusion in graphite → it takes a long time for Li concentration to equalize due to the distance Li has to travel.
- SLMP provides a localized Li distribution → much faster to reach equilibrium with SLMP treated electrode compared to foil treated one.

Unless you want to wait for days, use SLMP to lithiate your electrode – much faster diffusion

SLMP® Introduction into the Cell

Two general methods to apply SLMP

- Surface application
  - Coat an SLMP suspension on the surface of pre-fabricated anode sheet – no need to change the existing anode fabrication process
- Slurry application
  - Include SLMP in the slurry mix when the anode sheet is being cast – no additional step but the slurry solvent needs to be compatible with lithium

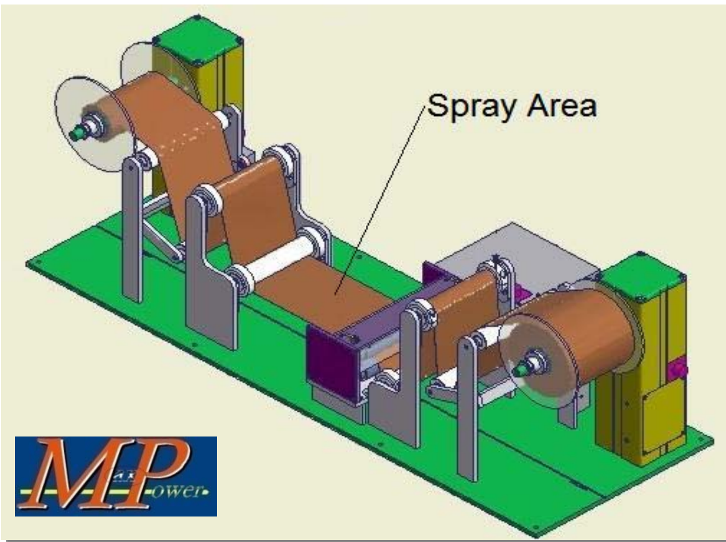
CLEAR

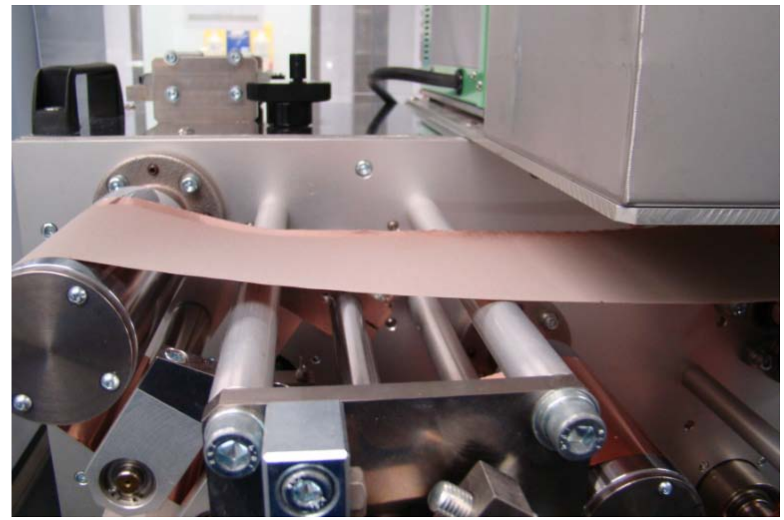
Center for Lithium Energy Advanced Research

- Equipped for demonstration of safe handling of the SLMP Technology
- Equipped for demonstration of multiple SLMP Application Methods using customers" electrodes
- Equipped for making laminated full lithium-ion cells

Spray Application Study-Demonstration (Anode)

Industrially Scalable Processes





- Set-up designed for D-cell production with SLMP® Technology incorporated
- under US Army contract W15P7T-06-C-P242

- Slurry based
- Micro Gravure coating method