Final Report

DOE Contract Award: DE-EE0006868

Dramatically Improve the Safety Performance of Li ion Battery Separators and Reduce the Manufacturing Cost Using Ultraviolet Curing and High Precision Coating Technologies

Miltec UV International

Gary Voelker, Project Director
Dr. John Arnold, Principal Investigator
146 Log Canoe Circle
Stevensville, MD 21666
Phone:410-604-2900; Fax: 410-604-2906
Email: gvoelker@miltec.com, jarnold@miltec.com
Teaming Members:
Celgard
Argonne National Laboratory

Start Date: October 1, 2014
End Date: June 30, 2017

EXECUTIVE SUMMARY

Miltec UV International and its partners, Celgard Inc, and Argonne National Laboratory (ANL) undertook this project to improve the safety of operation of Lithium ion batteries (LIB)and at the same time significantly reduce the manufacturing cost of LIB separators. The project was very successful in demonstrating the improved performance and reduced cost attributed to using UV curable binder and high speed printing technology to place a very thin and precisely controlled ceramic layer on the surface of base separators made of polyolefins such as Polyethylene, Polypropylene and combinations of the two as well as cellulosic base separators.

The underlying need for this new technology is the recently identified potential of fire in large format Lithium ion batteries used in hybrid, plug-in hybrid and electric vehicles. The primary potential cause of battery fire is thermal runaway caused by several different electrical or mechanical mechanisms; such as, overcharge, puncture, overheating, compaction, and internal short circuit. During thermal runaway, the ideal separator prevents ion flow and continues to physically separate the anode from the cathode. If the temperature of the battery gets higher, the separator may melt and partially clog the pores and help prevent ion flows but it also can shrink

which can result in physical contact of the electrodes and accelerate thermal run-away even further.[1]

Ceramic coated separators eliminate many of the problems related to the usage of traditional separators.[2] The ceramic coating provides an electrically insulating layer that retains its physical integrity at high temperature, allows for more efficient thermal heat transfer, helps reduce thermal shrinkage, and inhibits dendrite growth that could create a potential short circuit.

The use of Ultraviolet (UV) chemistry to bind fine ceramic particles on separators is a unique and innovative approach primarily because of the instant curing of the UV curable binder upon exposure to UV light. This significant reduction in drying/curing time significantly reduces the cost of a ceramic coating. Another innovation is high precision, high speed, printing techniques that can apply a unique pattern of ceramic particles on base separators. The pattern will maximize ionic conductivity and minimize ceramic coating weight and thickness, while retaining the benefits of increased puncture strength, reduced thermal shrinkage and no decomposition.

This project has met all of its milestones and has been successfully completed. This completion has enabled Miltec UV to take the final steps leading to the commercialization of an innovative technology that will result in ceramic coated separators that can be manufactured and sold from the U.S., with increased production capacity, reduced cost, and improved battery safety.

ACCOMPLISHMENTS

The objective of this project was to further develop and demonstrate the use of Ultraviolet (UV) curing technology to reduce the cost of manufacturing Lithium ion battery ceramic coated separators by more than 50% while improving the porosity of the ceramic coating and retaining or improving the safety attributes. Previously identified UV curable binders and associated curing technology was shown to reduce the time required to cure separator ceramic coatings from tens of minutes to less than one second. This revolutionary approach results in dramatic increases in process speeds and significantly reduced capital cost, operating cost, and energy consumption. In addition, the use of patterns applied with high speed coating technology coupled with thinner separator bases has the potential to significantly improve the safety performance of ceramic coated separators as well as reduce the cost of separators in a Lithium ion battery.

This project employed an iterative process of technology evaluation, implementation, testing, and resulting optimization. Multiple samples of ceramic coated separators were prepared using a combination of various UV curable binder chemistries and printing patterns. The coated separators were evaluated initially by Celgard LLC and ANL during the first budget period and during the second budget period numerous separator types including PE, PP, UHMWPE and trilayer and cellulosic; some manufactured using wet processes and some using dry processes were coated by Miltec UV and returned to the separator manufacturers for evaluation. The evaluations both at Miltec UV and the separator manufacturers included: shrinkage at elevated temperatures (130C-180C) , Gurley air permeability, and adhesion with tape tests and rub tests to ascertain

---

[1] S.S. Zhang. A review on the separators of liquid electrolyte Li-ion batteries. Journal of Power Sources 164 (10) 351-364 2007

[2] Patent #US 6432586 B1. Z. Zhang. Celgard. 2000

minimal loose particles on the surface of the coated separator. In addition, selected samples were made into cells and tested for performance.

The specific performance goals are shown in the table below.

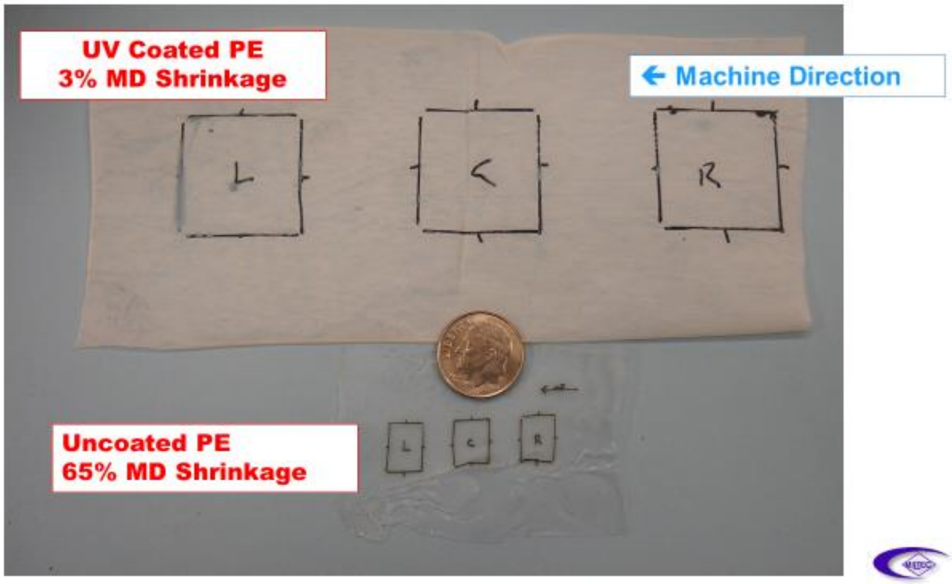
Performance Goals

Base Separator Material	16 µm Trilayer, PP and PE
Ceramic coating thickness and material	4 µm Aluminum Oxide (0.5-1 µm diameter.)
Gurley # (permeability) of coated separator	<10% increase over base uncoated separator
Shrinkage, Trilayer, and PP	MD <5% at 1 h, 150^{o}C TD <3% at 1 h, 150^{o}C
Ceramic coating cost	<\$0.20 /m^{2}
Reduced thickness base separator	6-10 µm

As shown in Figure 1 below, the performance goals related to the use of a UV binder for shrinkage and permeability preservation for PP were all met or exceeded. The interim goal of the projet for PE was designated as 5% at 130C and that value was obtained with the exception of one PE separator of 5 µm thickness. The 5 µm thick separator with a 1 µm thick costing reduced the shrinkage from 24 % to 7.5% at 130C.

	Uncoated		Shrinkage			**Coated**		Shrinkage		
	Thickness, µm	Gurley's	130	150	180	Thickness, µm	Gurley's	130	150	180
PP	16	12	12.50%			6	21	1.10%		
trilayer	20	19	23.10%	29.30%		4	23		0.70%	
PE	14	6.7		40%		3+	9		1.60%	
Cellulose	25	1.4		0%		3+	2.5		0%	
UHMWPE	14	6		55%		4	11	(double sided coating of 2 µm)		4 %
PE	12	8.8	13.80%			1	11.1	2.20%		
PE	5	4.3	24.30%			1	5.9	7.50%		

Figure 1. Demonstrated Results



UV Ceramic Coated 16 µm PE Separator barely shrinks after 0.5 hour @ 180°C.

One goal of the project was to investigate the use of electron beam radiation treatment of a very thin (6 to 10 µm) PE or PP to improve physical strength by causing crosslinking of the polymers. It was learned that EB treatment did not adequately improve the strength of either dry process PE or PP after numerous attempts with different treatment intensities and durations. In November, 2015 Miltec UV had a Go-NoGo Decision meeting with the DOE on all elements of the project. Based on past success, the EB work was judged as a No-Go and removed from continued funding.

SUMMARY of SPECIFIC PROJECT ACTIVITIES

The specific milestones for the project are shown below in the contract milestone chart. All milestones were successfully completed. Following is a summary of the specific activities achieved by budget period.

Milestone	**Planned Completion Date**	**Status**
Budget Period 1		
Complete Project Management Plan	10/16/2014	complete
Complete UV curable binder characterization	12/15/2014	complete
Complete UV Curable Binder formulation corrected for printing applications	03/15/2015	complete

Complete Printing Pattern Characterization	06/24/2015	complete
Separator Coating Laboratory Testing Complete	08/24/2015	complete
Complete Coated Separator Electrochemical Evaluation (Go/No-Go)	09/30/2015	complete
Budget Period 2		
Complete Initial Printing Press application Validation Tests	12/15/2015	complete
Initiate Purchase of Commercial Scale Press	03/18/2016	complete
Complete Press Design	06/24/2016	complete
Begin Press Shakedown	09/26/2016	complete
Complete Final Printing Press Tests	06/26/2017	complete
Complete Cost Model	12/10/2016	complete
Complete Cost Reduction Analysis	03/12/2017	complete

During the first budget period the iterative testing was done first with hand drawn samples and then using a Laboratory Bench Coater (LBC), Figure 2. The LBC is a reel to reel system capable of coating and UV curing 120mm wide material using a specially designed coater capable of coating from .5 – 4+ microns thickness. Mixing techniques applicable to solvent-free slurries that ensure homogeneous mixing and viscosities compatible with high speed coating techniques were developed along with separator coating techniques.

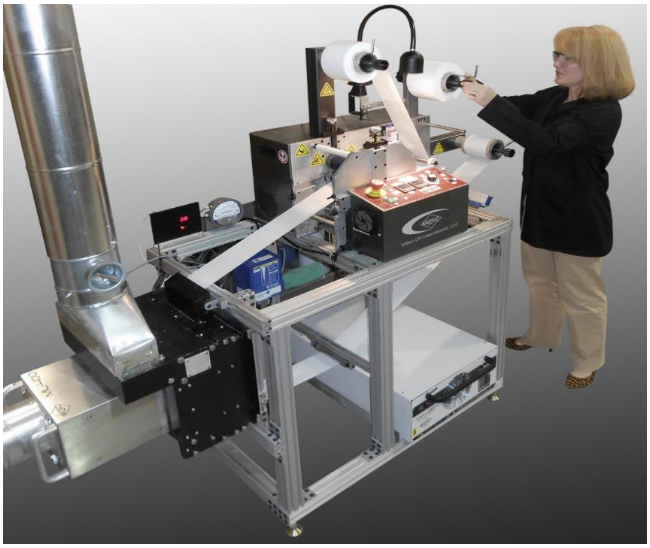


Figure 2. Laboratory Bench Coater (LBC)

- Flexo coater with reel to reel control, single UV lamp, 120mm width and 100 fpm capability
- Developed UV coatings for PE, PP, UHMWPE, cellulosic, and Trilayer separators with <5% shrinkage at 150^{o}C and Gurley increases ≤ 10%. Similar results at 180^{o}C with Trilayer
- Printed patterned coatings for reduced vehicle weight and higher ion flow, while maintaining shrinkage <5% at 150^{o}C and 180^{o}C

During the second budget period the hand drawn and LBC sample preparation continued and provided the design parameters for a commercial scale coater/ UV curing system. The commercial scale coater/UV curing system called the CX400 was designed specifically to handle super thin polyolefin separator material with superior web handling, edge control, tension control and high speed precision coating. The CX400 was designed to handle 440 mm wide separator material and operate at 400 fpm and 10 micron separator material. Miltec has successfully coated 5 micron thick separator material on the CX400. The CX400 has minimum unsupported web and a chill drum to achieve precise tension and separator temperature control.

- Designed to reduce tension-stress issues:
    - Large rolls
    - No stress due to heat or UV curing (chill drum)
- Web fully supported from nip to coating, drying, curing, rewind to eliminate unsupported web stress
- Designed for 10 µm polyolefin (successfully handled 5 µm separator)
- Small footprint offers maximum manufacturing flexibility.
- Precise thickness control (<1 µm)

Figure 3. Commercial scale coater, CX 400

RESULTS and PRODUCTS DEVELOPED

Publications

Miltec UV made various public releases of results during the period of performance of the contract. These include:

- Presentations at each of the DOE Annual Merit Reviews sponsored by the Vehicle Technology Office in June of 2015,2016, and 2017.
- Gary Voelker and Dr. John Arnold gave a presentation on the merits of UV binder for ceramic coated separators to the DOE USCAR representatives from Ford, Chrysler, GM and EPRI in Detroit May 17, 2017
- Miltec UV had an exhibit with visuals and a video presenting the progress on UV binder for ceramic coated separators at the International Battery Conference, Fort Lauderdale, FL in March 2017.
- Dr. John Arnold gave a presentation titled *UV Coating Processes to Enhance Li Ion Battery Performance and Reduce Costs* to the Electrochemical Society meeting at National Harbor Fall 2017.
- Miltec UV had an exhibit with visuals and a video presenting the progress on UV binder for ceramic coated separators at Battery Show,Novi, MI September 2017.

Web Site

Miltec UV has a fully operating website presenting details on the performance and potential for ceramic coated separators. http://www.miltec.com/technology/battery/uv-ceramic-coated-separators/

Networks or collaborations fostered

The Miltec business model for commercialization of the use of UV curable binder for ceramic coated separators is for Miltec UV to sell coating and UV curing equipment based on the design of the prototype unit the CX400 developed under this contract and to either sell the UV curable binder or license the formulation chemistry to potential customers. In pursuit of this business model Miltec UV fostered multiple collaborations during the course of the contract. These collaborations were primarily with separator manufacturers who provided Miltec with rolls of their separator material which Miltec coated with ceramic coatings (primarily alumina of different characteristics) using the CX400. The coatings were of different thicknesses and some desired coating on one side and others were costed on both sides. These approximately five collaborations are continuing and involve multiple separator manufacturers in the United States and Asia. In addition, Miltec is collaborating with Lithium ion battery manufacturers that are considering internalizing the coating of separators in lieu of buying coated separators.

Inventions

Miltec UV Patent 9,680,143 covering the invention of using a UV curable binder for adhering a ceramic coating on a separator for a Lithium ion Battery was filed before project award October 2014 and was granted June 13, 2017.

UV Ceramic Coated Separator

Miltec successfully used the commercial scale CX400 to coat and UV cure a 2 um thick ceramic coating on both sides of a potential customers UHMWPE (14 um thick) separator film. Most importantly the uncoated separator had a shrinkage of 55 % at 150oC and the ceramic coated separator shrunk less than 5 % after 10 minutes at 180C. The High Pressure Gurley for the uncoated material was 6 s and the coated Gurley's were 11 s. A total of 1000 meter of coated separator was delivered to the potential customer. At the conclusion of the DOE contract Miltec was preparing a budgetary cost estimate for a machine(s) for the potential customer.

Conventional ceramic coated separators available today are typically made with water based solvent and roll or dip or gravure coaters. Slow process speeds compared to UV curing and lengthy drying ovens accompany today’s conventional technology. The printing technology chosen by Miltec provides both high speed and very precise coating thickness control (± 1 µm) .

Printing inks are typically applied in a thickness range of 1 to 5 µm. The precision of the placing of graphics or text is taken for granted. Precision of all printing methods are beyond the edge accuracy of any roll coater or slot die coater. Thickness control is equally precise. A change of 0.1 µm thickness will change the color of the print from one edge of the sheet to the other side. Such errors are unacceptable in the printing industry. Commercial label printing (200-400 feet per minute) and newspaper printing run faster (over 1000 feet per minute) than current separator coatings.

Besides preventing or reducing thermal shrinkage, other advantages have been realized for ceramic coated separators (Figure 4). One, improved long term capacity retention; which is believed to be related to a process where the aluminum oxide particles in the ceramic coating provide a place for electrolyte decomposition products to deposit. Since these decomposition products are coating the separator, they do not end up coating the anode. It is dangerous for these decomposition products to coat the anode. Decomposition products reduce the anode capacity, and unbalances the battery. Any foreign deposits on the anode limit the amount of lithium that the anode can absorb (intercalate). If the lithium coming off the cathode cannot go inside the reduced area (partially coated) anode, then the excess lithium is likely to electroplate lithium metal on the outside of the anode, leading to the growth of lithium metal dendrites. Not only can the dendrites puncture the fragile separator; with continued growth, they can create an explosive conductive path between the anode and the cathode.

All Ceramic Coated Separators

- **Reduce shrinkage**
- **Increase toughness**
- **Reduce dendrite growth/penetration**
- **Improve Long Term Cycling Capacity (by scavenging by products before landing on anode area)**
- **Impede Thermal Runaway**

UV Ceramic coated Separators

- **Do not appreciably reduce porosity**

Figure 4. Safety reasons for using ceramic coated separators and additional reasons for considering a UV ceramic coated separator.

The thermoset property of crosslinked UV binders gives them higher temperature resistance and greater chemical and oxidation resistance. We believe these properties lead to greater voltage stability and oxidation resistance from electrolyte degradation products. Figure 5 shows a 4.8 V cell with excellent cycling stability.

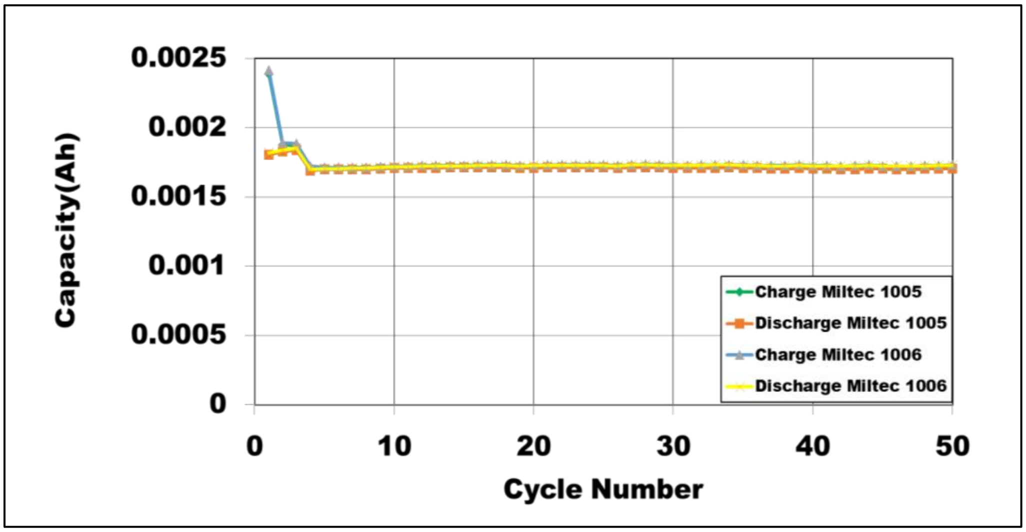


Figure 5. Shows cycling data for a couple Li(Mn1.5Ni0.5O_4)-LTO, cells. This is a 4.8V cell with a UV ceramic coated separator. Data from Argonne National Laboratory.

Pattern Printed UV Ceramic Coatings

Mimicking the known electrode coating process, the original ceramic coatings were applied with a slot die coater and solvent based chemistry. As coatings became thinner and greater control was needed other methods like roll coating and gravure coating processes gained popularity. As an additional process advancement we incorporated the flexographic process (Figure 6) with our UV process. UV will work with roll and all forms of gravure, but there are advantages to the flexographic process.

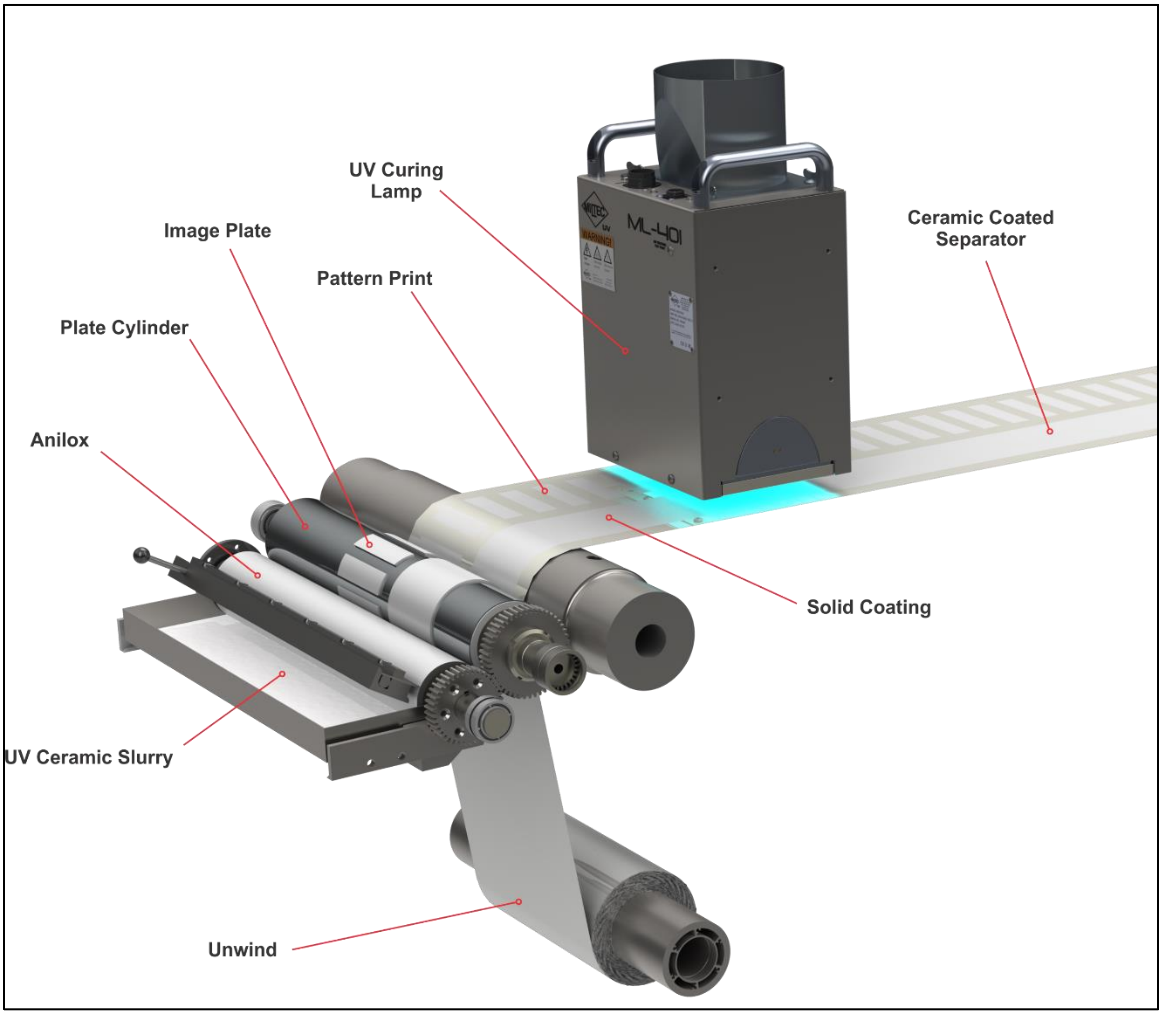


Figure 6. In the flexographic process, the anilox meters the coating to the image plate which like a rubber stamp transfers the image to the separator. As shown, the left side is printing a pattern and the right side is printing a continuous coating.

There are many advantages to the flexographic process. Although we introduced the flexographic process to the separator industry, this is the main printing process for the printing of labels in the United States. Product labels contain far more spectacular and hidden features than other types of print. The accuracy of the flexographic process far exceeds that of the separator industry. Note the separator film does not go through a bath, when the press starts and stops the plate cylinder engages and disengages the film. This makes film and coating change overs, cleaning, and many other processes quick and easy.

Besides introducing the concept of flexographic printing to the separator industry, we introduced the concept of printing ceramic patterns instead of the conventional solid coatings. The primary advantage of the patterned ceramic coating is that it allows more ion flow than the solid coating, while providing less shrinkage and more insulation than that of the uncoated separator. Many patterns were printed and tested for shrinkage. The pattern shown in Figure 7 where the cross hatch is line with the MD and TD directions of the roll was most effective at reducing shrinkage. Besides the advantage of ion flow and shrinkage reduction, there is 39% reduction in coating weight for the pattern shown in Figure 7 versus that of a solid coating.

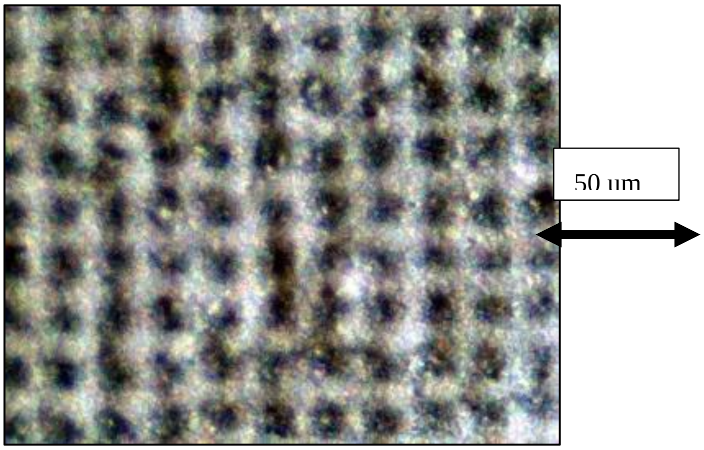


Figure 7. Image of UV ceramic coated separator. The white ridges are the rigid coating that inhibits thermal shrinkage and holes allow more ion flow.

When we initially proposed the idea of pattern coatings, the only possible objection we heard was that the differential ion flux through the separator might lead to dendrite growth. We felt this was an unfounded concern, as all separators have a differential ion flux. A patterned coated separator adds tortuosity and so it should not have this problem.

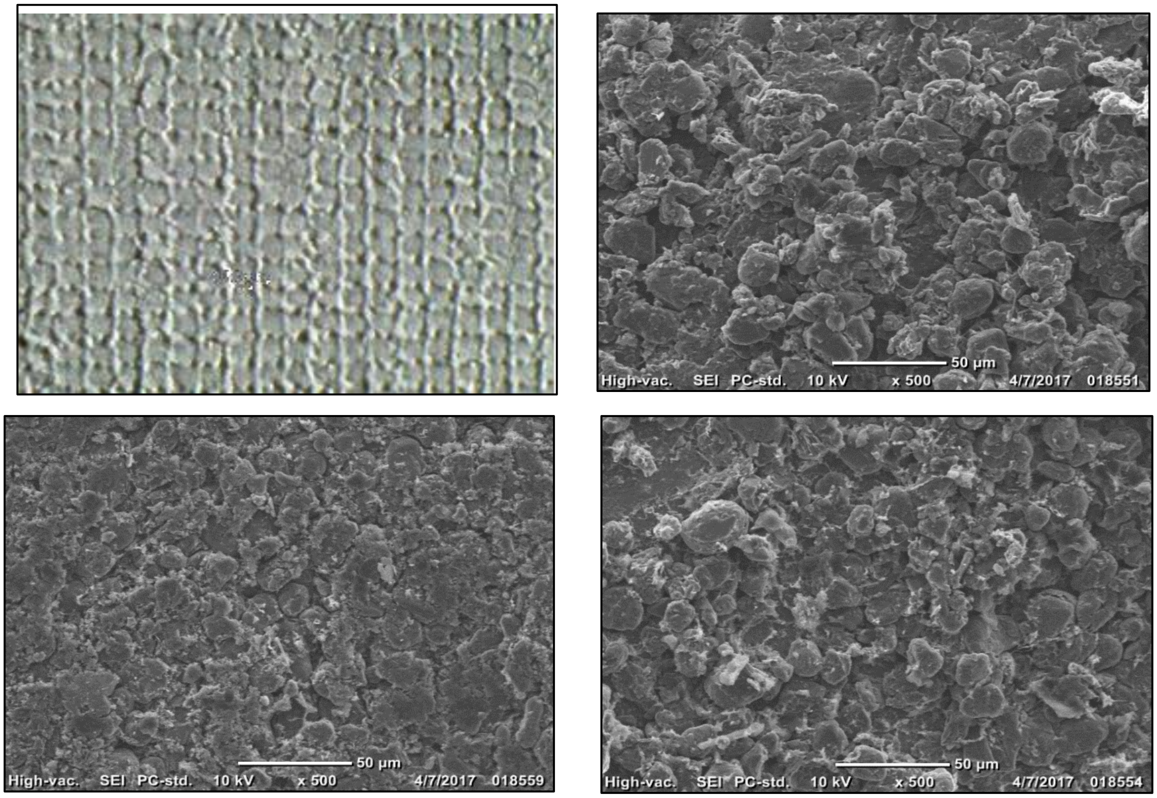


Figure 8. Deeply lithiated graphite anode shows no mirror pattern of patterned coated separator. 10 x 10 Pattern Coated separator (upper left). Lithiated anodes with uncoated separator (upper right), solid coated separator (lower right), and pattern coated separator (lower left).

So, we created full cells that would create dendrites to test this theory. Coin cells were constructed of a lithium-metal cathode and a graphite anode. This provides an infinite source of lithium to create dendrites. After 300 cycles dendrites clearly grew. However, the dentrite growth showed no mirror pattern of the printed separator nor was there difference between the anodes for the uncoated and coated separators (Figure 8). Therefore, we conclude that pattern printed ceramic coatings on separators do not lead to dendrite growth.

UV Extreme Temperature Coatings to protect against fire in nail penetration test

A well-known battery safety test is the nail penetration test. It is a dangerous test. Basically, a nail is driven into the battery. The bigger the battery, the more dangerous the test. There are many aspects to this test, but since we are coating separators, we wanted to see what could be done with a separator coating to help a battery pass this test. For this we developed the Miltec solder gun separator test.

Instead of a nail, we penetrate the separator with a 335^{o}C soldering gun. Details are shown in Figure 9. So there is enough time for reproducibility, we push the soldering gun though the separator so the 5-mm barrel of the gun goes through the separator—the barrel of the gun is a uniform 5-mm, unlike the solder tip which is a cone.

We mounted the soldering gun on a drill press, so we could precisely push the soldering gun to the same depth (10 mm) each time. We hold it there for 5 seconds. There is less sample to sample error in 5 seconds than 1 second push. The drill press safely moves the soldering gun along the same vertical path and to the same depth every time.

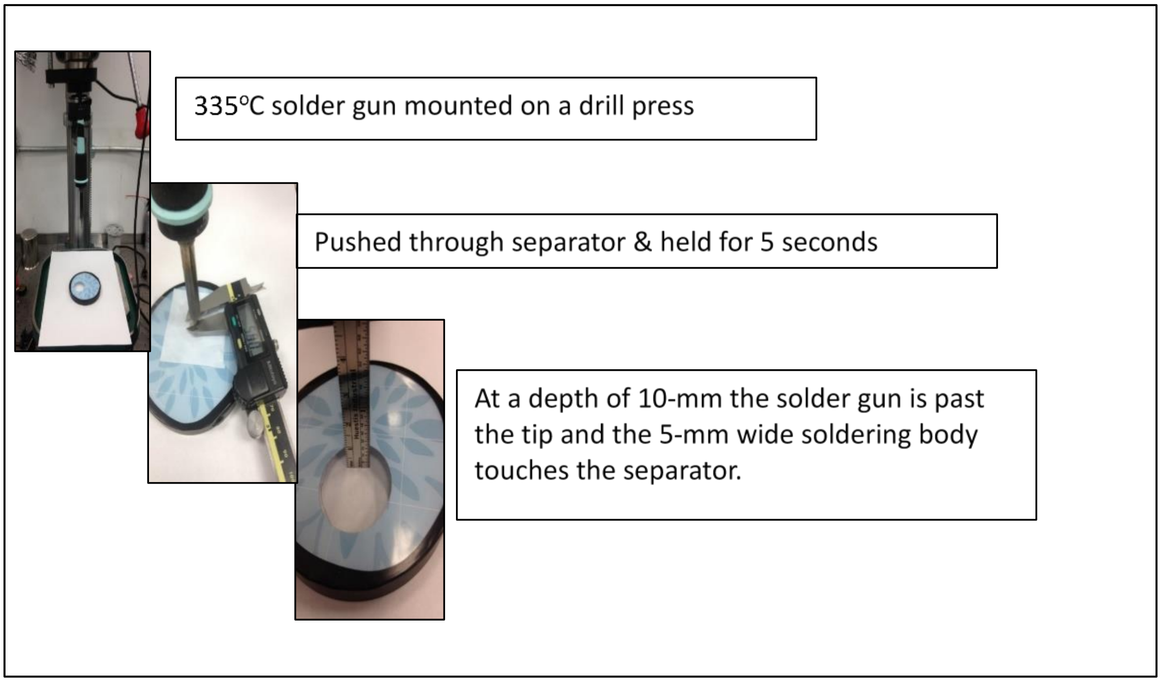


Figure 9. To simulate what happens to the separator in a nail penetration test, we poke the separator with the 5-mm diameter hot body of the soldering gun—not just the tip.

After removing the soldering gun, we measure the diameter of the hole. Remember the diameter of the hole 5-mm.

Solder Gun Separator Test Results When we tested the uncoated 16 um PP separator, the resulting hole is 11.0 mm. As expected, the PP separator shrinks away from the soldering gun. If we put UV ceramic coating on one side of the sheet, we can reduce the size of the hole, if we put a UV ceramic coating on both sides of the sheet, we further reduced the size of hole (See Table I). We developed a proprietary extremely heat resistant UV ceramic coating that reduces the shrinkage to the size of the soldering gun barrel. This heat resistant coating works on all polyolefin separators (Figure 10).

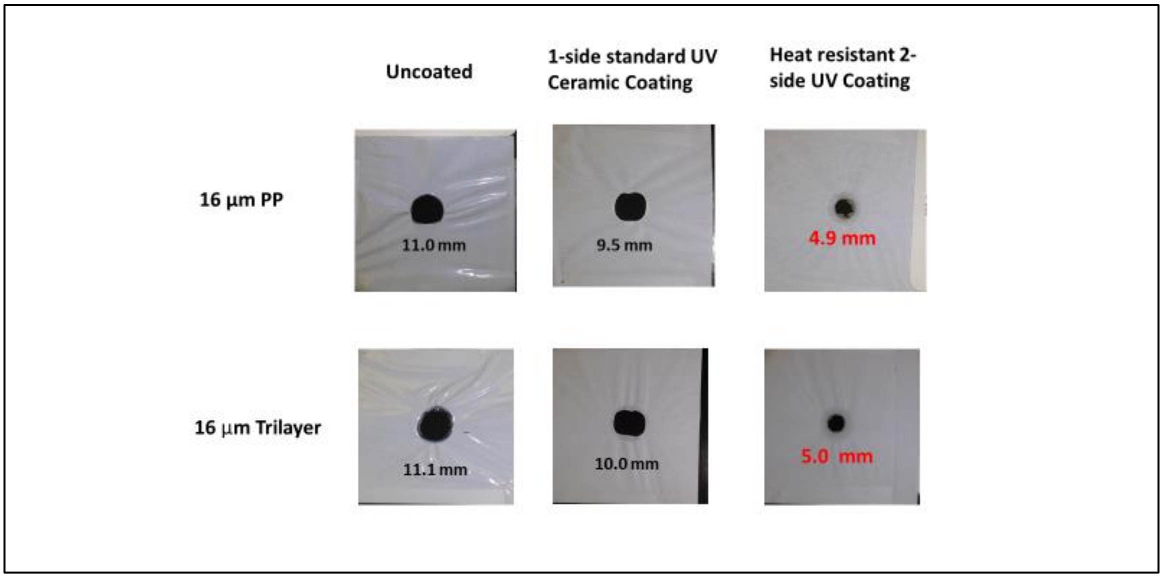


Figure 10. Results show 2-sided UV heat resistant coating prevents the hole produced by a 5-mm soldering gun from growing, whereas the uncoated separator rapidly melts and shrinks away. This may simulate what happens to the separator in the nail penetration test.

With the right UV ceramic coating, we might reduce and slow the ion tidal wave catastrophe in the nail penetration test

TABLE I. 5-second Solder Gun Penetration Produced the Following Holes in the Separator

Base Separator	Uncoated	1-side Standard Ceramic Coated	2-side Standard Ceramic Coated	2-side Extreme Heat Resistant Ceramic Coating
16 µm PP	11.0 mm	9.5 mm	7.8 mm	4.9 mm
16-µm Trilayer	11.1 mm	10.0 mm	8.2mm	5.0 mm

Manufacturing Cost Savings

Miltec UV successfully completed the milestone to *Complete Cost Reduction and Capacity Addition Analysis*. The milestone required that Miltec exercise the previously completed cost model to determine the costs associated with conventional and UV curable bindings and to determine the cost savings resulting from using a UV binder technology.

The cost model developed by Miltec is an excel based spreadsheet that calculates the cost of coating a polyolefin separator with ceramic particles using a UV curable binder to adhere the particles to the separator. The model includes the ability to vary all the essential parameters contributing to the final cost to coat the separator in $/m^2 of coated material with either single or double-sided coating.

The input parameters include:

Raw Material Cost: Alumina, UV Curable Binder - $/lb.

Coating Parameters:

- Coating thickness microns
- Alumina density g/cm3
- UV binder density g/cm3
- Slurry water content %
- Slurry UV binder content %
- Slurry alumina content %

Capital Equipment Costs

- Mixing equipment
- Coating and UV curing machine
- Maintenance
- The cost of capital on an annual basis is calculated using a Fixed Charge Rate to account for depreciation, investment, insurance, taxes, return on investment, etc.

Operating Costs

- Labor personnel, Labor Rates, Electricity Rate, Electricity consumption
- Scrap rate
- Building rent, HVAC, utilities

Operating Parameters

- Machine Process speed
- Coating Width
- Machine shifts per day
- Hours per shift
- Work Days per year

The goal of the project was to reduce the cost to coat to $.20/m2 compared to the nominal $.50 - $1.00/m2 being charged in the open market as a premium for coated separator versus uncoated separator. We believe that in both a conventional and a UV coating and curing system, the dominant cost representing 55-65% of the coating cost is the material costs. The cost savings attributable to a UV system lies in the reduced capital and operating costs due to lower capital costs, smaller footprint, and faster speeds. Provided below is a sample of exercising the cost model with specific assumptions resulting in an estimated coating cost of $.20/m2.

Sample Output Ceramic Coated Separator Cost Model			
Operating Assumptions		Material Costs	
Coating thickness	3 microns	Alumina	$20/lb
Coating/curing Speed	328 fpm (100 m/m)	UV Binder	$15/lb
Width	17.2" (440 mm)	Capital Costs	
Shifts per day	3	Mixing Equipment	$150,000
Fixed Charge Rate	26%	UV Coating nd Curing System	$1,300,000
Output	18,648,000 m2/yr		
Coating and Curing Cost			
Materials	$.13/m2		
Capital	$.021m2		
Operating	$.056/m2		
Total	$.20/m2		

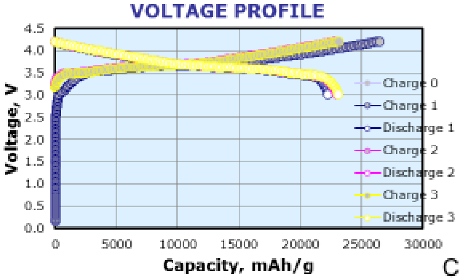
Miltec is also working on the feasibility of a class of alumina which is significantly less expensive on the market. Four samples were prepared and submitted to ANL for longer term cycling in pouch cells. The samples were numbered 1242,1242,1243, and 1245. The table below shows that 1242 was an uncoated Celgard C210 and the other 3 were coated on one side with a 4 µm alumina coating. 1243 was coated with the standard alumina typically costing in the range of $20/lb. 1244 and 1245 were coated with alternate alumina based ceramics with volume sales prices in the ranges of $2.50/lb and $1.50/lb, respectively. Using the same assumptions as above, the resulting cost for a coated separator in $/m2 is $0.10/m2 and $0.09/m2 respectively. The ANL prepared pouch cells were single sided NMC vs. graphite GenII with formation at 3 cycles at .1C and cycling between 3-4.2V at rates of .05C,.0.1C,0.2C,0.5C,1C,2C;3 cycles each and longer term at C/3. The pouch cells are now under long term cycling tests at 1C.

Sample		Alumina	Cost $/lb	$/m2
1242	uncoated			
1243	4um	std	$ 20.	$ 0.20
1244	4um	alt 1	$ 2.50	$ 0.10
1245	4um	alt 2	$ 1.50	$ 0.09

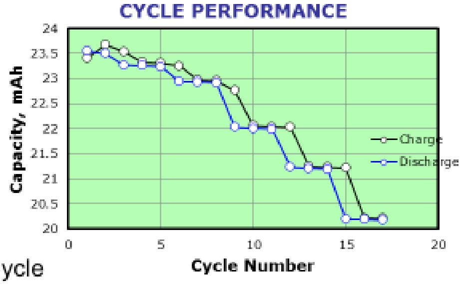
Figure 11 ANL cycling results for alternate less expensive alumina

1242 Uncoated

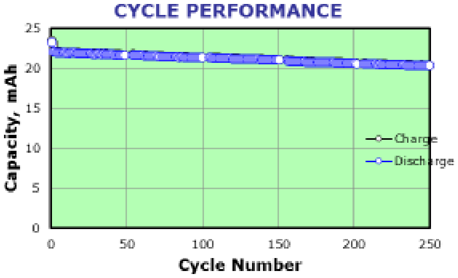
Formation



Rate

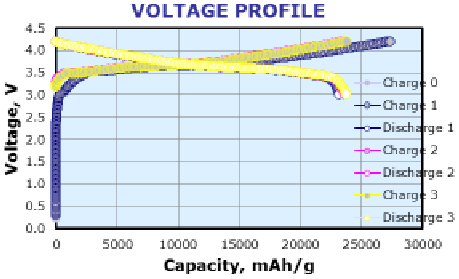


Cycle

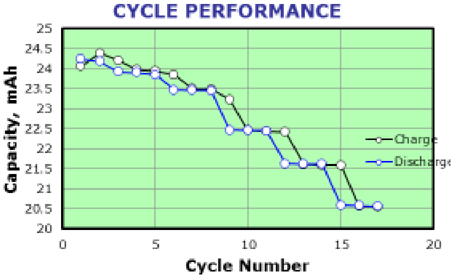


1243 Standard Alumina

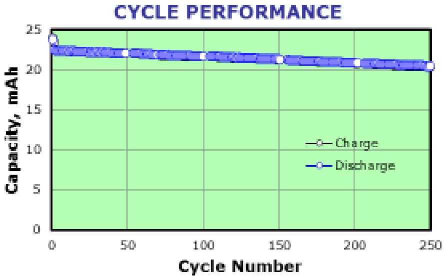
Formation

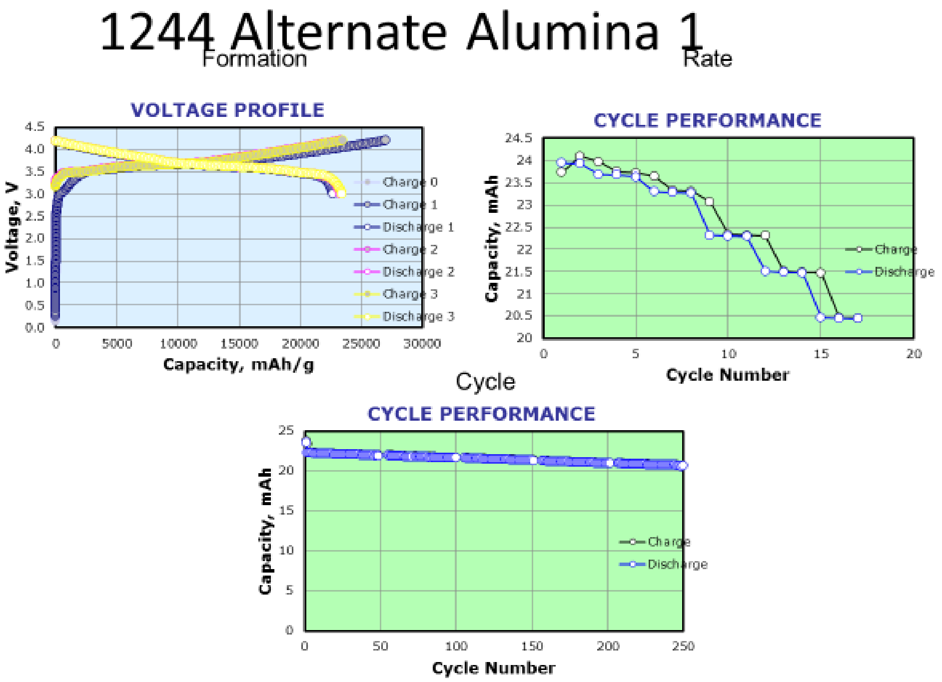


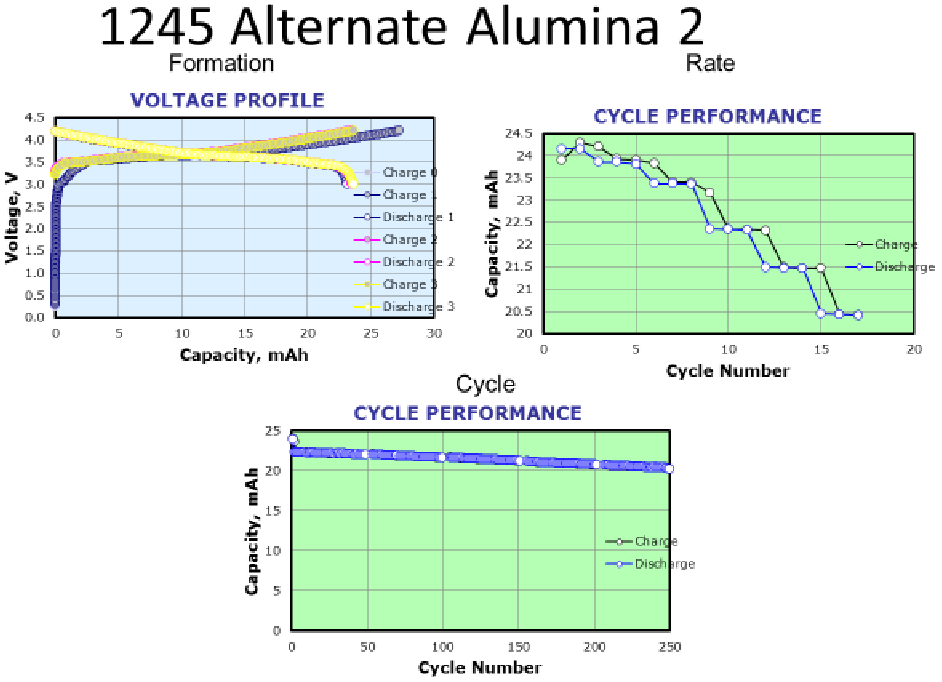
Rate



Cycle







As shown in the charts above, the voltage profile, rate cycle performance, and 250 cycle long term cycling performane are equivalent for the 4 samples thus representing the potential opportunity to significantly reduce the cost of ceramic coated separators.