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Batteries and UltraCapacitors

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Table of Contents

SBIR Rights Notice.....	1
Identification and Significance of the Problem or Opportunity and Technical Approach	3
Significance of the Opportunity	3
Technical Approach.....	6
Miltec UV, ACTEGA Kelstar Corporate R&D and Phase I SBIR	7
Miltec UV SBIR Phase I, ANL.....	7
Anticipated Public Benefits	7
Phase I Technical Results	8
UV Curable Binder Identification and Qualification.....	8
Coin Cell Performance with UV Curable Binder Cathode	11



Identification and Significance of the Problem or Opportunity and Technical Approach

Significance of the Opportunity

A significant reduction in the cost of Lithium ion batteries is a major goal of the Department of Energy (DOE) Vehicle Technologies Program (VT). Reducing the cost of these storage devices could accelerate the use of HEV, PHEV, and EV vehicles in the transportation sector and result in significant oil savings and reduced environmental emissions in the U.S. Lithium ion batteries are also making inroads into the electric grid storage market where reduced cost could increase the market penetration and increase energy savings.

The technical feasibility of using Ultraviolet (UV) curing technology to manufacture Lithium ion battery electrodes has been proven during SBIR Phase I.

One of the major cost elements of today's Lithium-ion batteries is the cost of manufacturing the electrodes. The major contributors to the manufacturing cost of these electrodes is the large amount of capital invested in the drying ovens, and the time, energy, and operating costs required to operate them, including the recovery costs of very large quantities of Volatile Organic Compound (VOC) solvents. The typical cathode is comprised of a matrix of active material particles such as LiMn_2O_4 , LiFePO_4 or Lithium Manganese Cobalt Oxide (NMC) and Carbon for enhanced conductivity bound to themselves and the current collector (typically 10 to 20 micron thick aluminum foil) by a small quantity of a specialized nonreactive thermoplastic polymer such as Polyethylene Oxide (PEO) or Polyvinylidene Fluoride (PVDF). This requires a multiple step manufacturing process. In the first step, the polymer and a VOC solvent such as N-Methylpyrrolidone (NMP) are mixed. The polymer solvent solution is then mixed with the Lithium compound active material and Carbon resulting in a slurry or paste that is coated on the current collector. This often requires a mixture of 45% or more by weight solvent to fully dissolve the polymer. This coating is then dried in a thermal oven which slowly evaporates the solvent and leaves the final cathode coating on the current collector. This coating is then calendered to a final electrode coating thickness nominally of 20 to 100 microns. Thinner coatings are typically applied in higher power applications and thicker coatings are typically



applied in higher energy applications. The calendaring is required to control the void percentage (typically 30-35% as a goal) and to control thickness. The driers consume natural gas or electricity and the VOC's must be recovered. The thermal driers are up to 100 meters long with residence times of several minutes for complete drying of the electrode coating. The driers and attendant equipment for VOC recovery represent a very large capital investment, well above \$10 Million for a typical electrode manufacturing plant. The electrode manufacturing line speed is typically the limiting factor in the processing speed associated with manufacturing a Lithium ion battery. Typical electrode speeds are from 12 to 24 feet per minute with some projected systems capable of 35 feet per minute. These faster systems however will require dryers longer than a football field, compared to a comparable UV total curing system of 12 to 14 feet in length operating at 100, 200, or a possible 400 feet per minute.

The Lithium ion battery anode manufacturing process is essentially the same except in most cases the anode coating is a form of Graphitic Carbon such as Meso Carbon Micro Beads (MCMB) or graphite coated amorphous carbon with some manufacturers adding small quantities of Lithium compounds. The anode current collector is typically 7 to 20 microns thick copper foil.

Ultracapacitors go by several different names (including "Electric Double-Layer Capacitors (EDLCs)" and "supercapacitors") and are used for many different applications. They are being prominently considered for use in conjunction with Lithium ion batteries in PHEV and EV applications. Ultracapacitor electrodes are very similar to Lithium ion battery anodes (high surface area carbon or graphite is a typical carbon form used) and are manufactured using essentially the same solvent based drying process except that the Ultracapacitor current collector is more typically aluminum and the coating thickness is more like that of a high energy Lithium ion battery, in the range of 75 to 100 microns. The focus of the Miltec UV commercialization plan is to first demonstrate and commercialize UV curing technology in the Lithium ion battery manufacturing industry; first in the U.S. and then worldwide. Pursuit of Ultracapacitor manufacturing will be a secondary but also important commercialization effort.

Historically, similar solvent based coating techniques were used for the application of various organic coatings in several industries such as wood and furniture finishes, ink printing, sheet metal coatings, fiber optic coatings, paper and plastic package coatings, CD's, DVD's, several automobile parts such as headlight reflectors, circuit boards, ceramic coatings, and many other coating applications. The introduction and application of Ultraviolet (UV) and Electron Beam (EB) curable materials has resulted in dramatic cost savings in those industries. In a straightforward UV example, a mixture of UV curable liquid monomers, oligomers, dispersants, if required, and a photoinitiator are coated on the subject substrate (wood, metal, cloth, paper, etc) and then exposed to UV radiation. When exposed to appropriate wavelength and intensity UV radiation, the photoinitiator generates free radicals that in turn cause the monomers and oligomers to polymerize and cross-link in a fraction of a second to the desired polymer. No solvent is used. In the case of Lithium ion battery electrode manufacture using UV curing technology small quantities of a liquid carrier may be required to reduce the coating viscosity



for ease of application to the current collector. However, this small quantity of liquid carrier evaporates immediately under the UV lamps, most likely will not have to be recovered, and if it must be recovered it is very easily accomplished from the cooling exhaust air flow from the UV lamp housing.

In an EB application the same curable monomers and oligomers are coated on the substrate but without the photoinitiator. The photoinitiator is not required because free radicals are generated by the electron beam. EB systems are typically used for thicker coatings because of their ability to penetrate to greater coating depths. EB systems are however typically more expensive to install and to operate. Miltec UV and its commercialization partners have the capability to apply EB curing technology, but the success to date of using the less costly UV curing at coating thicknesses to 75 microns and the ability to do multiple layer coating with UV technology has lead the team to de-emphasize this approach.

The effective capital cost of a UV curing system could be 1/20th to 1/100th today's solvent based system per unit area of electrode produced. In addition, reduced operating costs, energy costs, solvent recovery costs, and manufacturing facility costs, and significantly increased processing speeds and improved productivity with two sided coating and curing make a 50% reduction in electrode manufacturing cost an achievable goal.

The electrode manufacturing cost reductions associated with UV curing technology are attributable to several cost saving benefits:

1. The curing takes place in a fraction of a second instead of tens of minutes as required in a solvent based thermal drying system. This has the potential to dramatically increase the speed of a continuous manufacturing line (typically speed is increased by a factor of 10-100). Fiberoptic cables are for example coated at a processing speed up to 900 feet per minute. In the case of a Lithium ion battery electrode the limiting speed will most likely be the coating speed limitations. We expect today's coating technology coupled with UV curing technology as applied to Lithium ion battery electrodes to achieve easily 150 feet per minute and likely 200 feet per minute. During Phase II other very high speed coating techniques will be evaluated that can possibly achieve 400 fpm.
2. The UV curing technique involves no solvents to dissolve the polymer. It may require a carrier /wetting agent but in much smaller quantities. The wetting agent is used to carry or disperse the binder but it vaporizes almost instantly in the UV curing environment. VOC's with their attendant cost, recovery and/or disposal and associated environmental concerns are minimized.



3. The capital cost of a UV curing system is expected to be less than 1/10th the cost of a thermal drying system that it might replace in a retrofit application. There is no drying oven used at all. However this does not take into account the effective reduced capital cost because of the dramatically increased processing speed. For example, in the case of a Lithium ion battery electrode manufacturing process, if a UV system operating at 200 feet per minute replaced a solvent based system operating at 20 feet per minute, one UV unit, which by itself costs 1/10th the dryer, would replace 10 solvent based units. This is in effect a reduction by a factor of 100 in capital cost per unit of electrode produced. In addition, today's solvent based systems use single side coating followed by drying. The single coated electrode is then coated on the opposite side and dried again in a drying oven. This causes the two sides to have different exposures to the drying oven; the first side coated is exposed to the oven twice and the second coated side is only exposed once. In a UV curing system it is anticipated that in effect two sided coating will be accomplished. One side will be coated and UV cured followed within seconds by the opposite side being coated and UV cured. This effectively reduces the capital cost by another factor of 2. It is expected that this two-sided coating process will improve the consistency of electrode coatings. Each side will be subjected to the same conditions. It is also expected that productivity will be improved due to the reduced amount of lost material if the process is out of tolerance. The amount of lost material resulting from a shutdown is significantly less in a curing unit of a few feet length as opposed to a curing unit of hundreds of feet.
4. The footprint of a UV curing system is typically one tenth or less that of a thermal drying system. In the Lithium ion battery electrode application we expect the footprint for the UV curing system to be about 1/20th that of a thermal drying system.
5. The energy consumption of a UV curing system is typically one half or less that of a thermal drying system. Only electricity for the UV lamps and cooling blowers is consumed instead of fuel to be burned such as natural gas.

Technical Approach

Using funding from Corporate R&D, SBIR Phase I, and a parallel DOE Vehicles Technology Program cost-shared contract, the basic feasibility of using UV curing technology to produce Lithium ion battery electrodes at speeds over 200 feet per minute has been shown.



Miltec UV, ACTEGA Kelstar Corporate R&D and Phase I SBIR

1. Demonstrate that UV curable binder can retain binding characteristics and remain inert in Lithium ion battery environment.
 - a. Electrolyte immersion tests of UV cured binder only coatings.
 - b. Cyclic Voltammetry tests of UV cured binder only coatings.

Miltec UV SBIR Phase I, ANL

2. Demonstrate that UV cured binder can be used to produce cathodes for a coin cell with performance equal or better than a PVDF type cell
 - a. Demonstrate mixing and UV curing at 87% Li compound, 5% Carbon and 8% binder
 - b. Demonstrate coating and UV curing to 75 microns and 150 fpm
 - c. Demonstrate satisfactory adhesion with crosshatch and tape test
 - d. Demonstrate acceptable conductivity
 - e. Demonstrate coating and UV curing multiple layers for potential use in very high energy applications.
 - f. Demonstrate acceptable initial charge and discharge and long term cycling performance of coin cells made with UV cured binder containing cathodes.

Anticipated Public Benefits

Batteries are a critical enabling technology for the successful introduction of very fuel efficient vehicles such as HEV's, PHEV's and EV's. The commercialization of these vehicles can dramatically reduce the U.S. consumption of oil and reduce our dependence on imported oil, which now represents over 50% of our total consumption. Lithium ion battery technology is fast becoming the chosen technology for these fuel efficient vehicles of the future. Several major auto manufacturers including BMW, Mercedes Benz, Nissan, General Motors, Toyota, Hyundai, and Ford as well as several smaller manufacturers have announced their selection of Lithium ion battery technology for various significantly improved mileage vehicles. However, they have also identified Lithium ion battery cost as a specific barrier to wider spread commercialization. The vision for this project is to develop and commercialize a Lithium ion battery manufacturing process that can reduce the process manufacturing cost of the electrodes by 50% or more. The DOE Vehicles Technology Program Annual Report on Energy Storage Research and Development cites a 50% reduction in manufacturing costs to be needed for a more cost effective PHEV. In addition, because of the dramatic reduction of the use of VOC's, the manufacturing process itself is more environmentally friendly. U.S. Lithium ion battery and Ultracapacitor manufacturers would be the direct beneficiaries of introducing this technology followed by the auto manufacturers who would use the reduced cost batteries and Ultracapacitors followed by the general public who would be more apt to buy fuel efficient vehicles at a reduced cost.



Phase I Technical Results

Miltec UV and its Phase I subcontractors, Argonne National Laboratory and ACTEGA Kelstar, have shown the technical feasibility of using UV curing technology to manufacture Lithium ion battery electrodes.

UV Curable Binder Identification and Qualification

Miltec UV and ACTEGA Kelstar identified, developed, and tested unique UV and EB curable binders (patent pending) that retain adhesion and other necessary properties after the rigors of being exposed to a Lithium ion battery electrolyte at full strength for two weeks at 140 degrees F. The possibility of using UV curable binders in Lithium ion batteries had not been considered previously because selected UV cured polymers had failed to survive the battery electrolyte environment.

ACTEGA Radcure & Kelstar scientist, Dr. John Arnold, now the Principal Investigator on this project and a Miltec UV employee, discovered a unique set of UV curable chemicals that were proven to be compatible with a Lithium ion battery environment with the adhesion qualities of PVDF.

A patent application was filed in October 2010. Under the SBIR Phase I effort significant research and development was conducted to identify and qualify a group of UV curable binder components. The two tests chosen to confirm the UV binder components ability to be a satisfactory binder in a Lithium ion battery were an immersion test and a Cyclic Voltammetry Test (CV).

A UV curable binder mix is comprised of a blend of oligomers, monomers, dispersants, if needed, and a photoinitiator. Upon exposure to UV radiation, the photoinitiator (very small quantities of 2% or less of the binder mix) releases free radicals which cause the oligomers and monomers to polymerize and cross link to a solid binder. Dispersants are added in very small quantities to reduce viscosity and enhance uniformity of the Carbon and Lithium compounds in the mixture and the deposited coating. A UV curable binder mix is deemed qualified if it retains full adhesion qualities and remains absolutely chemically inert during exposure in a battery and contains no constituents that interfere with the electrochemical performance of the battery.

Miltec UV working with ACTEGA Kelstar and Argonne National Laboratory have identified and qualified 5 oligomers, 4 monomers, 4 photoinitiators, and 6 dispersants for use as constituents in UV curable binders for Lithium ion batteries. These constituents can be used in varying combinations to optimize and tailor the binder to the coating particles and current collector.



In the immersion test a mix of oligomers, monomers, dispersants, and photoinitiators are mixed and coated approximately 5-10 microns thick on an aluminum sheet and UV cured at 150-200 fpm. The UV cured samples are immersed in electrolyte for 2 weeks at 140 degrees F. A UV curable binder mixture that passes the immersion test retains outstanding adhesion while exhibiting no weight gain or loss, discoloration, cracking, curling, swelling or other signs of chemical reaction. Dozens of candidates were tested to arrive at the matrix of constituents that have been qualified.

Those samples that passed the immersion test at Miltec UV were then subjected to CV testing at ANL. A typical test condition and representative test results for qualified constituents are shown below.

Dozens of test results like those shown below confirmed the ability of the successful UV curable binder constituents to be acceptable in a Lithium ion battery when compared to PVDF. The CV test results confirm that the UV curable binder components, like PVDF, remained chemically inert while subjected to the high intensity electron flows caused by the voltage cycles. The suite of qualified UV curable constituents provide the capability to work with varying cathode and anode particle sizes, curing rates, curing depths, viscosities, aluminum adhesion qualities, and binder flexibilities. It was also shown that the UV curable binders could operate at voltages well above the limits of today's electrolytes.



Cyclic Voltammetry Test Conditions

Coin cell: CR 2032

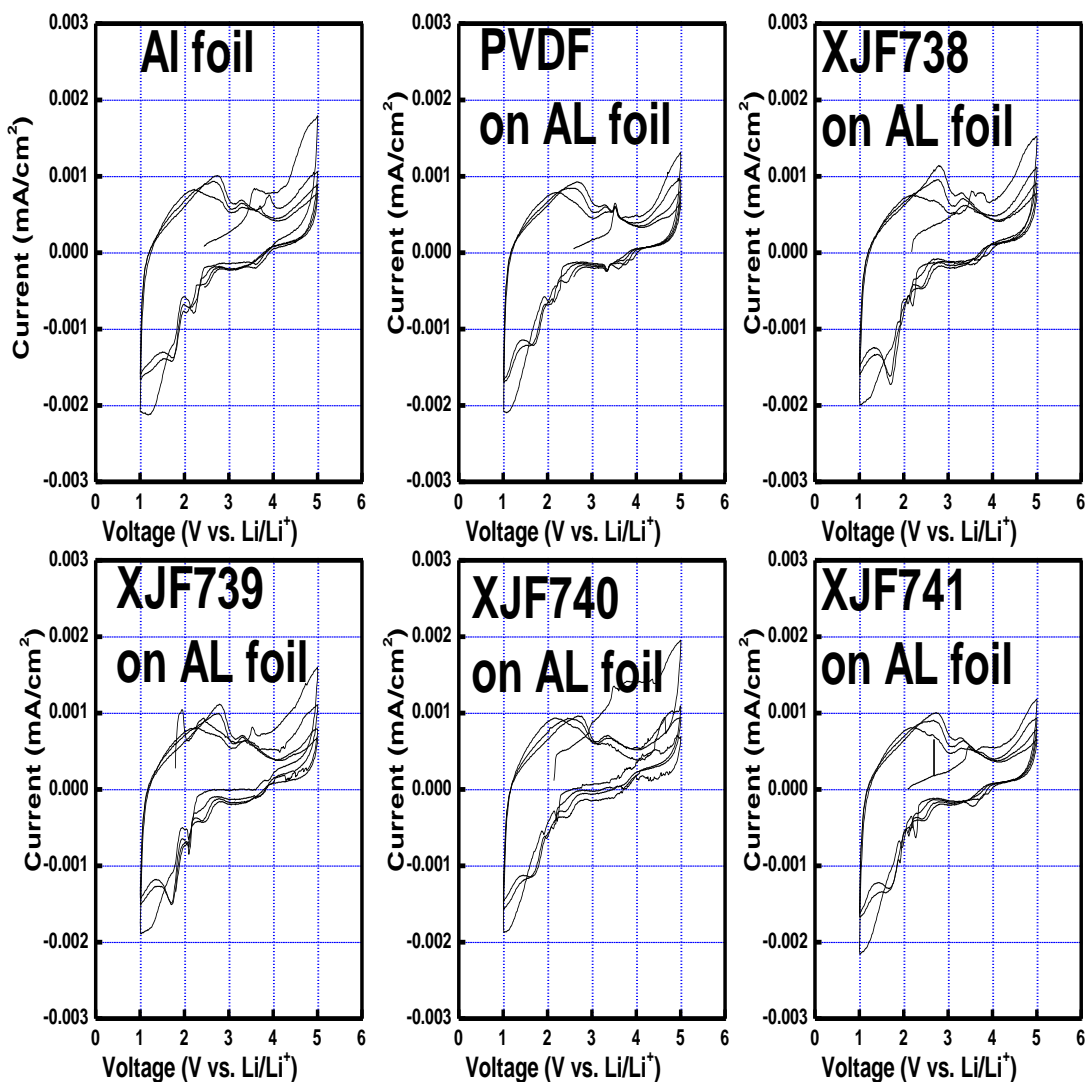
Lithium metal as counter electrode

Electrolyte: 1.2 M LiPF₆ in EC: EMC (3:7 in weight)

CV: 0.1 mV/s between 1-5 V at room temperature

Instrument: Solartron analytical 1400 cell test system

		Total thickness	Thickness of the binder
Mitec	Al foil	~26 μm	
Self-made	PVDF on Al foil	~28 μm	2 μm
Mitec	VJF738	~30 μm	4 μm
	VJF739	~28 μm	2 μm
	VJF740	<27 μm	<1 μm
	VJF741	<27 μm	<1 μm



Coin Cell Performance with UV Curable Binder Cathode

Following the qualification of a family of UV curable binder constituents, the next step was to develop the processes for mixing, coating, and UV curing a mixture of Lithium compound,



carbon and binder coated on a current collector. NMC was chosen as the initial active cathode material. The goal was coating at 50 microns (75 microns has been successfully demonstrated as well as multiple coatings to higher thicknesses) thickness with 87% NMC, 8% UV curable binder, and 5% Carbon on untreated Aluminum current collector at 150 fpm. New mixing techniques were required to achieve these goals. Conductivity/resistance of the UV cured cathode coating was used as a screening tool prior to subjecting samples to coin cell tests at ANL. A gold plated, constant pressure, resistance measuring apparatus was built to specifications given to us by a battery manufacturer. Bulk resistance of 0.35 ohms was set as a maximum resistance for a 1.76715 cm² die cut sample. Most samples were in the 0.1 to 0.3 ohm range.

The test conditions for the ANL coin cell tests are shown below.

Room temperature (about 20 °C)

Half cell (Li metal as anode) Coin cell 2032

Electrolyte: 1.2 M LiPF₆ in EC:EMC (3:7 in weight)

Separator: Celgard 2325

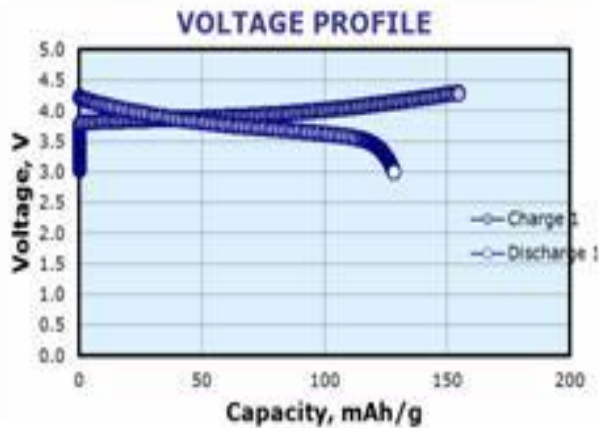
Assemble in He-glove box

Electrochemical equipment: Maccor 4400

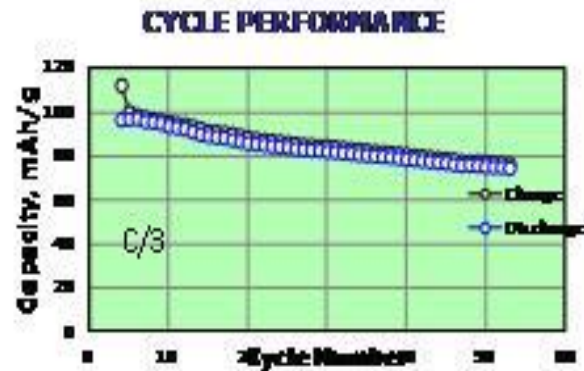
The initial charge discharge, capacity and the cyclic performance of two recent samples, one coated with a single layer of 50 micron thickness uncalendered and one with a two layer coating, calendered, are shown. It is important to note that the performance of a cell using uncalendered electrode samples is very similar to one using calendered electrode samples. In a conventional solvent based system, 45% or greater by weight of a solvent is used. When the solvent evaporates, significant voids are left by the evaporated solvent. Calendering is a necessity to achieve porosity that minimizes the voids to the point of still having adequate space for the electrolyte. The calculated voids in the uncalendered sample using UV curable binder and a small amount (approximately 10% by weight) of carrier/wetting agent is 32% after UV curing. The second sample used a cathode that was prepared in two steps. Approximately 25 microns was coated and UV cured and then a second 25 micron coating was applied over the first and UV cured. This sample was calendered to 30% voids.



Single Layer



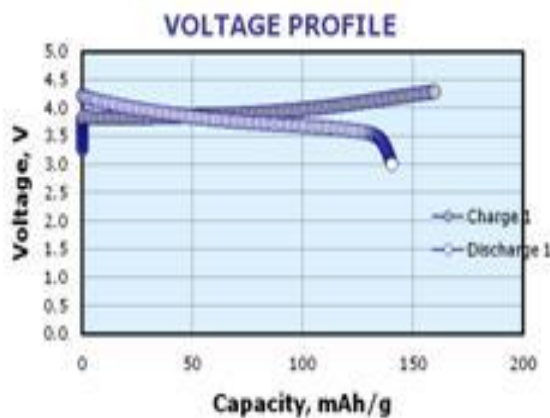
Coating Thickness = 50 microns
 Calendered = No
 Loading: 87% NMC 8% Binder 5% Carbon
 Cured: 2 HPI Lamps X 550wpi @ 100fpm
 Initial Charge/Discharge: 154/128 mAh/g
 Void = 32%



Research and development is continuing under the VT contract to improve the capacity of the cells at the higher charge/discharge rates. As mixing, and coating and calendering techniques have improved, the conductivity of the tested coin cells has improved along with improved capacity. The Miltec UV team is learning that using UV curable binder requires a slightly different approach to mixing and coating and calendering to achieve very high conductivity and capacity. Significant progress is being made and confidence is high that the goal of a cell with performance equal or greater than the baseline PVDF cells will be achieved.



Double Layer



Coating Thickness = 20 microns
 Calendered = Yes
 Loading: 87% NMC 8% Binder 5% Carbon
 Cured: 2 HPI Lamps X 550wpi @ 100fpm
 Initial Charge/Discharge: 163/142 mAh /gm
 Void = 30%



The sample above was coated with a nominal thickness of 25 microns, UV cured at 100 fpm and a second layer of nominal 25 microns was coated over the surface of the first and UV cured at 100 fpm. This coin cell shows good performance after calendering to 30% voids. Further research and development is being conducted to optimize performance with UV curable binder as a function of coating thicknesses and calendering. These results indicate that accommodating thicknesses from tens of microns to a hundred microns or more is very doable using UV curing technology. The resistance measurement for the double layer was only slightly



higher than the resistance of a single layer of the same thickness. One reason for experiencing equal or better performance for a layered coating is that the second layer covers any minute bare or thin spots in the first layer. The lack of solvent causes the uncalendered void % for a UV cured electrode to be significantly less than a conventional solvent based electrode.