Dry Processed, Layered, Flexible Lithium-Ion Manufacturing Process

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Abstract

The dry PVDF electrode process, developed under a DLA BATTNET project, provides improved electrical performance compared to solvent-based electrodes. The process allows multiple electrode layers, tailoring active material particle size. Conductive additives and polymer loadings can provide significant improvements in life, power and cell capacity. This paper will briefly go over the ETP process and explore the improvements that a controlled tailored anode and cathode electrode system can provide. Performance of commercial solvent cast electrodes will be compared with that of single coat dry process electrodes, then multi-layered electrode technology will be evaluated while defining the improvements that occur in high performance battery cells.

Keywords: Lithium-ion; layered separator, low-cost lithium-ion manufacturing; just-in-time manufacturing; solventless; solvent free; lithium-ion manufacturing; dry process; batteries.

Introduction

From 2012 to 2015, ETP worked under a DLA BATTNET Project. ETP Inc. was tasked to develop an electrode manufacturing process for Lithium-Ion batteries, which would enable just-in-time capability and small order delivery for the Defense Community. Under the STP task ETP was to demonstrate a pre commercial pilot process for a totally dry, solvent free manufacture of electrodes (Figure 1). It turned out that an important ancillary benefit of the ETP solvent-free process was that production costs were lowered substantially. Additionally, the process allows fabrication of electrodes with multiple layers, each of which can have their own composition. This can lead to performance enhancements in cells using dry-processed electrodes.

Concept

The ETP process is based upon the concept of a charged fluidized bed, depositing onto a grounded electrode current collector. The electrodes materials (active materials, additives and polymer binder) are suspended in a fluidized bed, charged electrostatically (10s of kV), and then sprayed onto a heated and grounded metal foil current collector. The loose deposit is then calendered to a desired thickness and porosity. The deposition/calendering stages can be repeated multiple times to achieve the desired thickness and capacity, and if desired, apply layers with differing properties (porosity, composition, etc.).

The process reduces initial capitalization costs by 50%, while providing an ongoing cost savings of greater than 30%. The cost of manufacturing is lowered as the process allows for the total elimination of solvents, slurry preparation, drying and solvent recovery. Facility costs are lowered as the method requires a much smaller footprint compared to conventional manufacturing techniques.

The same binder and active materials used in conventional lithium-ion batteries are used in the ETP solvent-free manufacturing of electrodes, leaving no issues with non-compatible components being added to the cell to limit life or hinder performance.

Figure 1. Pre-Production Manufacturing Line.

This line has successfully produced both cathodes and anodes for lithium-ion batteries. It has also been used for bipolar lead acid batteries and several lithium primary chemistries. Performance of test cells has been at or better than the level of commercially made electrodes.

The ETP process can be effectively used with all common active materials and particle sizes for both cathodes and anodes. It has also demonstrated the ability to spray ceramic separator layers on the

surface of electrodes, eliminating the need for a discrete component separator.

Description of the Process

The dry process consists of multiple stations where the active material is applied on either a single or dual sided onto the current collector (Figure 2). The stations can be reduced or increased to accomplish the design of the electrode with thicknesses ranging from the width of individual active material particles to much greater thicknesses (> 0.1 cm). The electrode thickness is built up in a single pass through the roll to roll process.

Active materials, binders and conductive carbons are dry blended and applied in an electrostatic spray. Each successive layer is added to the preceding layers. Calendering can be performed between layers or after final coating. A schematic of a single sided coating is shown on the left sides of Figure 3 and Figure 4. An electrode prior to calendering is shown in Figure 5.

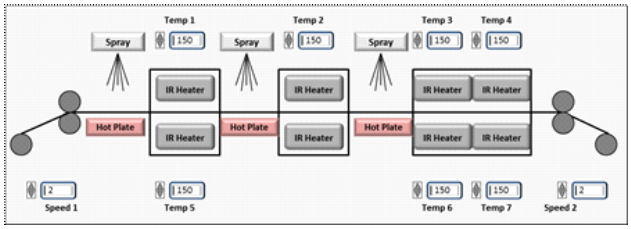

Figure 2. ETP Dry Process Flow Schematic.

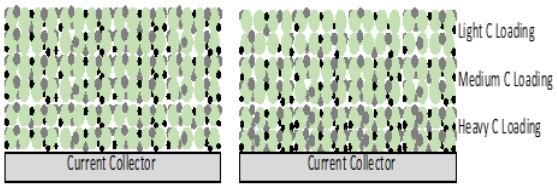

Figure 3. Depiction of Electrodes with Uniform Composition (Left) and with Layers of Variable Composition (Right).

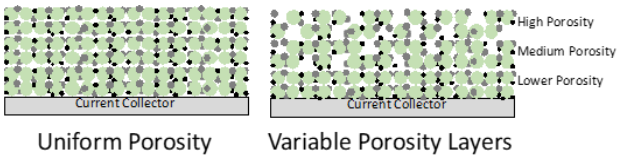

Figure 4. Depiction of Electrodes with Single Layer and Multiple Layers with Variable Porosity.

The temperatures are controlled such that the PVDF polymer does not flow. It is the intent to keep the polymer out of the pores of the active material so as not to fill them with polymer. This has shown to provide substantially higher rate capability compared with solvent cast electrodes.

Keeping the active materials dry enables the ability to start and stop the machine, or change over active materials or continuous runs hindered only by the changing of the foils.

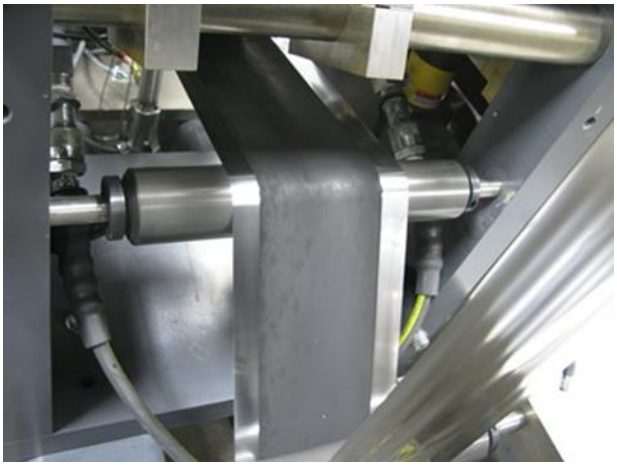

Figure 5. Electrode Before Calendering.

Dry blending is quicker and more cost effective than solvent blending. The finished electrodes are dry as they exit the process and can be slit or cut and built into cells immediately. This lowers the amount of work in process inventory along with lowering the probability of damage to WIP due to further handling and storage.

ETP is presently in the process of switching over to an alternative spraying system. The existing Wagner systems demonstrated uniform coating and strip coating capabilities but they were not as effective at patch coating capability. The lag of active material internal to the coating gun made precision start and stops difficult to manage. The Wagner equipment did provide a working demonstration of the capabilities of uniform very thin to thick capability and may be used on dedicated high volume manufacturing lines. Even they demonstrated that micron control could be achieved with uniform powder feed.

The advantage of the existing dry powder delivery system is that the equipment and in particular the nozzles are very low cost and can be designed and built using 3-D modeling. The tips wear very slowly and have a great deal of flexibility.

ETP typically increases the level of polymer and conductive carbons on the base layer. This improves adhesion of the active materials to the foil. The second and subsequent layers can be thicker with less polymer percentages. The layers can also be tailored to optimize performance as will be discussed in the next section.

ETP has been developing a sprayed ceramic separator. This allows a lower amount of polymer to be used in the separator. This has been shown to

provide an improved safety separator. The ceramic separator collapses as thermal runaway begins with the PVDF liquifying and entering the pores of the ceramic. This limits ion transport to allow a slower failure.

Th existing prototype machine (Figure 1) can handle 8” wide foil and can coat up to 40 feet per minute spraying wo sides.

Multi-Layer Capability

ETP’s solvent-free electrode fabrication process has the capability of applying the electrode in multiple layers with multiple compositions. This powerful aspect of the process allows battery manufacturers to optimize the electrode for improved performance, especially in applications requiring high power and energy output.

The standard industrial practice at present is to make electrodes by mixing the electrode constituents in powder form (active materials, carbon additives, polymer binder) in an organic liquid which dissolves the binder, and then coating the slurry onto metal foil current collectors. After drying and compressing, the electrode usually has fairly even composition throughout the electrode thickness.

An even distribution of materials through the electrode thickness though is often not ideal. For example, the current flowing through the solid electrode material is highest at the back of the electrode, so the conductive carbon content would be ideally higher at the back of the electrode.

This is easily accomplished using ETP’s solvent-free process. Several layers are sprayed onto the current collector, each with a different composition. The bottom layer would have higher carbon content, to reduce voltage drop during high power operation. In contrast, the single-layer (solvent-cast) electrode will have a more uniform carbon content profile. The carbon content at the front of the electrode is the same as that at the bottom, where higher carbon content is most needed.

Figure 3 shows schematically how this might take place. On the left is a single layer electrode. On the right is one with three different layers, with increasing carbon content nearer the current collector.

Other performance variables can also be affected by using layers of differing compositions. For example, porosity can also be changed from one layer to another. Higher porosity reduces the resistance caused by current flow through the electrolyte. In some cases (for example at lower temperatures), the electrolyte resistance can reduce cell voltage. The porosity at the front of the electrode could be increased, where electrolyte current flow is highest. This would improve overall cell performance. Figure 4 illustrates the multi-porosity layers concept.

The powerful design flexibility offered by ETP’s solvent-free process extends to the use of different or mixed active materials and carbon powders of differing sizes (depicted in the figures by the grey and black spheres of differing sizes). All in all, use of the ETP process allows quantum upgrading of Li-ion cell design and performance.

An additional advantage of the ETP process is the improvement in distribution of the binder throughout the electrode structure. Presently the binder precipitates preferentially toward the back of the electrode, due to the nature of the evaporation process. This is not necessarily an advantage. Improved binder distribution can be accomplished by elimination of the solvent used in the casting process. Instead, the binder levels, and the location of the binder, can be controlled, further improving electrode and cell performance. Figure 6 shows a 2.8 C discharge of an LTO anode-limited cell, where both electrodes were made using the ETP solvent-free process. Comparison with cells made with solvent-cast electrodes of comparable loadings, show performance is at least equivalent.

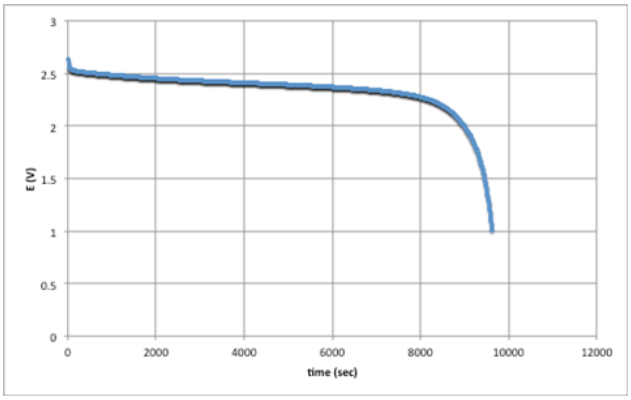

Figure 6. LTO Anode-Limited Cells with and Initial Specific Capacity of 0.485 mAh/cm^2

Solid State Battery Processing

Solid state batteries show significant promise but seem to be suffering from interfacial resistance between the electrolyte and the active material. ETP has recently begun an internal project to use dry process solid state electrolyte and active materials. Again, ETP has chosen to process the materials completely dry and use a modified spray coating process to make composite electrode/separators. This has required elevated temperatures to enable the manufacture of quality electrodes along with operation inside of a glove box. It is our plan to move this process to a dry room in the future.

Summary

The cost and time advantages of the use of the dry fabrication process developed by ETP are well-established. Perhaps overlooked have been significant performance advantages, which can be achieved by applying multiple electrode layers with different properties. Additionally, depositing a ceramic-polymer separator on the surface of electrodes greatly improves electrode alignment and safety.

Finally, at the present time much effort is being expended to find ways to effectively fabricate all solid-state lithium-ion cells. It is widely believed that solid electrolyte cells cannot be made effectively when a solvent-casting manufacturing approach is used to make electrodes. The use of the ETP dry process avoids the problems of using a solvent-based process, which include a residual and resistive film that remains on the surface of the solid electrolyte.

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