I. Executive Summary
Lithium ion batteries use a separator which wets out poorly with commonly used electrolytes. This can cause problems especially in emerging applications such as electric vehicles where the battery size is larger than in legacy applications such as consumer electronics. From this arises a need for a separator with improved wettability compared to current commercial polyolefin materials. Approaches used in the past are discussed and the benefits and deficiencies of those methods are highlighted. Nonwoven separators, based on hydrophilic nanofibers present a potential solution to wettability concerns.

II. Issues with Wettability
In lithium-ion battery manufacturing, a prerolled or prestacked thin-layered porous electrode assembly is placed inside the cell container and then liquid electrolyte is injected into the nearly complete battery assembly. A precision pump fills the cells, then vacuum applied to ensure the electrolyte completely permeates the pores in the separator and electrodes. Poor compatibility between the electrolyte and the porous film separator can lead to incomplete filling or extended manufacturing times. Two issues with poor wettability can result: 1) it can take increased time to fill the wound battery with electrolyte, and 2) the distribution of the electrolyte in the cell can be uneven, leading to poor long-term stability of the battery. Another consequence of poor wettability is decreasing the battery load capacity, i.e. maximum charging/discharging currents are relatively low.

The wettability issue is a growing concern as larger batteries are being produced for electric vehicle applications. Any un-wetted active material will cause an underutilization of electrode capacity and increased electrolyte resistance. Due to the metal current collectors in a lithium-ion battery being foils, the transport of the liquid electrolyte occurs in a highly directional manner through the thin porous channel formed by the electrode materials and separator. The wettability issue becomes more critical for large capacity electrodes that are being developed for vehicle applications, where the entrance area is limited, and the transport distance increases for the electrolyte.

Several advantages have been proposed as resulting from a battery separator with improved wettability. Improved wettability could lead to better cycle performance with increased capacity retention and better rate capability. Both can be attributed to facile ion transport and improved interfacial compatibility between the electrodes and the separator.

III. Past Studies of Wettable Separators
Current commercial separators for lithium-ion batteries are porous polyolefin films, both polyethylene (PE) and polypropylene (PP). These separators are reliable for most portable electronic applications but they suffer from a limitation for some emerging uses. The polymer separators are not compatible with conventional electrolytes that include polar solvents, such as ethylene carbonate, propylene carbonate and gamma-butyrolactone, due to hydrophobicity and low surface energies of the polyolefins which lead to wetting problems.
Several approaches have been attempted to address these concerns, including coating with a gel polymer electrolyte (1-3), using a wetting agent (4) and grafting hydrophilic functional groups onto the membrane surface (5). Each has limitations that have prevented their general applicability.

Separators modified with gel polymer electrolytes have complex multi-step processes and expensive modification with hydrophilic monomers. Wetting agents improve wettability but cannot ensure electrolyte retention. Membranes may be hydrophilic only temporarily as liquid electrolytes could wash away the wetting agents upon repeated cycling or storage. Finally, permanent grafting of hydrophilic functional groups is sufficient for the surface modification of polyolefin membranes. However, specialized, expensive equipment is required to implement that technology. These drawbacks have generated continued interest in alternative methods to achieve a wettable separator.

Several studies have shown the performance of batteries using separators with improved wettability. In one study (6), ethylcellulose-coated polyolefin separators were produced through a dipping and extraction process. The electrolyte wettability is greatly improved compared to an uncoated separator which leads to an increase in capacity retention from 28 to 99 %. The improved wettability is attributed to the high polarity of the ethyl cellulose layer.

A cellulose-based composite separator for use in a high performance battery was developed by Zhang et al (7). The composite separator improved electrolyte retention, with better interface stability and enhanced ionic conductivity. A battery produced with the separator exhibited better rate capability and cycling retention than that for a PP separator. The cell with the composite separator delivered stable cycling performance and thermal dimensional stability even at 120 C.

Plasma treatment has been reported to improve wettability of polyolefin separators as reported by Kim and Lim (8). The surface of a PE membrane was modified with acrylonitrile via plasma-induced coating. The plasma-modified PE membrane exhibited increased ionic conductivity, good wettability, and enhanced interfacial adhesion between the electrodes and the separator. Lithium-ion polymer cells fabricated with the plasma-modified PE membrane exhibited better cycle performance compared to an unmodified PE membrane.

Aromatic polyethers can be made into highly wettable separators by blending with polyethylene oxide (PEO) and then removing the PEO (9). The wettability and also pore structure can be controlled by both side chemical structures on the aromatic polyethers and also by the blend ratio with PEO. The separator showed increased thermal stability and good cycle life, with somewhat lower rate capability compared to polypropylene dry process separator.

Dopamine can be self-polymerized on the surface of polypropylene separators via a solution immersion method to improve the interfacial hydrophilic wettability and also discharge performance (10). In their study, the dopamine modified separator shows improved strength, lower water contact angle, higher electrolyte uptake capacity, lower ac impedance, lower internal resistance and higher rate capability.

Another approach that has been recently used has been to mass produce cellulose acetate microfibers using force spinning, followed by alkaline hydrolysis treatment (11). Membranes of randomly oriented, fully interconnected and highly porous (75%) three dimensional fibrous networks structure can be created. Compared to commercially available polypropylene membranes, they show higher ionic conductivity, higher thermal stability, better wettability and lower interfacial resistance.
IV. Current Commercial Solutions

The Figure shows the wettability observed with a Dreamweaver separator compared to a standard polyolefin separator, showing dramatic differences in wettability. The DWI materials wet out dramatically faster which may assist in the manufacturing cycle to build lithium-ion batteries. In addition, the faster wetting achieved by Dreamweaver nanofiber-based separators demonstrates higher ionic transport. This can lead to longer lasting batteries, as well as higher energy density and higher power batteries. Further, the higher ionic transport may allow batteries to undergo faster recharge.

![Dreamweaver Separator vs Polyolefin Separator](image)

Other companies address wettability differently. One company incorporates a surfactant or wetting agent into the separator to improve the wettability, which adds significantly to the price of the separator. While this may improve the initial wettability, there is no guarantee the surfactant will remain on the film surface during the battery production process or through cycling. Most other technologies suffer limitations which beg the question of a separator that has a more permanent hydrophilic nature than is provided by current polyolefin separators, either modified or unmodified.

V. Summary and Conclusions

Emerging applications, such as electric vehicles suffer the most from the inherent incompatibility between conventional lithium ion electrolytes and separators, because the size of the batteries for electric vehicles is larger than for consumer electronics uses. The separator designed to meet the needs of one market may not optimize performance for another. It would be very advantageous if the same separator could satisfy both the wettability requirement as well as the need for an increased thermal stability or high temperature performance also required for electric vehicles. Such a separator could have a huge impact on the electric vehicle market.
Modification of existing materials has not proven to be an effective way to address the concerns. A separator produced by Dreamweaver has shown a dramatic improvement in wettability compared to other separators. As such, it offers a unique opportunity to deal with challenges presented by new markets for lithium-ion batteries.

VI. References