WILD CAT SUPERTEMP® ELECTROLYTES
Wide Temperature Range Electrolyte Formulations for Start-Stop Vehicle Applications

Over the last decade, many governments have implemented more stringent regulations on vehicle fuel economy and CO\textsubscript{2} emissions. For example, European targets for new passenger cars reduce emissions to 130g CO\textsubscript{2} per kilometer by 2015, with further reduction to 95g by 2021. Start-stop vehicle engines, which shut off during stops for traffic or at a light, play an important role in achieving these targets. These vehicles require a battery with sufficient power to re-start the engine over a wide range of conditions and sufficient energy to run the lights, air conditioning, etc. on the vehicle when stopped. Therefore, these batteries need deliver high power when starting the car at low temperature, but also have good high temperature stability. In general, the power capability of the batteries suffers at low temperature due to 1) increase in viscosity of the electrolyte resulting in slower Li\textsuperscript{+} diffusion, 2) decrease in conductivity of the electrolyte, 3) decrease in conductivity of the solid electrolyte interphase (SEI) on the anode, and 4) decrease in diffusion of Li\textsuperscript{+} through the electrode materials, especially the anode.

Solutions to the low temperature problem generally consist of adding solvents with very low melting points and/or low viscosity to the formulation which keep the formulation from freezing or reduce the viscosity at low temperature. However, these solvents tend to be detrimental to high temperature stability, required to meet the lifetime requirements of the vehicle batteries. Alternative solutions to the low temperature problem include addition of electrolyte additives that affect the SEI formed on the anode. Some effects that may benefit low temperature power include thinner SEI layers or chemical compositions with higher Li\textsuperscript{+} ion conductivity at low temperature. Electrolytes with no SEI additives can show good low temperature performance (low impedance) because thin/poor SEIs are formed. However, these formulations show very poor high temperature stability. Conventional SEI additives such as vinylene carbonate (VC) or lithium bis(oxalato)borate (LiBOB) improve the quality of the SEI, but increase the low temperature impedance.

Wildcat has developed electrolyte formulations that improve the power performance at low temperature, but improve or maintain the high temperature cycle life relative to baseline electrolyte formulation. Wide temperature range formulations were developed for both NMC//graphite and NMC//LTO electrode chemistries.

Wildcat's strategic approach focused on both improved solvent compositions and new SEI additives. Test protocols included area specific impedances (ASI) determined at multiple states of charge (SOC) from hybrid pulse power characterization (HPPC) testing at 25°C (pulse/regen), -10°C (pulse/regen), and -25°C (pulse), as well as -30°C cold crank testing where the voltage at the end of a 30 sec pulse was tracked. High temperature stability was determined from a two week 60°C (100% SOC) storage test where ASI was measured before (initial ASI) and after storage (2\textsuperscript{nd} ASI).

Figure 1. Solvent composition has strong effect on reducing low temperature impedance (blue/purple is best result, gray/red is worst).
An example of the power of Wildcat’s high throughput approach is shown in Figure 1, which demonstrates the effect of solvent composition on -25°C ASI in NMC//graphite cells. Purple/blue areas in Figure 1 represent the lowest impedance at low temperature, and are desirable. Wildcat has identified a number of optimal solvent formulations with good low temperature performance. It does not appear that obvious trends can be established as solvent composition is varied. Therefore, many formulations need to be evaluated to identify the best solvents and solvent ratios.

For any particular solvent combination, additives have a profound effect on both low and high temperature performance. Wildcat has discovered a number of effective additive chemistries that enable large improvements in low temperature impedance and high temperature stability. Figure 2 shows an example of a set of additives that improve -25°C impedance at 50% SOC for NMC//graphite. When no additive is used in the solvent formulations, a low ASI is obtained (~220 Ω-cm) due to a thin or poor quality SEI. However, this formulation will have poor high temperature stability. Typically, VC, LiBOB, or both may be added to improve the high temperature stability. However, as shown in Figure 2, addition of these additives increases the low temperature ASI. Wildcat SEI additives 1 through 9 demonstrate reduced ASI at -25°C relative to formulations containing typical additives such as VC or LiBOB on NMC//graphite electrodes.

Results of the high temperature storage tests for a subset of additives are shown in Figure 3, where ΔASI is the growth in area specific impedance after the two weeks at 60°C/100% SOC. As expected, the formulation with no additives showed poor high temperature stability as evidenced by a large ΔASI. Addition of 1% VC also shows poor thermal stability. However, LiBOB substantially improves stability within almost no growth of ASI during high temperature storage. Addition of LiBOB to a formulation that contains VC also has high thermal stability. However, as previously shown – formulations containing VC or LiBOB have poor performance at low temperature. Wildcat additives 1 through 9 show excellent high temperature stability, similar to LiBOB, but ALSO maintain low impedance at low temperature on NMC//graphite electrodes.
During the discovery efforts, Wildcat identified many additives that improve low temperature performance without high temperature stability. Conversely, Wildcat also discovered many additives that improve high temperature stability, but are worse at low temperature. However, the combination of high and low temperature additives sometimes results in remarkable improvements in both metrics. An extensive high throughput study was performed with additive combinations including materials that performed well at low temperature, at high temperature, and at both conditions to find the best wide temperature range solutions.

Improved wide temperature range electrolytes were optimized by Wildcat with up to a 30% improvement in both low temperature impedance and high temperature storage. In Figure 4 shows the magnitude of improvement on both metrics. The dashed lines are the control formulations with 1% VC/0.5% LiBOB (black) or 0.5% LiBOB (red). Wildcat formulations A and B significantly decrease the ASI at -25°C (x-axis) while simultaneously maintaining a low ASI after 60°C storage for two weeks (y-axis). Additional formulations C and D reduce low temperature impedance while maintaining similar high temperature stability to the 0.5% LiBOB control. Results on these and other improved wide temperature range electrolytes were reproduced in large format cells at a battery company.

Wildcat also developed successful wide temperature range electrolytes for NMC//LTO cells. LTO operates at a much higher potential than graphite, such that an SEI is not expected to form using typical electrolytes. However, the high temperature stability of electrolytes on LTO tends to be very poor due to the catalytic nature of Ti$^{3+}$ in the charged state. Thus, solvent effects were expected to be much more important in electrolyte development for this system. However, Wildcat discovered important synergies between solvents and additives that provide improvements to both low temperature impedance and high temperature stability.

Since no SEI is necessary on the LTO due to its higher potential, most current electrolytes used with LTO contain propylene carbonate (PC) rather than ethylene carbonate (EC) as the high dielectric constant solvent due to PC’s lower viscosity and freezing point. Wildcat evaluated alternatives to PC in combination with a variety of low viscosity solvents (Figure 5), and identified promising alternatives to PC. While additives were initially assumed to be less
important to achieving good performance over a wide temperature range, Wildcat discovered a number of novel molecules that yielded remarkable improvement in combination with optimized solvent combinations. A strategy similar to the successful approach with NMC//graphite was used, in which the effects of individual additives on high temperature and low temperature performance were determined separately. From these results, additive combinations in a matrix of solvent formulations were designed and tested that were expected to show benefits at both temperature extremes.

Figure 6 shows the improvement at high and low temperature for a variety of additive/solvent combinations (different symbols). The non-PC based solvent formulation without additives reduces both the -25°C ASI and the growth of ASI during the high temperature storage. However, addition of additives can result a further reduction of nearly 40% from the starting PC-based formulation. In addition, the novel additives and solvent combinations result in very low ASI growth during the 60°C storage, demonstrating excellent high temperature stability.

Wildcat’s high throughput workflow was successfully utilized to rapidly identify electrolyte formulations with wide temperature performance on two different active material pairs. The unique high throughput workflow automates the entire discovery process, including material synthesis, electrode preparation, electrolyte formulation, cell assembly and testing - enabling the screening of hundreds of cells/week. Wildcat’s high throughput approach has been proven in multiple battery development projects, including the development of oxide and phosphate cathodes, and high voltage electrolytes for rechargeable batteries, high power carbon fluoride cathodes and electrolytes for primary batteries. The company has >90 collaborative research projects with large material suppliers, cell manufacturers, and OEMs and three DOE grants. In 2012, Wildcat was named one of the 50 most innovative companies by MIT Technology Review.