# Electrolytes for Lithium-ion Batteries with Wide Operating Temperature Range

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Lithium-ion batteries have been extensively investigated as power sources for electric vehicles due to their high energy density. Electric vehicle applications require a superior retention of performance (10-15 years of calendar life) over a wide range of temperatures (-30 to 60 °C). The electrolyte used in commercial lithium-ion batteries are composed of $LiPF_6$ dissolved in organic carbonates or esters, among which ethylene carbonate (EC) is a required component due to the importance of EC in the formation of the anode solid electrolyte interphase (SEI). However, $LiPF_6$ is very sensitive to environmental moisture and has poor thermal stability. Furthermore, EC leads to poor performance at low temperature due to its high melting point.

Lithium difluoro(oxalato)borate (LiDFOB) is a promising alternative lithium salt for lithium-ion battery electrolytes. The ligand exchange reaction of LiDFOB to generate Lithium tetrafluoroborate ($LiBF_4$) and Lithium bis(oxalato)borate (LiBOB) was investigated by Nuclear Magnetic Resonance (NMR) spectroscopy. A thermally induced equilibrium exists between LiDFOB, $LiBF_4$ and LiBOB and the equilibrium favors LiDFOB.

A novel salt, lithium tetrafluorooxalatophosphate [$LiPF_4(C_2O_4)$, LiFOP] was developed. It has much better thermal and hydrolytic stability and performance retention upon accelerated aging. This unique combination of properties makes LiFOP an interesting alternative to $LiPF_6$. The cycling performance of LiFOP electrolyte is compared with $LiPF_6$ electrolyte in the presence of several different electrode materials. In order to develop a better understanding of the sources of performance differences between LiFOP and $LiPF_6$, the surfaces of the electrodes have been analyzed after cycling.

Propylene carbonate (PC) is a good candidate for improving low temperature performance due to a low melting point, and comparable dielectric constant compared to EC. Unfortunately, replacing EC for PC in a $LiPF_6$ battery, results in continuous electrolyte reduction and exfoliation of the graphite anode. This problem can be solved by using LiFOP with PC. To confirm reversible cycling behavior of LiFOP/PC electrolytes, the cycling properties were investigated with a natural graphite anode and either $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ or $LiFePO_4$ cathodes. A comparison of the low temperature cycling performance of $LiPF_6$/EC electrolyte and LiFOP/PC electrolyte was also conducted.

**References**

1. Liu Zhou, Wentao Li, Mengqing Xu, Brett L. Lucht, *Electrochemical and Solid-State Letters*, 14 (11) A161-A164 (2011).

2. Liu Zhou, Swapnil Dalavi, Mengqing Xu, Brett L. Lucht, *Journal of Power Sources*,196 (2011) 8073– 8084.

3. Liu Zhou, Brett L. Lucht, *Journal of Power Sources*, 205 (2012) 439– 448.