Materials & Coatings

Use of Additives to Improve Performance of Methyl Butyrate-Based Lithium-Ion Electrolytes

A number of formulations are identified.

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This work addresses the need for robust rechargeable batteries that can operate well over a wide temperature range. To this end, a number of electrolyte formulations have been developed that incorporate the use of electrolyte additives to improve the high-temperature resilience, low-temperature power capability, and life characteristics of methyl butyrate-based electrolyte solutions. These electrolyte additives include mono-fluoroethylene carbonate (FEC), lithium oxalate, vinylene carbonate (VC), and lithium bis(oxalato)borate (LiBOB), which have been shown to result in improved high-temperature resilience of all carbonate-based electrolytes.

Improved performance has been demonstrated of Li-ion cells with methyl butyrate-based electrolytes, including 1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 v/v %); 1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 v/v %) + 2% FEC; 1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 v/v %) + 4% FEC; 1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 v/v %) + lithium oxalate; 1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 v/v %) + 2% VC; and 1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB. These electrolytes have been shown to improve performance in MCMB-$LiNiCoO_2$ and graphite-$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ experimental Li-ion cells.

A number of $LiPF_6$-based mixed carbonate electrolyte formulations have been developed that contain ester co-solvents, which have been optimized for operation at low temperature, while still providing reasonable performance at high temperature. For example, a number of ester co-solvents were investigated, including methyl propionate (MP), ethyl propionate (EP), methyl butyrate (MB), ethyl butyrate (EB), propyl butyrate (PB), and butyl butyrate (BB) in multi-component electrolytes of the following composition: 1.0M $LiPF_6$ in ethylene carbonate (EC) + ethyl methyl carbonate (EMC) + X (20:60:20 v/v %) [where X = ester co-solvent]. ["Optimized Carbonate and Ester-Based Li-Ion Electrolytes," *NASA Tech Briefs,* Vol. 32, No. 4 (April 2008), p. 56.] Focusing upon improved rate capability at low temperatures (i.e., –20 to –40 °C), this approach was optimized further, resulting in the development of 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 v/v %) and 1.20M $LiPF_6$ in EC+EMC+EB (20:20:60 v/v %), which were demonstrated to operate well over a wide temperature range in MCMB-$LiNiCoAlO_2$ and $Li_4Ti_5O_{12}$-$LiNiCoAlO_2$ prototype cells

This work was done by Marshall C. Smart and Ratnakumar V. Bugga of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1).

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Li-Ion Cells Employing Electrolytes With Methyl Propionate and Ethyl Butyrate Co-Solvents

These electrolytes can be applied to hybrid electric vehicles that incorporate wide-operating-temperature-range cells.

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Future NASA missions aimed at exploring Mars and the outer planets require rechargeable batteries that can operate at low temperatures to satisfy the requirements of such applications as landers, rovers, and penetrators. A number of terrestrial applications, such as hybrid electric vehicles (HEVs) and electric vehicles (EVs) also require energy storage devices that can operate over a wide temperature range (i.e., –40 to +70 °C), while still providing high power capability and long life. Currently, the state-of-the-art lithium-ion system has been demonstrated to operate over a wide range of temperatures (–30 to +40 °C); however, the rate capability at the lower temperatures is very poor. These limitations at very low temperatures are due to poor electrolyte conductivity, poor lithium intercalation kinetics over the electrode surface layers, and poor ionic diffusion in the electrode bulk.

Two wide-operating-temperature-range electrolytes have been developed based on advances involving lithium hexafluorophosphate-based solutions in carbonate and carbonate + ester solvent blends, which have been further optimized in the context of the technology and targeted applications. The approaches employed include further optimization of electrolytes containing methyl propionate (MP) and ethyl butyrate (EB), which are effective co-solvents, to widen the operating temperature range beyond the baseline systems. Attention was focused on further optimizing ester-based electrolyte formulations that have exhibited the best performance at temperatures ranging from -60 to +60 °C, with an emphasis upon improving the rate capability at –20 to –40 °C. This was accomplished by increasing electrolyte salt concentration to 1.20M and increasing the ester content to 60 percent by volume to increase the ionic conductivity at low temperatures.

Two JPL-developed electrolytes — 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 v/v %) and 1.20M $LiPF_6$ in EC+EMC+EB (20:20:60 v/v %) — operate effectively over a wide temperature range in MCMB-$LiNiCoAlO_2$ and $Li_4Ti_5O1_2$-$LiNiCoAlO_2$ prototype cells. These electrolytes have enabled high rate performance at low temperature (i.e., up to 2.0C rates at –50 °C and 5.0C rates at –40 °C), and good cycling performance over a wide temperature range (i.e., from –40 to +70 °C). Current efforts are focused upon improving the high temperature resilience of the methyl propionate-based system through the use of electrolyte additives, which are envisioned to improve the nature of the solid electrolyte interphase (SEI) layers.

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