Materials & Coatings

Improved Wide Operating Temperature Range of Li-Ion Cells

Applications include electric vehicles, where high-energy-density and high-power batteries are needed that can operate at low temperature.

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Future NASA missions aimed at exploring the Moon, Mars, and the outer planets require rechargeable batteries that can operate over a wide temperature range (–60 to +60 °C) to satisfy the requirements of various applications including landers, rovers, penetrators, CEV, CLV, etc. This work addresses the need for robust rechargeable batteries that can operate well over a wide temperature range.

The Department of Energy (DoE) has identified a number of technical barriers associated with the development of Li-ion rechargeable batteries for PHEVs. For this reason, DoE has interest in the development of advanced electrolytes that will improve performance over a wide range of temperatures, and lead to long life characteristics (5,000 cycles over a 10-year life span). There is also interest in improving the high-voltage stability of these candidate electrolyte systems to enable the operation of up to 5 V with high specific energy cathode materials.

Currently, the state-of-the-art lithium-ion system has been demonstrated to operate over a wide range of temperatures (–40 to +40 °C); however, the rate capability at the lower temperatures is very poor. In addition, the low-temperature performance typically deteriorates rapidly upon being exposed to high temperatures.

A number of electrolyte formulations were developed that incorporate the use of electrolyte additives to improve the high-temperature resilience, low-temperature power capability, and life characteristics of methyl propionate (MP)-based electrolyte solutions. These electrolyte additives include mono-fluoroethylene carbonate (FEC), lithium oxalate, vinylene carbonate (VC), and lithium bis(oxalate borate) (LiBOB), which have previously been shown to result in improved high-temperature resilience of all carbonate-based electrolytes. These MP-based electrolytes with additives have been shown to have improved performance in experiments with MCMB-$LiNiCoAlO_2$ cells.

A number of lithium-ion electrolytes having improved temperature range of operation were demonstrated. $LiPF_6$-based mixed carbonate electrolyte formulations that contain ester co-solvents have been optimized for operation at low temperature, while still providing reasonable performance at high temperature. In earlier work [see "Optimized Carbonate and Ester-Based Li-Ion Electrolytes" (NPO-44974) *NASA Tech Briefs*, Vol. 32, No. 4 (April 2008), p. 56], ester co-solvents, including methyl propionate (MP), ethyl propionate (EP), methyl butyrate (MB), ethyl butyrate (EB), propyl butyrate (PB), and butyl butyrate (BB), were investigated in multi-component electrolytes of the following composition: 1.0 M $LiPF_6$ in ethylene carbonate (EC) + ethyl methyl carbonate (EMC) + X (20:60:20 v/v %) [where X = ester co-solvent]. Focusing upon improved rate capability at low temperatures (i.e., –20 to –40 °C), this approach was optimized further [see "Li-Ion Cells Employing Electrolytes With Methyl Propionate and Ethyl Butyrate Co-Solvents" (NPO-46976), *NASA Tech Briefs*, Vol. 35, No. 10 (October 2011), p. 47], which resulted 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-$LiNiCoA1O_2$ and $Li_4Ti_5O_{12}$-$LiNiCoA1O_2$ prototype cells. In the current work, improved high temperature resilience, low temperature power capability, and life characteristics have been provided with methyl propionate-based electrolyte solutions [i.e., 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 v/v%)] possessing the additives described above.

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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Non-Toxic, Non-Flammable, –80 °C Phase Change Materials

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The objective of this effort was to develop a non-toxic, non-flammable, –80 °C phase change material (PCM) to be used in NASA's ICEPAC capsules for biological sample preservation in flight to and from Earth orbit. A temperature of about –68 °C or lower is a critical temperature for maintaining stable cell, tissue, and cell fragment storage.

Within this technical effort, two phase change fluids were developed with melting onset at –85 °C and –61 °C, and latent heat of fusion of 100 and 136 J/mL, respectively. The experimental results