

Safer electrolyte for lithium-ion batteries

Chi-Kyun Park and Robert Rubino
Greatbatch Medical
10000 Wehrle Drive, Clarence, NY 14031

Lithium-ion cells can swell and vent under abusive conditions because cell components such as electrolyte, anode and cathode release exothermic heat and gas¹. There is a limited understanding of how lithium-ion cells vent at elevated temperature. Thus, DSC of cell components in a hermetically-sealed stainless steel (SS) container² and a high pressure vessel test of electrolyte were performed. After DSC, the SS containers were cooled to RT and were punctured with a laser beam to create a hole in order to remove any gas that was formed during the DSC scan. The weight loss of the SS container was measured to determine the quantity of gas evolved by each cell component during the DSC study.

All of the major cell components, such as anode, cathode and electrolyte, released large amounts of exothermic energy (over 400 J/g) during DSC up to 400 °C. Electrolyte containing carbonate solvents released the most gas, over 70% of its original mass. Fully charged cathode and anode released gas equal to 4.6% and 3.9% of their original mass, respectively. This indicates that most of the gas generated at elevated temperature is from the electrolyte. Thus, electrolyte gas generation was studied based on various lithium salts and solvents. LiPF₆, LiBF₄, LiN(CF₃SO₂)₂, LiBETI and LiBOB were tested as the solute of the electrolyte²⁻⁵. In addition, various materials including flammable organics (carbonates and esters), and non-flammable organics [triphenyl phosphate (TPP), tetrachloroethylene (TCE), 1-ethyl-3-methyl imidazolium tris(pentafluoroethyl)trifluorophosphate (EMIT, ionic liquid)] were tested as the solvent of electrolyte.^{1,6,7}

The type of lithium salt significantly affected the exothermic heat of electrolyte decomposition by DSC. Gas generation with carbonate solvents was over 70% of the original mass regardless of lithium salt. Gas generation was mostly determined by the thermal stability of the solvent in the electrolyte. Among the solvents tested, GBL and TPP released the least amount of gas. However, TPP, a fire retardant, is a solid at room temperature and it provides poor cycle performance due to its poor stability on the graphite anode. In contrast, GBL did not effectively wet the polyolefin separator. In addition, GBL increased the self-discharge rate during storage and reduced the cycle life compared to carbonate solvents. Thus, it was necessary to use a co-solvent, such as 2-fluorotoluene (FT), for wetting the separator, along with additives, such as vinylene carbonate (VC) or poly(2-vinylpyridine-co-styrene), to improve the cycle performance of the cells.

A high pressure vessel was used to check the gas pressure of the non-aqueous electrolytes during heating up to 250 °C. As can be seen in Figure 1, electrolytes containing GBL, or a mixture of GBL and FT, had much lower vessel pressure than those with carbonate solvents (cyclic: EC, acyclic: EMC, DMC, DEC) or with a mixture of EC and GBL.

Lithium-ion cells containing GBL (major solvent), FT (co-solvent), and some additives exhibited similar cycle performance as the cells containing conventional carbonate solvents (Figure 2). Safety testing of the cells will be also reported.

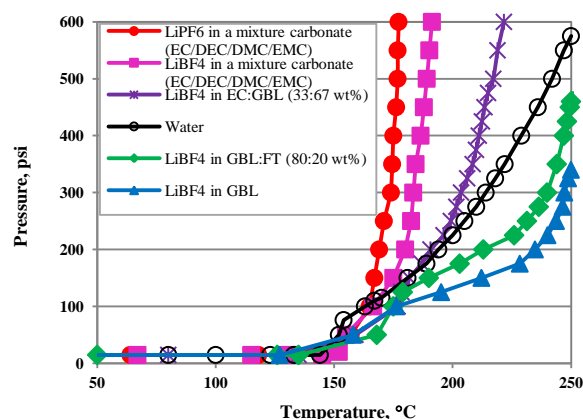


Figure 1. Gas pressure of the vessel based on electrolyte solvent at elevated temperature.

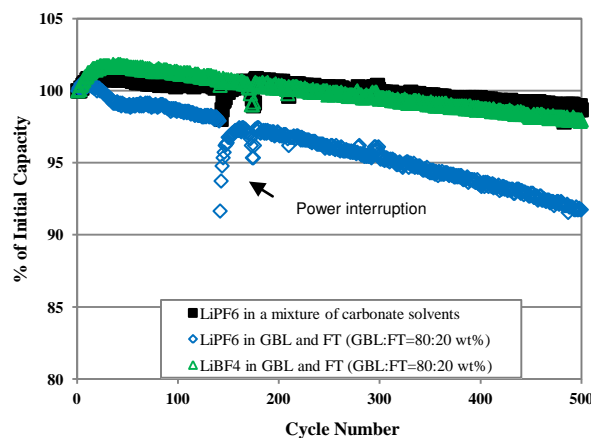


Figure 2. Cycle performance of Li_xC₆/Li_{1-x}CoO₂ cycled between 4.1V and 2.75V at C/2-rate

References

1. E. P. Roth and C. J. Orendorff, *Interface*, **21** (2), 45 (2012)
2. D. D. MacNeil and J. R. Dahn, *J. Electrochem. Soc.*, **150**, A21 (2003)
3. W. K. Behl and E. J. Plichta, *J. Power Sources*, **72**, 132 (1998)
4. T. R. Jow, K. Xu, M. S. Ding, S. S. Zhang, J. L. Allen, and K. Amine, *J. Electrochem. Soc.*, **151**, A1702 (2004)
5. C. Täubert, M. Fleischhammer, M. Wohlfahrt-Mehrens, U. Wietelmann and T. Buhrmester, *J. Electrochem. Soc.*, **157**, A721 (2010)
6. X. Xia, P. Ping, and J. R. Dahn, *J. Electrochem. Soc.*, **159**, A1834 (2012)
7. S. Seki, N. Serizawa, K. Hayamizu, S. Tsuzuki, Y. Umebayashi, K. Takei, and H. Miyashiro, *J. Electrochem. Soc.*, **159**, A967 (2012)