Performance Characterization of Lithium-Ion Cells Possessing Carbon-Carbon Composite-Based Anodes Capable of Operating Over a Wide Temperature Range

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Abstract:

NASA has interest in secondary energy storage batteries that display high specific energy, high energy density, long life characteristics, and perform well over a wide range of temperatures, in order to enable a number of future applications. Due to favorable performance attributes, lithium-ion technology has emerged as one of the most promising systems to meet these demanding performance requirements. Of these attributes, the ability to perform well over a wide range of temperatures (i.e., +40°C to –40°C) is, perhaps, the most challenging requirement to satisfy, especially at low temperatures. For this reason, at JPL we have focused our efforts on developing improved electrolyte formulations and demonstrating lithium-ion cells capable of operating over a wide range of temperatures. In this paper, we will present the results of the performance characterization of prototype lithium-ion cells that contain novel carbon-carbon composite anodes developed and fabricated by LiTech LLC. As part of the study, two different cell sizes were evaluated (4 Ah and 700 mAh) and the electrolyte type has also been varied with the intent of comparing the low temperature capabilities. The low temperature electrolytes studied include: 1.0 M $LiPF_6$ in EC + EMC (1:2 v/v %) [1], 1.4 M $LiPF_6$ in EC + EMC (1:3 v/v %) [2] and an electrolyte developed at JPL, 1.0 M $LiPF_6$ in EC + DEC + DMC + EMC (1:1:1:3) [3-4]. In addition to discussing the performance attributes at room temperature, the discharge characteristics at low temperature (with both charging at room temperature and at low temperatures), the impedance characteristics over a wide temperature range, and the polarization behavior of the cells will also be discussed.

Keywords: Lithium-ion cells; Novel carbon-carbon composite anodes; Low temperature electrolytes.

Introduction

MER Corporation (LiTech, LCC) has recently been actively involved in the development of novel carbon-carbon composite anode materials for lithium-ion battery applications. The carbon, graphite, carbon fiber, or "C-C composite" materials have the advantage of not containing any inactive materials, such as polymeric binders or metal substrates, allowing the entire electrode weight to become actively involved in the lithium-ion intercalation/de-intercalation process. [5-6] In addition, due to the fact that anode electrodes manufactured from the novel carbon-carbon composites do not contain metallic current collecting substrates, deleterious cell degradation reactions which can occur on over-discharge, such as copper dissolution, are eliminated. [7-8] Given the favorable attributes of these novel anode materials, which result in high specific energy and energy density, we were interested in evaluating the potential of this technology to meet JPL/NASA's future mission needs. In addition to requiring high specific energy and energy density rechargeable batteries, a number of future missions require energy storage devices which can operate over a wide temperature range. Thus, in collaboration with MER Corp., we undertook a study to assess the performance characteristics of a number of cells, in which the electrolyte type has been varied, with the objective of demonstrating improved low temperature capability

Experimental

A number of prismatic, pouch design cells were fabricated by MER Corporation (LiTech, LCC), consisting of carbon-carbon composite anode materials (as described above), $LiCoO_2$ cathode materials, and a number of ethylene carbonate (EC)-based electrolytes containing

$LiPF_6$. Initially, cells of 4 Ah capacity were evaluated which contained two different electrolyte types: a) 1.0 M $LiPF_6$ in EC + EMC (1:2), and b) 1.0 M $LiPF_6$ in EC + DEC + DMC + EMC (1:1:1:3 v/v %). Subsequent to this cell build, cells of 700 mAh size were fabricated which also contained two different electrolyte types: a) 1.4 M $LiPF_6$ in EC + EMC (1:3), and b) 1.0 M $LiPF_6$ in EC + DEC + DMC + EMC (1:1:1:3 v/v %). The cells were evaluated in terms of: i) the room temperature rate capability; ii) the discharge characteristics at low temperature (with both charging at room temperature and at low temperatures), iii) the impedance characteristics over a wide temperature range, and the iv) polarization behavior of the cells as a function of temperature. Charge-discharge measurements and cycling tests were performed with a Maccor battery cycler. A Tenney environmental chamber was used to maintain the desired temperature within $\pm$ 1°C for the cells.

Performance at Room Temperature

When the performance of the initial batch of 4Ahr cells was evaluated at room temperature, high specific energy was observed as anticipated. As illustrated in Fig. 1 in which the specific energy is displayed as a function of charge voltage, over 140 Whr/kg and 153 Whr/kg are delivered using a 4.10V and 4.20V charge voltage, respectively. This is especially noteworthy given the small cell size.

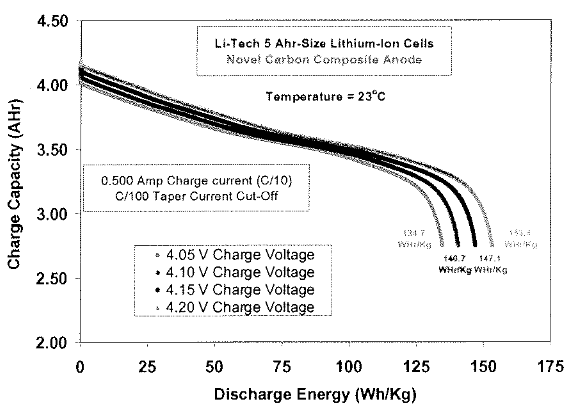

Figure 1. Specific energy of a MER 4 Ah cell containing the baseline electrolyte, 1.0M LiPF6 EC+EMC (1:2), at 23°C using different charge voltages and a C/10 discharge current to 2.75V.

Good rate capability of the cells was also observed at room temperature and found to be very similar for all of the electrolyte types evaluated. As shown in Fig. 2, over 92 % of the capacity delivered using a C/10 rate was obtained using a C/2 discharge rate (C rate designation based on nameplate capacity of 4.0 Ahr). This finding illustrates that reasonable rate capability can be obtained even without the presence of metallic substrates which serve as current collectors (e.g., copper foil).

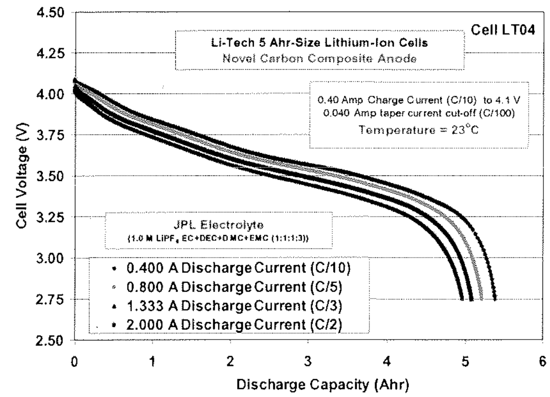

Figure 2. Discharge capacity as a function of discharge rate at room temperature of a MER 4 Ah cell containing a low temperature electrolyte (1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:3 v/v)

Discharge Characteristics at Low Temperature

Since many of NASA missions require good performance at low temperature, emphasis was placed upon evaluating the discharge characteristics of the cells at low temperatures (-20 to –60°C), using conditions of charging at both ambient and low temperatures. When the rate capability of one of the 4 Ahr cells containing the quaternary electrolyte was evaluated at –20°C (with both charge and discharge performed at low temperature), good performance was obtained with over 81% of the room temperature capacity delivered at a C/10 rate (4.374 Ahr), corresponding to over 122 Whr/kg. The cell also delivered reasonable performance using a C/2 discharge rate at –20°C (following a low temperature charge), corresponding to 74 Whr/kg and 60% of the room temperature capacity.

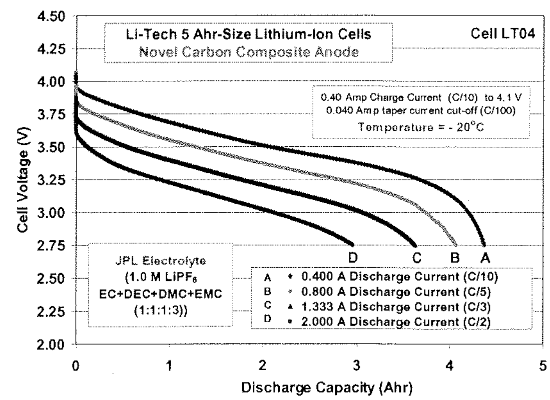

Figure 3. Discharge capacity as a function of discharge rate at –20°C of a MER 4 Ah cell containing 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:3 v/v).

As expected, higher discharge capacities were obtained when the cells were first charged at room temperature and then discharged at low temperature. Under these conditions, the cells were demonstrated to be capable of operating well down to very low temperatures. For example, a cell containing the quaternary low temperature electrolyte was observed to provide good performance to temperatures as low as –60°C using low discharge rates (i.e., C/20 rate) and a low end-of-discharge voltage (i.e., 2.0V rate). As illustrated in Fig. 4, over 80 Whr/kg was delivered at –40°C (3.718 Ah) and over 115 Whr/kg was delivered at –20°C (4.308 Ah) using a C/20 discharge rate.

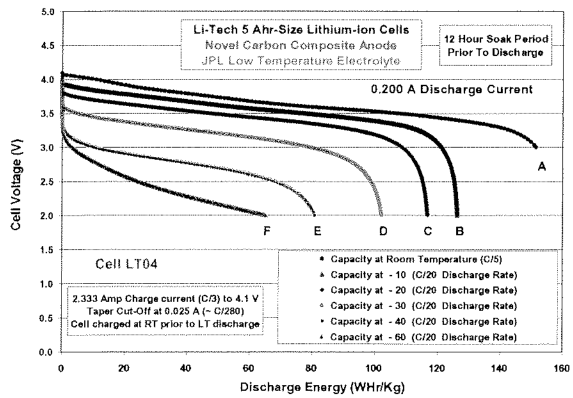

Figure 4. Discharge energy (Wh/Kg) as a function of temperature of a MER 4 Ah cell containing 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v %) electrolyte.

Effect of Electrolyte Type on Low Temperature Performance

As part of our study, we assessed the performance of a number of carbon-carbon composite-based LiTech lithium-ion cells with different electrolytes to determine the impact of electrolyte type upon the low temperature performance. At temperatures down to –20°C, all of the three low temperature electrolytes resulted in relatively comparable performance. However, when the cells were characterized below –20°C, especially using moderate rates (C/5 to C/20), the quaternary JPL electrolyte outperformed the binary electrolyte formulations. For example, as shown Fig. 5, the 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v %) electrolyte resulted in over 60% of the room temperature capacity when discharged at –40°C using a C/10 rate, whereas only ~ 40% of the room temperature capacity was deliver with the cells containing the binary mixture. Due to the fact that not all three electrolyte types were evaluated in the same cell size, the capacity was normalized in terms of the percentage of room temperature capacity for comparison purposes. Also apparent in Fig. 5 is the impact of cell size upon the low temperature performance, with the larger cell size resulting in slightly higher capacities. However, under the conditions studied, the electrolyte type had a more dramatic impact upon the observed performance.

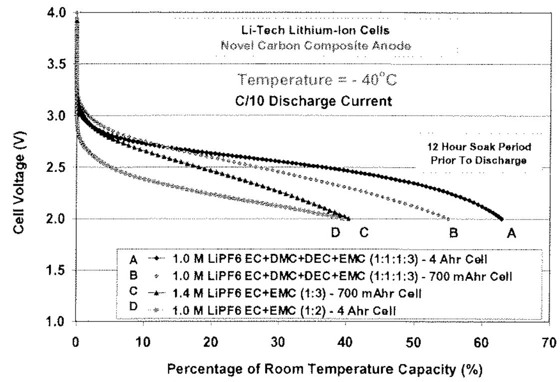

Figure 5. Percentage of the room temperature capacity delivered with cells containing different electrolytes at –40°C using a C.10 discharge rate.

This result can be rationalized, in part, by the fact that the quaternary electrolyte solution contains a lower proportion of ethylene carbonate (EC) (16.7 %), in contrast to the other two electrolytes which contain 33 % and 25% EC-content, respectively. Although high EC content typically results in highly conductive solutions at ambient temperature, due to the high dialectic constant and good Lewis basicity, at lower temperatures the high viscosity and high melting point of the solvent serve to reduce the ionic mobility. Another factor which can affect the low temperature performance, besides the ionic conductivity of the electrolyte, is the impact that the electrolyte type has upon the nature of the solid electrolyte interphase (SEI) layers on the electrodes, especially the carbon anodes, and the corresponding lithium intercalation/de-intercalation kinetics. Additional experiments, including electrolyte conductivity measurements and characterization in half-cells or three-electrode cells, must be performed on all three electrolyte types to determine the relative contributions of each factor.

As illustrated in Fig. 6, when the low temperature performance of a cell (700 mAhr size) containing the quaternary, low EC-content electrolyte is summarized in terms of discharge rate (C/5 to C/20) and temperature (-20 to –50°C), it is apparent that reasonable performance is obtained to –50°C using low rates (C/20). However, the discharge capacity precipitously falls upon using more aggressive rates at the very low temperatures (e.g. C/5 at –50°C and below). Thus, in order to achieve enhanced high rate performance at very low temperatures (< -50°C), further improvements in the low temperature electrolyte ionic conductivity and/or improvements in the lithium kinetics (in the bulk of the electrode materials and through the SEI layers) must be made.

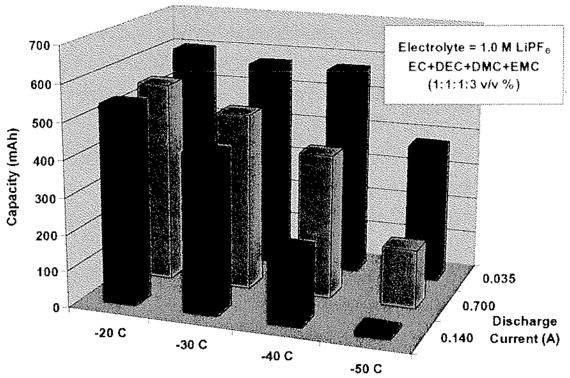

Figure 6. Discharge capacity as a function of discharge current and temperature for a 700 mAh LiTech lithium-ion cell containing a quaternary low temperature electrolyte, 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v %)

Conclusions

In this paper, we have presented the results of the performance characterization of prototype lithium-ion cells that contain novel carbon-carbon composite anodes developed and fabricated by LiTech LLC. As part of this study, two different cell sizes were evaluated (4 Ah and 700 mAh) and the electrolyte type has been varied with the intent of comparing the low temperature capabilities. When the rate capability of one of the 4 Ahr cells containing a quaternary electrolyte was evaluated at –20°C (with both charge and discharge performed at low temperature), good performance was obtained with over 81% of the room temperature capacity delivered at a C/10 rate, corresponding to over 122 Whr/kg. When the cells were evaluated at even lower temperatures, over 80 Whr/kg was delivered at –40°C using a C/20 discharge rate (room temperature charge). Comparable performance was obtained with all three different electrolytes at temperatures of –20oC and above; however, at lower temperatures (and especially using higher rates) the quaternary low temperature electrolyte was observed to out-perform the binary mixtures consisting of EC+EMC. This trend may be attributed to differences in electrolyte conductivity at these low temperatures and differences in the nature of the electrode SEI layers, and the resulting influence upon the lithium intercalation and de-intercalation kinetics. Experiments are on-going in an effort to resolve the more dominant of the two factors to further understand the influence of the electrolyte type upon the low temperature performance of lithium-ion cells. In summary, high specific energy cells containing a novel carbon-carbon composite anode material have been demonstrated to provide excellent low temperature performance when coupled with advanced low temperature electrolytes.

Acknowledgements

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, for an internal JPL research and technology development (R&TD) program to develop low temperature lithium batteries under contract with the National Aeronautics National Aeronautics and Space Administration (NASA).

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