Project Research — Development of a Supply/Demand Infrastructure for Next-generation Electric Power

Lithium Secondary Batteries with Reliable Safety

Background and Objective

Dispersed battery energy storage systems are expected to be used in residential applications (kWh-class) and on-site leveling operations of renewable power generation (MWh-class). Although lithium secondary batteries exhibit high energy density, energy efficiency, and rate capability, the determination of long duration life and reliable safety in large batteries is needed to perform installation on a system level. This subject shows the direction at which to build up lithium-ion battery performance during long-life operation using non-destructive and simple analysis techniques. In addition, this subject proposes the improvement of battery performance of all-solid-state lithiumion batteries using solid polymer electrolyte. The proposed battery is expected to improve safety, cost performance, and simple large battery production compared to the conventional lithium-ion batteries with flammable liquid electrolyte.

Main results

Lithium-ion Battery Evaluation: Development of Performance Evaluation Using Actual Operation Patterns

Although the life evaluation of lithiumion batteries is generally determined using constant current charge-discharge operation, actual operation includes complicated charge/ discharge patterns. We thus compared the capacity degradation between simulated leveling cycle patterns of photovoltaic (PV) power generation (real PV cycle operation) and constant current cycle operations. We assume that capacity degradation can separate cycle operation factors and duration factors. Further, we found that the extracted cycle degradation ratio was independent of operation patterns, which suggested that we could evaluate the battery degradation in actual operation by using a simple constant current operation protocol (Fig. 1) (Q11015).

2 Lithium-ion Battery Evaluation: Development of Degradation Component Evaluation

The understanding of battery performance degradation from basic battery components is important for precise battery life evaluation. We proposed to estimate the cathode component ratio from the derivative analysis of the voltage profile in (LiMn2O4: LMO)/(LiNi1/3Mn1/3C01/3O2:

NMC) mixed cathode materials without disassembling the cell. This procedure could also apply to the estimation of the degradation factor in the mixed cathode materials (Fig. 2) (Q11022).

Development of an All-solid-state Lithium-ion Battery: Achievement of Comparable Long Life to that of Commercialized Cells

All-solid-state lithium-ion batteries using solid polymer electrolyte have compatibility with the cathode and anode materials that were already used in conventional lithium-ion batteries. In addition, the proposed battery is expected to reduce the assembly cost and can produce large formats without difficulty. These features are superior to those of other all-solid-state batteries. We introduced an antioxidant into the electrolyte to reduce the side reaction between 4-V class cathode material (NMC) and solid polymer electrolyte with a suitable choice of lithium salts, and established 1,500-cycle operation using a lithium metal anode (Fig. 3) (Q11017) (Q11020). Furthermore, we assembled an allsolid-state lithium-ion battery using aluminum laminate housing, graphite anode, and NMC, and exhibited 500-cycle reversible operation (Fig. 4) (Q11014).



Fig. 1: Relative capacity retention of batteries in an actual PV cycle and constant cycle operation

Capacity retentions of the actual PV pattern cycle (\diamondsuit) , constant current cycle (\bigcirc) , and corrected capacity retentions without duration degradation factor (\diamondsuit : real PV pattern cycle, \boxdot : constant current cycle); the corrected results exhibited similar degradation trends, which suggested that we could estimate the battery capacity degradation of actual operation by using a simple constant current condition.



Fig. 2: Comparison of relative capacity in a degradated mixed cathode

Voltage profiles (cell voltage response to electrode capacity) exhibit each unique characters such that each electrode capacity ratio obtained from the derivative analysis (•) showed good corresponsive trends to those obtained from the loading weight ratio.



Fig. 3: Cycle performance of 4 V-class cathodes and lithium metal anodes

An optimized cell with a 4 V-class cathode, solid polymer electrolyte, and lithium metal exhibited the longest operation of 1,500 cycles.

Operation temperature: 60° C, capacity retention at an eight-hour rate



Fig. 4: Cycle performance of an all-solid-state lithium-ion battery using a 4 V-class cathode, solid polymer electrolyte, and graphite anode

An all-solid-state lithium-ion battery with electrode materials compatible with those of conventional lithiumion batteries showed good cycle performance comparable to that of commercialized lithium-ion batteries.

Operation temperature: $60^\circ\mathrm{C}\text{,}$ capacity retention at an eight-hour rate