SUMMARY OF Ph.D. DISSERTATION

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Title

Development of long-cycle-life lithium secondary batteries using graphite-coke hybrid carbon

Abstract

Recently, there have been increasing demands for better specifications of batteries used as the power supply for cellular phones and portable personal computers. These demands have arisen with the continuing advances in the performance of such devices. In addition, from an environmental viewpoint, much attention has been paid to the development of large-sized batteries for a power storage system that can be integrated with a clean power generation system.

These requirements form the background to develop 2 kWh class lithium secondary cells. In order to realize a long cycle life, various combinations of positive and negative electrode candidate materials were examined experimentally. At the same time, cycle deterioration factors were investigated during charge-discharge cycle tests.

First, the charge-discharge performance and cycle performance of carbon materials were examined and it was found that a graphite-coke hybrid carbon showed superior characteristics. Furthermore, the states of Li intercalated in carbons and Li compounds on the surface of carbons were analyzed by ^{7}Li NMR spectroscopy, and thus the different factors among graphite, coke and graphite-coke hybrid carbon were elucidated.

Next, in order to find the optimum combination for long cycle life, the x value in $LiNi_{1-x}Co_xO_2$ and the mixture ratio of graphite and coke were examined. Here, it was found that the combination of $LiNi_{0.7}Co_{0.3}O_2$ and graphite-coke hybrid (4/1) carbon showed superior performance in a charge-discharge cycle test, which was conducted under simulated load-levelling systems.

Furthermore, in order to clarify the factors of a battery's capacity fade, the batteries after 2000 and 2350 charge-discharge cycles were decomposed to analyze the positive and negative electrodes. It was confirmed that both the positive and negative electrodes showed 86 and 92% discharge capacity of the initial state, although after 2350 charge-discharge cycles the capacity deterioration of the battery showed 70% of initial discharge capacity. It was also confirmed that the impedance of the negative electrode further increased, which suggested an increase in the quantity of SEI consisting of LiF, Li_2CO_3, and polymers. By clarifying the use domain of the positive electrode in a battery after a long charge-discharge cycle test, it was found that the capacity fade was mainly caused by the decreased amount of active lithium available for charge-discharge and by the deterioration of rate performance caused by the increased impedance of the negative electrode.

Through this development, longer cycle life was achieved, beyond the limitations of conventional batteries. In addition, the clarification of the deterioration mechanism is valuable for the engineering that will be needed to solve future problems and to further advance cycle performance technology.