Floating charge voltage dependency on lithium-ion battery lifetime

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Introduction

More compact batteries are required to replace the lead-acid batteries currently used in applications such as telecommunications backup. Accordingly, lithium-ion rechargeable batteries (hereafter, Li-ion batteries), which boast a high energy density, are expected to significantly contribute to the compactization of batteries for use in telecommunications. As for application as a backup power source for telecommunications batteries, it is necessary to continually maintain a battery in a state close to full charge. The inputs of communication devices are direct current, and the range of input voltages is different depending on the device. Therefore, it is necessary to match the battery charge voltage to within that range. Li-ion batteries using manganese-spinel cathode material (1) were accordingly fabricated and float charged at four different voltages to investigate charge voltage dependency on battery lifetime.

Sample battery

In this examination, we fabricated 18650-type cylindrical Li-ion batteries (capacity: about 0.7 Ah) using an EC/DMC-based electrolyte and manganese-spinel positive material.

Experimental

The sample batteries were charged at four voltages (4.05 V, 4.10 V, 4.15 V, and 4.20 V). The environmental temperature during float charging was kept at 50°C. The sample batteries were discharged periodically at a current of 0.2 CA (25°C) and their capacities then ascertained.

Results

Figure 1 shows the charge voltage dependency of the initial capacity at discharge current 0.2 CA. There was no special difference seen at 4.15 and 4.2 V, though a tendency for the capacity to increase as the floating charge voltage became higher was seen from 4.05 to 4.15 V. We presume that an increase in capacity is not effective even if the floating charge voltage is raised because the voltage increases steeply at 4.15 and 4.2 V according to the characteristic of the manganese-spinel cathode material.

Figure 2 shows the lifetime of each floating charge voltage. The lifetime is defined as the duration at which the discharged capacity remains under 70% of the initial capacity. We found that the lifetime decreased greatly between 4.15 and 4.2 V, presumably due to the phenomenon of deterioration caused by electrolyte decomposition since this test was performed at 50°C. The lifetime at 4.05 V was slightly shorter compared with that at 4.10 and 4.15 V. The reason for this is uncertain.

From our current research (2), we reported the cause of deterioration in Li-ion batteries using manganese-spinel cathode material under float charge as follows. The cause is due to the increase in the thickness of the solid-electrolyte-interface (SEI) film that formed on the anode over time because the SEI film formation involves lithium ion consumption, which reduces the number of mobile lithium ions in the cell. The deterioration degree is too high for the amount of manganese elution from the cathode to increase. Therefore, we analyzed the element extracted on the anode by XPS and found that 430–740 times the lithium was detected in the deteriorated anode compared with the electrochemical equivalent of the extracted manganese. It also seems that the majority is an organolithium compound. We presume that the decomposition of the electrolytes etc. is promoted by the manganese extraction on the anode, which consumes the lithium in the battery and thereby accelerates the deterioration of the battery.

Reference

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(2) T. Tsujikawa, K. Yabuta, T. Matsushita, M. Arakawa, K. Hayashi, J. Electrochem. Soc.,158, 322 (2011).

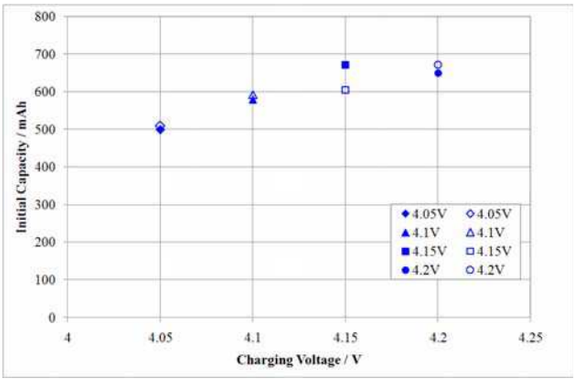

Figure 1. Charge voltage dependency of the initial capacity at discharge current 0.2CA

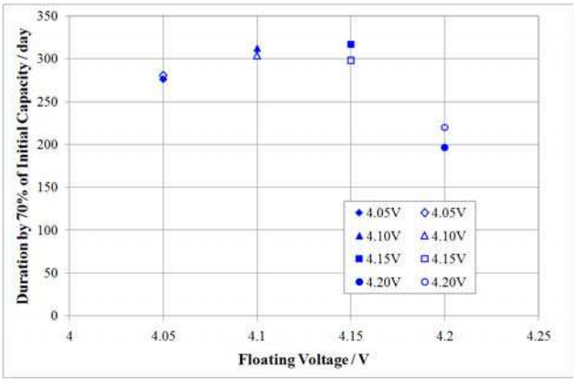

Figure 2. Lifetime in each floating charge voltage