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Development of High power and Long life Lithium secondary batteries

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Lithium-ion batteries have been widely used for lap-top PC, cellular phones and DSC applications as they have high energy density. Rising of environmental awareness, lithium-ion batteries are expected to be applied to automobile applications and electric energy storage use. For Plug-in Hybrid Electric Vehicle (PHEV) and Battery Electric Vehicle (BEV) applications, longer calendar life is necessary compared to the conventional usage.

The $Li(Ni,Co,Al)O_2$-based cathode, which is known to be a high capacity active material, showed better durability in storage tests and cycle tests than the other cathode materials ($LiCoO_2$, $Li(Ni,Mn,Co)O_2$).[1-3] For EV or home electric storage applications, we proposed a multipurpose standard module composed of 140 18650-type cylindrical cells with above-mentioned $Li(Ni,Co,Al)O_2$-based cathode.[1,3]

In order to enhance battery durability, deterioration behaviors of $Li(Ni,Co,Al)O_2$-based cathode / graphite cells (400 mAh cylindrical type) were investigated. The cells used in this investigation were composed of $LiNi_{0.76}Co_{0.14}Al_{0.10}O_2$ cathode, graphite anode, electrolyte and micro-porous polyethylene separator. Electrolyte was a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) with lithium hexafluorophosphate ($LiPF_6$).

Fig.1 shows the results of storage tests of the cells. Storage tests were performed at either SOC (State of Charge) of 30 or 90% and at temperatures of 25 or 60℃. As shown in Fig.1, the change ratios in capacity and DC-IR (Direct Current Inner Resistance) depended on SOC and temperature, respectively.

Fig.2 shows the results of charge/discharge cycle tests of the cells. Cycle tests were performed in voltage range of 3.60 to 4.05V at either operated current rates of 2 or $1I_t$ and at temperatures of 25 or 50℃. As shown in Fig.2, the change ratios in DC-IR depended on temperatures while no significant correlation between capacity fade and operated current or temperature was observed.

In order to identify the causes of deteriorations in capacity and DC-IR, tested cells were disassembled after storage and cycle, and then various analysis were performed by using scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and so on. We will discuss in detail about deterioration mechanisms from these analysis data.

References

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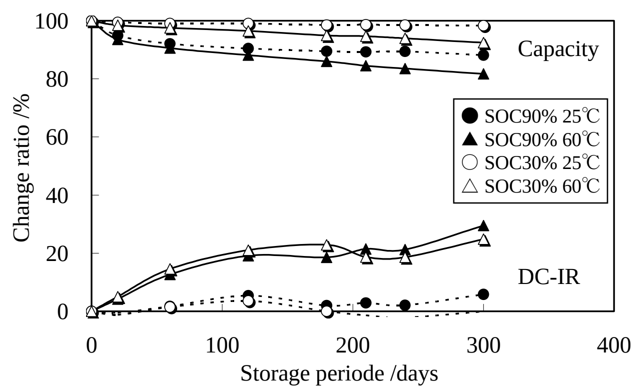

Fig.1 Storage characteristics of tested cells. Closed and open symbols indicate stored SOC of 90 and 30%, respectively. Circles and triangles indicate stored temperatures of 25 and 60℃, respectively. The vertical axis indicates the change ratio in discharge capacity or DC-IR with respect to the initial value.

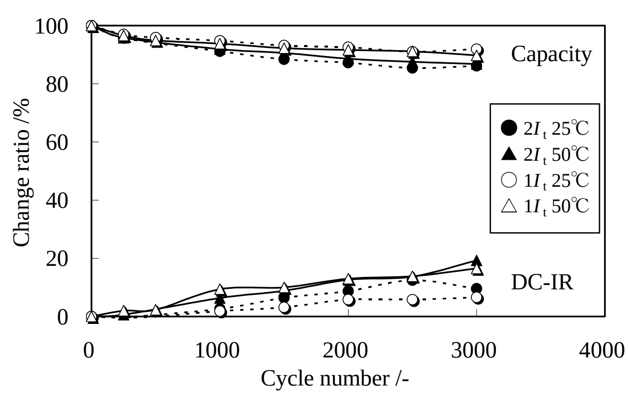

Fig.2 Charge/discharge cycle characteristics of tested cells. Cycle tests were performed in voltage range of 3.60 to 4.05V. Closed and open symbols indicate operated current rates of 2 and $1I_t$, respectively. Circles and triangles indicate ambient temperatures of 25 and 50 ℃, respectively. The vertical axis indicates the change ratio in discharge capacity or DC-IR with respect to the initial value.