Dilation Behavior of Anode Material for Lithium-ion Secondary Battery

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Introduction

It is well-known that graphite material for the anode of Lithium ion secondary battery shows dilation/shrinking during Li intercalation/de-intercalation. Besenhard et al. have observed the dilation/shrinking of a HOPG with their spring-dilatometer system[1]. Although the theoretical amount of expansion for a graphite particle is below 10% if c-axis dilates, the composite anode made by graphite particles and polymer binder shows more amount of expansion. Ohzuku et al. have reported the composite anode shows abnormal expansion during first Li intercalation.[2] It is important to recognize dilation phenomenon of the anode when designing battery such as prismatic cell or laminate cell. We found that the dilation of composite anode is due to (1) non-electrochemical swelling of anode, (2) reversible dilation/shrinking of electrode during intercalation/de-intercalation, (3) irreversible dilation due to SEI film formation.

Experimental

As the new type of carbon materials, spherical synthetic graphite (MCMB, Osaka-gas Chemical), synthetic graphite (SFG44, Timical), spherical artificial graphite A, and B (MCC) were used in this study. The crystal intensity ratio for z-axis to the x and y-axis (110/004) was measured using X-ray diffraction-meter (JEOL JDX-3500). This intensity obtained is shown in Table.1 with material properties.

Carbon electrode was prepared by coating slurries of the above new type carbon powder and water-soluble binder (Carbonpowder/SBR/CMC=96.5/2/1.5, 10mg/cm^2) on copper foils. The electrode thickness after drying at 130℃ for 10hrs , "Spring-back", and the thickness after soaking in electrolyte for 36hrs, "Swelling" were measured, base on the thickness just after pressing electrode. Throughout the measurements of swelling and dilation, the spot of electrolyte was wiped out. After drying, electrode swelling thickness was measured by the micrometer (Mitsutoyo Degimatic Indicator). All cells were charged and discharged in the potential range of 0-1.5V vs. Li/Li$^+$ for 4 cycles and stopped at 300 mAh/g at 5th cycle. The dilation of electrodes was measured at this point.

Results and Discussion

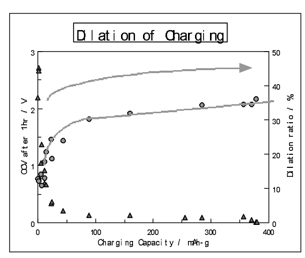
We observed the thickness-back after drying electrodes (Spring-back process) and that after soaking electrodes in electrolyte (Swelling process). In this study, we found that the amount of spring-back depends on line-pressure when the electrode presses and that the amount of swelling is almost constant irrespective of the kinds of material (Table.1). In case of spherical artificial graphite B, the electrode suddenly dilates at the lower capacity and does slowly at higher capacity during the intercalation process. During the de-intercalation process, electrode shrinks and shows the same locus with that of intercalation, but the electrode thickness was not returned to the initial thickness even if the voltage sweeps to the 1.5 V vs. Li$^+$ (Fig.1). The thickness is recovered when the voltage is up to the 2.0 V vs. Li$^+$ (Fig.2). This reason might be due to SEI film dissolution. From this result, we considered that SEI film formation also effects on the electrode dilation. The net dilation (the amount which subtracts spring-back and swelling from apparent dilation) decreased with the increase of the 110/004. This is caused by the relaxation of dilation towards the three-dimensional direction, accompanying with Li-GIC formation.

Conclusions

We found that there were two processes in the dilation of anode for Li-ion secondary battery in this study. One is "irreversible dilation process", and the other is "reversible dilation process". In the irreversible dilation process, spring-back and swelling are contained. The reversible dilation is controlled by the amount of charge and crystal orientation of electrode. Moreover, this also contains the effect of SEI film formation.

Table.1 Properties of anode materials.

Sample Name	Mean Diameter (μm)	Crystal Orientation (110/004)	Tap Density (g/cc)	Specific Surface Area (m2/g)	Line-pressure @1.5g/cm3 (Kg/5cm)	Spring-back (%)	Swelling (%)	Net dilation (%)
MCMB	22	0.122	1.47	0.9	960	12	6	41
SFG44	20	0.002	0.52	5.2	220	3	4	35
Graphite A	25	0.037	1.04	2.1	250	3	5	34
Graphite B	20	0.008	1.08	2.6	210	2	5	34



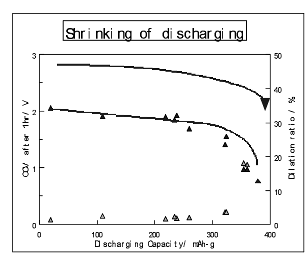


Fig.1 Dependence of charging capacity and dilation ratio. (Left)

Fig.2 Dependence of discharging capacity and dilation ratio. (Right)

References

[1]J.O.Besenhard, M.Winter, J.Yang, and W.Biberacher, J. Power Sources, 54, 228 (1995).

[2]T.Ohzuku, Y.Orita, and Y.Makimura, Abstract of the 42nd Battery Symposium, Yokohama, Japan, 1A19 (2001).