# Development of Surface Modified Carbon Anode Material for High-Power Lithium-Ion Battery

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Since Lithium ion battery was commercialized in 1991, 19 years has passed. So far Lithium ion battery has been mainly used for mobile application such as Note book PC, Cellular phone and so on. Therefore Lithium ion battery has contributed to "Smaller" "Lighter" and "Longer operating time" for this mobile apparatus.[1)] As anode material, Graphite has bees applied for most of battery due to enable for high energy density. Hitachi Chemical Co. Ltd has developed high performance artificial graphite anode material "MAG" in 1999, which has high discharge capacity especially under harsh circumstances (high current density, low temperature). After that the energy density of mobile apparatus has increased progressively. [2)]

Recently, the promotion of Lithium ion battery for high power application such EV/HEV and power tool is going on due to environmental and performance reason.[3)] In these applications high power density has more priority than energy density, as well as long life (cycle and storage). In general pure Graphite anode material shows poor power and cycle by formation of membrane (called "SEI"), and it was formed by the decomposition of electrolyte with active site on Graphite at first cycle. And it has high resistance and unstable morphology during cycle. Amorphous carbon such as hard carbon has good power and longer life in comparison with Graphite due to high stability with electrolyte. However this material normaly shows poor energy as disadvantage compare with Graphite anode. Accordingly appearance of highly performed Graphite anode material is expected. So Hitachi Chemical has started to develop "Surface Modified Graphite (SMG)" which coated by amorphous carbon on Graphite surface to remove active site.

In this investigation, as Graphite Core, Spherical Natural Graphite by Chinese producer "A" were selected. Coal Tar Pitch and Specified resin was used as precursor of coated amorphous carbon. As a modification way, „Wet" process using solvent and „Vapor" process which ware developed by Hitachi Chemical originally were investigated.

As powder character SEM, TEM observation, BET surface by $N_2$ were measured to clarify micro- macro structure. As electrochemical properties charge-discharge capacity, Direct current resistance (DCR) and cycle life were measured by coin cell which apply Li-metal as counter and reference. In coin cell anode was prepared with 1% of SBR binder and 1% of CMC.

SEM and TEM micrographs of surface modified Natural Graphite were shown in Fig.1.
The particle keeps spherical shape and surface is very smooth after modification. Crystal structure in surface shows two different morphologies clearly. Against highly oriented linear crystal structure (Needle like structure) was observed in core, the surface is composed by random like. Although the boundary is divided clearly, any crevice is not observed.

Powder character for natural Graphite before and after modification were shown in Table 1. The relation with degree of modification (amount of amorphous) and modification method were investigated. By surface modification, as amorphous contents increase, particle size also increased and BET surface decreased. Comparing modification method vapor method shows lower particle size and BET surface in same amorphous contents. It is considered amorphous coating was made not only on surface but also void in inside of particle by vapor, against by dry method amorphous was covered mainly on surface.

DCR is closely related to power input and output in battery and it is very important property for EV/HEV which require instant driving accelelation, and measued result was shown in Fig2. It is considered that the resistance in anode is related by some factor such as particle shape, conductivity of particle and surface condition.[4)] In this investigation DCR measurement was made in full charged stage, so SEI was formed on anode. Accordingly in this investigation DCR would be influenced by mainly SEI. In generally Graphite forms thicker SEI caused by much active site. In this investigation, comparing blank (N1) surface modification has the effect to decrease DCR. It is caused from Surface Modified Graphite leads to less SEI formation. However larger amorphous contents show higher DCR. It is considered that much amorphous has higher resistance than SEI. Comparing modification method Vapor shows less DCR. It was also caused from inter-site amorphous coating. It was also reasonable that finer particle shoes lower DCR due to much diffusion pass for Li ion.

As purpose of the development in anode material for high power Lithium ion battery, surface modification for Graphite was investigated. It was observed this technology has good contribution for decreasing of resistance in anode, and it leads to the improvement of power for Lithium ion battery directly. As detail conditions lower amorphous coating and finer particle have effect for it as well as vapor way.

**References**


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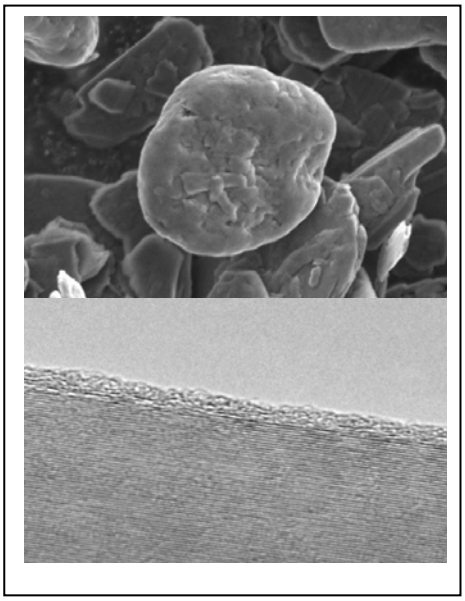

Fig1.SEM and TEM of „SMG“

| No. | N1 | N2 | N3 | N4 | N5 |
|---|---|---|---|---|---|
| Core | Spherical Natural Graphite | | | | |
| Degree of Modification (%) | Non | 2 | 4 | 2 | 2 |
| Modification Method | Non | Dry | Dry | Vapor | Dry |
| APS of Sample | 10.2 | 10.8 | 11.7 | 10.4 | 7.3 |
| BET surface (m2/g) | 6.5 | 5.5 | 2.8 | 5.2 | 8.4 |

APS: Average Particle Size (micro meter)

Table1. Powder Character of Before/After Modification

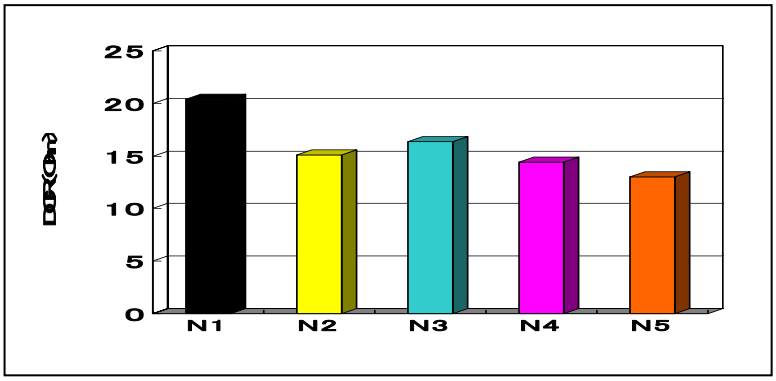


Fig.2 DCR Evaluation Result