Soft Carbon-coated Hard Carbon Beads as a Lithium-ion Battery Anode Material

Masaki Yoshio,* Hongyu Wang,[†] Kenji Fukuda,[††] Takeshi Abe,[†] and Zempachi Ogumi[†]
Department of Applied Chemistry, Saga University, 1 Honjo, Saga 840-8502
[†]*Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501*
[††]*Research Center, Mitusi Mining, 1-3 Hibikimachi, Wakamatsu-ku, Kitakyushu 808-0021*

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Thermal vapor decomposition (TVD) process has been applied to coat soft carbon onto the surface of hard carbon beads. The resultant spherical hard–soft carbon composites with "core-shell" structure demonstrate better electrochemical performance than the starting hard carbon beads as anode materials in lithium-ion batteries. The effect of TVD-carbon shell on the electrochemical performance was correlated with some physical properties.

Today graphite is commonly used as the anode material in commercialized lithium-ion batteries mainly because of its low and flat working voltage. From the viewpoint of capacity, a disordered carbon becomes a strong contender as well as graphite among the big family of carbonaceous materials. We have prepared hard carbon beads by the carbonization of naphthalenesulfonate–formaldehyde (NSF) resin and correlated the electrochemical performance with some carbonization factors.[1] But there is still a long way before the practical use of hard carbon beads in lithium-ion batteries. It is expected that lithium transportation in hard carbons is very slow since lithium clusters are stored in the small pores made of disorderly-stacked graphene layers, thus lithium diffusion routes inside hard carbons are long and winding, which is in big contrast with the straight-forward way for easy lithium movement between graphite layers. If the hard carbon was charged at higher rates, while lithium insertion into hard carbon from the outer surface is too sluggish to keep up with current's pace, the voltage will drop down rapidly and touch 0 V against lithium metal. In such cases, lithium metal is likely to plate on hard carbon surface and cause hazards. But the bulk of hard carbon is only partially lithiated and shows lower capacity. To ensure adequate lithium storage, hard carbon could be charged at slow rates to a low voltage (even several millivolts lower than lithium metal) or held at some low voltage for rather long time after being charged with constant current.[2–4] In addition, it is well known that the electric conductivity of hard carbon generally is not so high. Hard carbon beads construct the electronically conducting network merely through point contacts between adjacent small spheres so that the potential/current distribution on the hard carbon electrode is highly inhomogeneous. This will cause local high-density current flow, which decrease the lithium capacity of hard carbon beads drastically.

To solve the above problem, one way is modification of the surface of hard carbon beads. In our previous studies, we have applied TVD technique to coat soft carbon onto the surfaces of natural graphite and Si particles, respectively.[5–9] It is expected that the TVD-carbon on the surface of hard carbon beads shows higher electric conductivity values than hard carbon. Then lithium enters into the carbon spheres all over the surface rather than the contacting points. Moreover, lithium ions appear to transport more quickly in the TVD-carbon phase because of the high orientation of graphene layers.

In this letter, we will show that the TVD-carbon coating could not only greatly improve the electrochemical performance of both natural graphite and Si, but also helps for hard carbon.

NSF resin-derived hard carbon beads have been prepared as described in Ref. 1. NSF carbon beads were spread as a thin layer (<3 mm) on a graphite substrate inside a quartz reaction tube. Benzene vapor was carried by N_2 flow and fed into the reaction tube. Generally the temperature of the reaction tube was controlled at about 850 °C. At such high temperature, benzene decomposed and deposited onto the surface of carbon beads as a TVD-carbon layer. TVD process lasted for about 30 min, and then the heating power was switched off. Partly TVD-carbon coated carbon beads powders were collected after the temperature of the reaction tube cooled down. The gathered powders were softly ground by a pestle and mortar lest the TVD-carbon layer was destroyed. The TVD process was repeated at least four times for NSF carbon beads in order to make a complete and uniform coverage. Soft carbon amount of the resultant composite carbon beads was evaluated by measuring the weight increase after TVD. In this study, the weight of the soft carbon "shell" almost equated to that of the hard carbon "core." The electrochemical test conditions were similar to those reported in Ref. 1.

Figure 1 compares the discharge curves of some NSF carbon beads with and without TVD treatments. It can be observed that for most carbon beads samples (except for the sample carbonized at 700 °C), TVD-carbon coating enlarges the reversible capacity more or less, especially at low voltage range (<0.2 V). The reversible capacity of NSF carbon beads carbonized at 1300 °C increase a little after TVD treatment. The beneficial effect of TVD can be attributed to the increase in the electric conductivity of carbon beads. Figure 2 compares the bulk resistance of NSF carbon beads powders with and without TVD treatment under the pressure of $50\,\mathrm{kg/cm^2}$. The decrease in the resistances after TVD treatment can be considerably observed for most NSF carbon beads samples. In the case of NSF carbon beads carbonized at 1300 °C, the extent of decrease in bulk resistance is very small, which just parallels its tiny increase in reversible capacity. On the other hand, we also observed the decrease in irreversible capacity after TVD treatment, which can be ascribed to two facts: first, the inertness of TVD-carbon towards the electrolytes decomposition;[5] second, the increase in particle size and decrease in surface area of carbon beads. It is a general consensus that the irreversible capacity is almost proportional to the surface area of carbon.[10] It should be noted that TVD-coating brings decrease of irreversible capacity and increase of current. For exam-

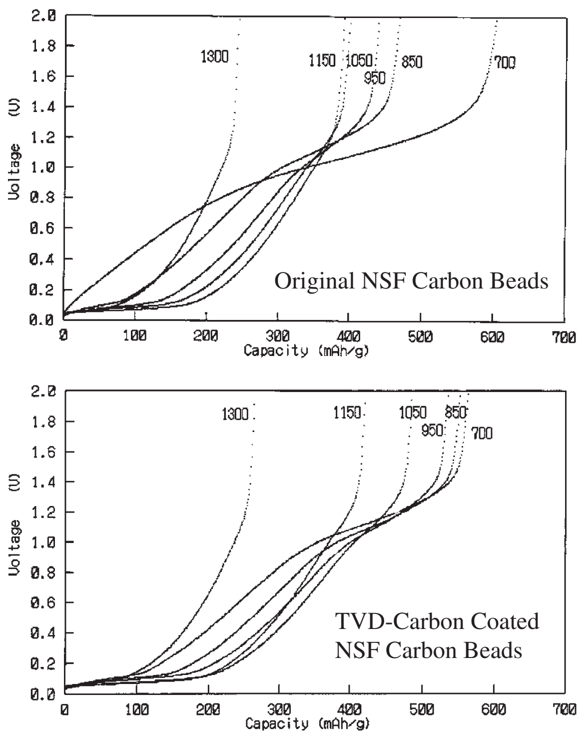

Figure 1. Discharge curves of some NSF carbon beads carbonized at different temperatures before and after TVD treatments. Charge: 0.1 A/g constant current to 10 mV vs Li, constant voltage charge at 10 mV for 48 h. Discharge: 0.1 A/g constant current (4-5 C rate).

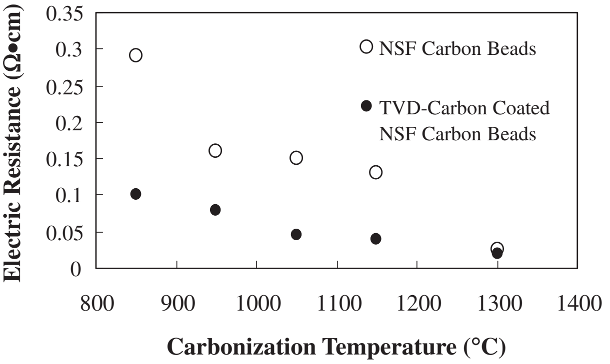

Figure 2. Bulk resistances of NSF carbon beads powders with and without TVD treatment under the pressure of 50 kg/cm^2.

ple, the first discharge capacity, reversible capacity and current efficiency for 900 °C-carbonized NSF bead are 708 mAh/g, 418 mAh/g, and 59.1%. In contrast, corresponding values for TVD-coated NSF carbon beads are 700 mAh/g, 536 mAh/g and 77%. That is, irreversible capacity is decreased from 290 to 164 mAh/g after TVD-coating.

The climb-up amplitude of coulombic efficiency after TVD carbon-coating ranges from 8 to 30%. Therefore, the performance of NSF carbon beads can be pronouncedly improved by TVD treatment in terms of both reversible capacity and coulombic efficiency.

Actually, we have obtained satisfactory TVD-carbon coated NSF hard carbon beads anode materials via controlling the experimental conditions such as carbonization factors, TVD procedures and NSF resin molecular weight. Figure 3 compares the discharge curves of natural graphite and our champion sample for TVD-carbon coated NSF carbon beads. The key preparation conditions included: (1) molecular weight of NSF around 7000, (2) abbreviation of the neutralization procedure using ammonia water in the synthesis for NSF, (3) addition of 20 wt % of phenol resin into NSF, and (4) both the carbonization and TVD temperatures at 900 °C, and so on. The superiority of TVD-carbon coated hard carbon beads can be obviously seen in this sample. Its discharge curve consists of a low-voltage plateau and a sloping part. The reversible capacity corresponding to the plateau almost equals to the whole reversible capacity delivered by natural graphite. Furthermore, the working voltage of the plateau is lower than that for natural graphite. The sloping part of the discharge curve may be valuable, which can indicate the residue capacity during discharge of lithium-ion batteries. In contrast, the voltage of natural graphite jumps up rapidly at the end of discharge. So far, we have shown the effect of TVD-carbon coating on the electrochemical performance of NSF carbon beads. Further research work is needed to make hard carbon-based anode materials suitable for lithium-ion batteries.

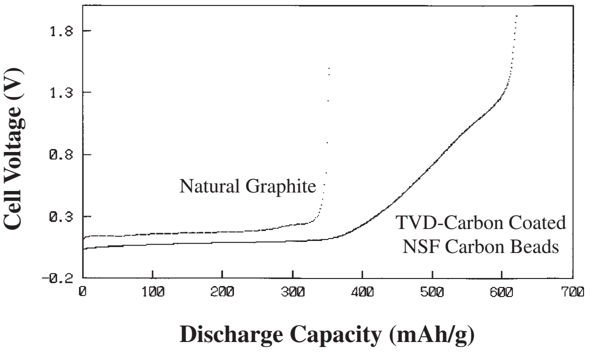

Figure 3. Discharge curves of natural graphite and "optimum" TVD-carbon coated NSF carbon beads.

References and Notes

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