



Development of efficient carbon anode material for a high-power and long-life lithium ion battery

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ABSTRACT

The Li ion battery with high power and long life is required for the hybrid electronic vehicle. A new carbon anode material called "ICOKE" has been prepared by the graphitization of coke at ca. 2000 °C and is shown to have excellent pulse charge/discharge characteristics and long cycle performance. The charge/discharge reaction mechanism of ICOKE was investigated in detail based on the result of cyclic voltammetry and X-ray diffraction profile change of ICOKE before and after charging. As a result, it was found that Li-intercalation reaction to ICOKE proceeds without forming higher stage compounds and the 1st and the 2nd stage compounds are directly formed.

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1. Introduction

About 15 years have passed since the Li ion battery using carbon as the anode was commercialized. During the first few years, the electrochemical performance of most carbons was investigated. In Fig. 1, the discharge capacities of various carbons reported by several research groups at the Japanese Battery Symposium held in 1993–1994 are plotted as a function of the heat-treatment temperature of the carbons [1]. It can be seen that the discharge capacity of carbon is almost determined by the heat-treatment temperature regardless of the kind of carbon material and the tendency was also reported by Zheng et al. and discussed with disorder probability P' [2–4].

The carbons listed in Fig. 1 can be systematically classified into three groups. The first group consists of the carbons prepared below ca. 1000 °C. They show a higher capacity than the theoretical value of 372 Ah/kg owing to the presence of LiC_6 . However, the cycle performance is notably poor and the initial coulombic efficiencies are less than ca. 80%. For this reason, their electrochemical characteristics are hardly studied now. The second group consists of what are called "artificial graphites", which are graphitized above ca. 2500 °C. Since such carbons have high crystallinities, natural graphite should also be included in this group. In general, these graphites show excellent cycle performance, high capacities of 350–370 Ah/kg, and coulombic efficiencies higher than 90%. There-

fore, graphite is commercially used as the anode of most Li ion batteries which are used in many electronic devices such as mobile phones, computers, and digital cameras. The third group consists of turbostratic carbons, heat-treated between ca. 1100 and 2500 °C. In this temperature range, the discharge capacity shows a minimum value at ca. 1800 °C. Very few researchers have, therefore, studied the characteristics of these carbons, and their detailed electrochemical performance still remain unknown.

In conventional studies and development of the carbon anode, improvement of capacity, initial coulombic efficiency, and cyclability have been emphasized from the viewpoint of use for mobile electronic devices. However, research activities for large-scale Li ion batteries have recently increased in order to apply them to hybrid electronic vehicles. Such applications require a carbon anode with high-power density and long-life performance. From this viewpoint, Fig. 1 does not indicate which carbon is the best. The author and Ozaki have recently found that the third group of carbons, i.e., carbons heat-treated at 1800–2400 °C, show excellent characteristics in terms of high-rate charge/discharge performance and cyclability [5,6] and have named it "ICOKE".

In the present study, the charge/discharge reaction mechanism of turbostratic carbons graphitized at ca. 2000 °C with high power and excellent cyclability were examined by means of cyclic voltammetry and X-ray diffractometry.

2. Experimental

As a starting material for preparing the carbon anode, pitch coke (supplied by Osaka Gas Chemical Co., Ltd.) was used. The pitch

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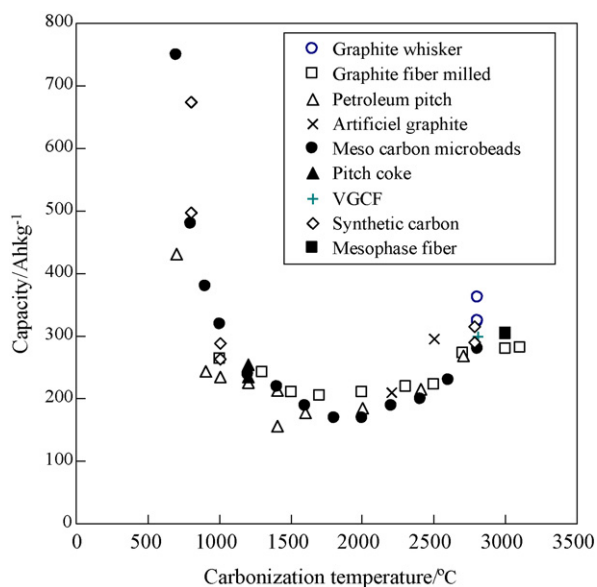


Fig. 1. Relationship between the carbonization temperature and capacity of several carbons.

coke was heat-treated in a temperature range of 1400–2800 °C in Ar atmosphere. Hereafter, “heat-treated pitch coke” will be abbreviated as ICOKE, followed by its heat-treatment temperature: for instance, “ICOKE2000” for the specimen heat-treated at 2000 °C. The term “ICOKE” will be used as a generic name for the improved coke for anode material.

Electrochemical measurements were made, using three-electrode test cells. A lithium metal was used as a counter and a reference electrode, so that the carbon electrode was positive in this cell system. However, the terms “charge” and “input” for Li-intercalation (cathodic reduction) and “discharge” and “output” for Li-deintercalation (anodic oxidation), will be used in connection with a practical rechargeable lithium battery. The electrolyte used was a 1 M LiPF₆/ethylene carbonate+methyl ethyl carbonate (1:1). First, in order to determine the capacities of the heat-treated ICOKEs, the cells were charged down to 0.01 V at a constant current density of 1 mA/cm² and then kept at a potential of 0.01 V, the total charging time being 12 h (CC-CV mode). Then, the cells were discharged in a potential range of 0.01–2 V

at a constant current density of 1 mA/cm² (CC mode). Based on the capacity thus obtained, the charge value of 1 C was determined and the input/output rate performance was measured. The input rate performance was measured by plotting the discharge capacity as a function of the charge current density in a range of 0.2–10C. The anode was first charged at a constant current in the 0.2–10C range down to 0.01 V and was then slowly discharged at a fixed current of 0.2C up to 2 V. That is, the charge capacity was estimated from the discharge capacity by slow discharging, while the output rate performance was measured by plotting the discharge capacity as a function of the discharge current density in the 0.2–10C range. The anode was first charged at a fixed current density of 0.2C down to 0.01 V and was then discharged by varying the current in the 0.2–10C range up to 2 V. Cyclic voltammetry was carried out in a potential range of 0–1 V at a sweeping rate of 2 mV/min. The X-ray diffraction profiles of charged/discharged carbon anodes were measured with the RINT2000 Diffractometer (made by Rigaku Co., Ltd.). The samples were covered with a Be filter during the run, so that they did not decompose by humidity. In order to compare the electrochemical performances of ICOKE with those of other carbons, several other graphites were selected. The natural graphite (SNO, average diameter is 6 μm from SEC Carbon Co. Ltd), graphitized mesocarbon microbeads (MCMB6-28 from Osaka Gas Chemical Co. Ltd.), and artificial graphite (SFG-44 from TIMCAL Ltd.) were used.

3. Results and discussion

Fig. 2 shows the output performance of ICOKE2200 and natural graphite. The ICOKE2200 shows only 300 Ah/kg at 0.3 C, while natural graphite shows 370 Ah/kg, being nearly equal to the theoretical value. However, above 3 C, the capacity of ICOKE2200 is larger than that of natural graphite. Fig. 3 shows the input performance of the same samples. Below 0.5 C, natural graphite shows a higher capacity, while above 1 C, ICOKE2200 shows a higher capacity. These data indicate that ICOKE2200 is a suitable material for the anode of a high-power battery.

Fig. 4 compares the input/output for ICOKE2000 and 2200 with those of several other graphites (natural graphite SNO, graphitized MCMBs, and artificial graphite SFG-44). In the range below 0.5 C, natural graphite shows higher input characteristics, while ICOKE2000 and 2200 show higher input characteristics above 0.5 C. The output performance of natural graphite is also

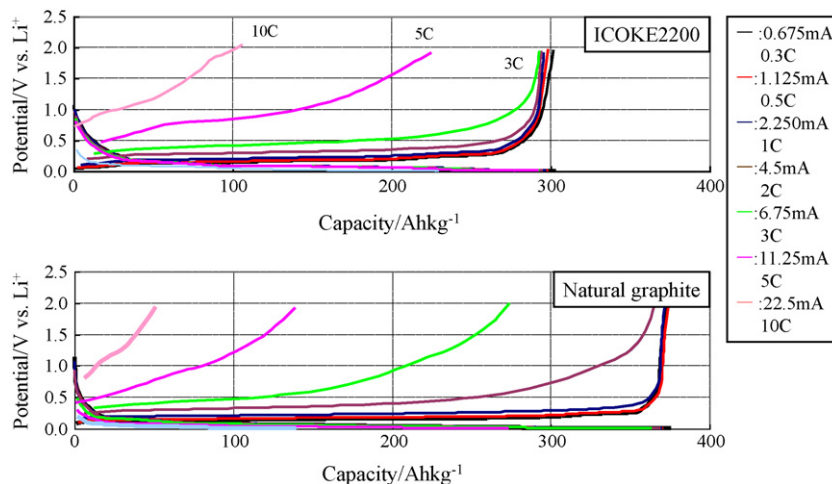


Fig. 2. Comparison of output performance between ICOKE2200 and natural graphite.

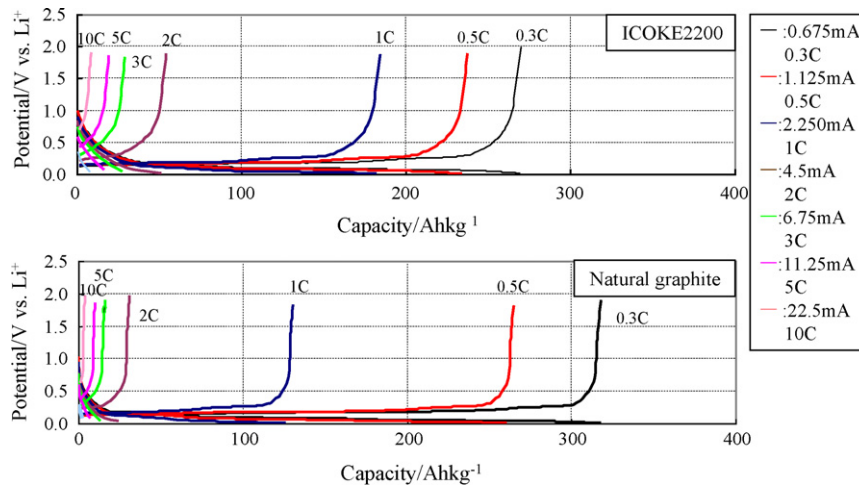


Fig. 3. Comparison of input performance between ICOKE2200 and natural graphite.

superior to that of ICOKEs below 2C. Above 2C, the capacity of natural graphite decreases abruptly and ICOKEs show a higher capacity. The carbonization temperature dependence of the input/output power of ICOKEs is shown in Fig. 5. It can be seen that the ICOKE carbonized at higher temperatures shows a higher capacity in the lower rate region. On the other hand, in the higher rate region, the capacity decreases with increasing carbonization temperature. In other words, the relationship between the capacity and the input power is in trade-off. A similar tendency can be observed for the output power.

Figs. 6 and 7 show the cyclic voltammograms of natural graphite and ICOKEs heat-treated at 1700–2200 °C, respectively. In the case of natural graphite, one can observe three peaks at 0.2, 0.09, and 0.04 V of cathodic side potential. Previously, in order to identify the

reactions corresponding to these peaks, the author analyzed the intermediate compounds formed at potentials between the peaks by X-ray diffraction and concluded that these peaks were assigned to the higher stage formation reaction, the transformation reaction of stage 3 to 2 Li-intercalated graphite, and stage 2 to 1, respectively [7]. The three anodic peaks at 0.13, 0.18, and 0.23 V of potential are considered to correspond to the reversible reaction. On the other hand, in the case of ICOKE2000, the most important point is that the reduction peak at ca. 0.2 V, which was observed for natural graphite, disappeared. It indicates that the charge reaction for ICOKE was not the conventional Li-intercalation reaction from a higher stage compound to a stage 1 compound via stage 2 or 3 but the direct intercalation reaction of stage 1 or stage 2 without going through a higher stage. Such a result was also reported by Zheng [2–4]. It would be one of the reasons that the input power per-

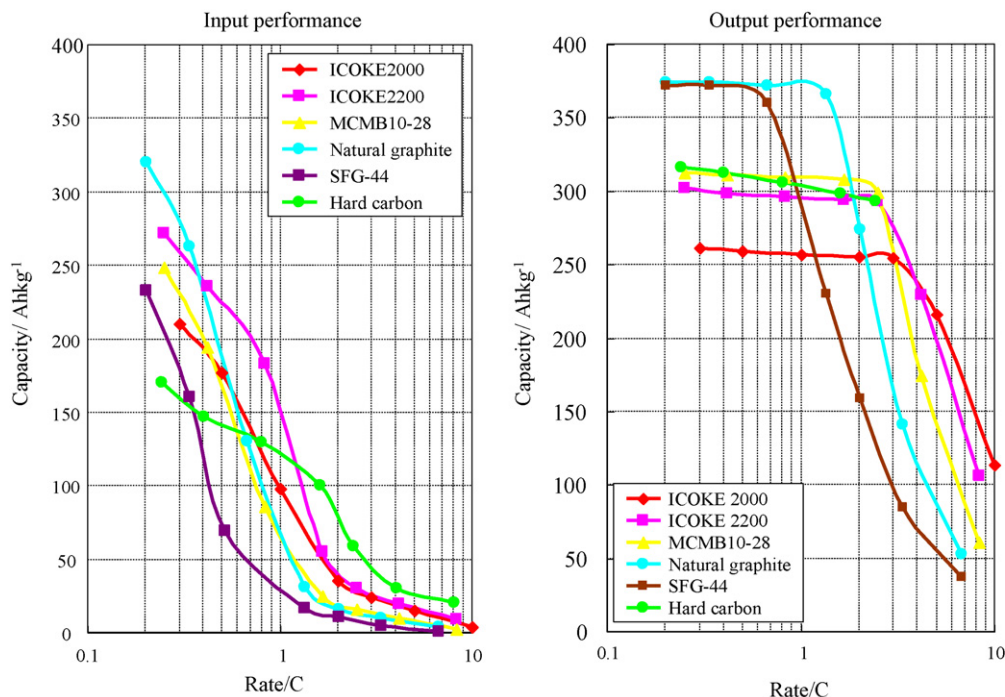


Fig. 4. Dependence of the input/output power performance of several carbons on the charge/discharge current rate.

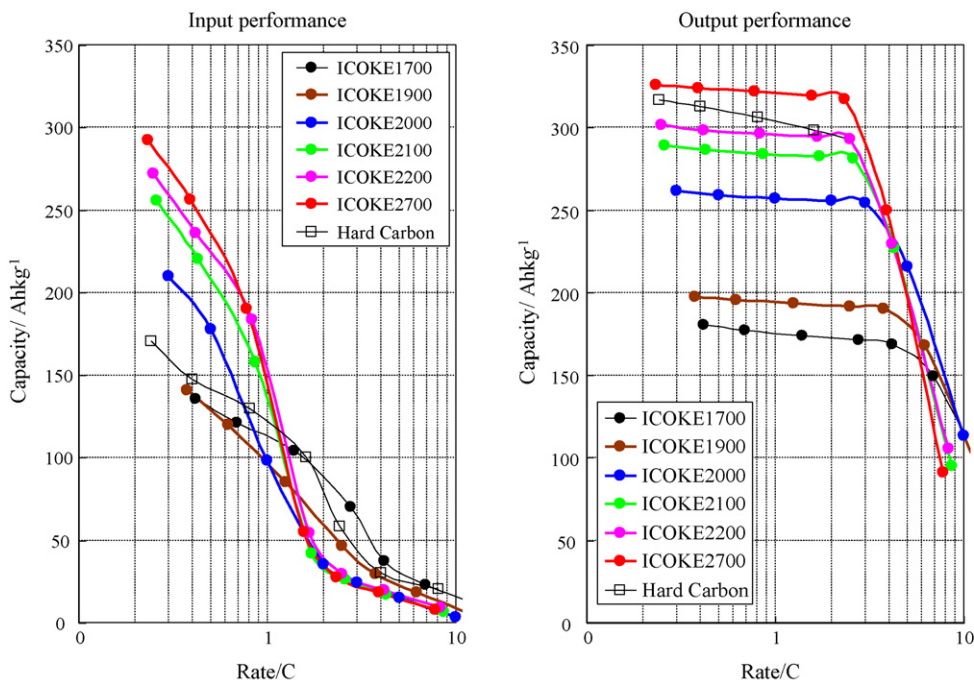


Fig. 5. The carbonization temperature dependence of the input/output performance of ICOKEs.

formance of ICOKE is superior to that of other graphite materials. Another important point is that an unknown shoulder anodic peak is observed at 0.03 V. This peak is also observed for other ICOKEs graphitized at different temperatures, 1400–2800 °C as shown in Fig. 7. This peak may be related to the high-rate discharge reaction. Fig. 8 shows the change of 002 diffraction profiles of ICOKE2000 and natural graphite by the electrochemical Li-intercalation reaction. The solid and dashed lines in the figure denote the profiles of ICOKE2000 and natural graphite, respectively. In the latter case, the sandwich thickness increased by 10% from 0.335 nm to 0.367 nm by the charge reaction compared with only a 6% increase from 0.34 nm to 0.36 nm observed in the former case. The degree of extraction/de-extraction along the vertical axis caused by the charge/discharge reaction for ICOKE is smaller than that for natural graphite. Therefore, the structural degradation of ICOKE decreases and as a result, its cycle life will be enhanced. Fig. 9 shows the change of 002 diffraction profiles of ICOKE2000 and natural graphite by the electrochemical deintercalation reaction. The most important point is that the peak position of the fully discharged ICOKE (profile E) slightly shifted from the original ICOKE position (Profile F). This indicates that the interlayer spacing of ICOKE that has been charged and discharged once is increased. This may be one of the reasons that the input/output performance of ICOKE is excellent.

Generally, fully charged graphite based on LiC_6 has a golden color. However, the color of fully charged ICOKE2000 is not golden but metallic bronze and the discharge capacity is only about 250 Ah/kg. This indicates that the in-plane ordering and electron density of LiC_x are quite different from those of natural graphite. The stacking sequence of most carbon materials heat-treated at ca. 2000 °C is generally turbostratic, being far from that of natural graphite, what is called the AB-stacking structure. The author previously estimated the graphitizability and the projected probability function of the first nearest carbon layer plane from the X-ray diffraction profile of mesocarbon microbeads based on Warren's theory [8,9] and found that the two adjacent carbon layer planes in the turbostratic stacking form the moiré pattern correspond-

ing to the misorientation angle ϕ between the two layers [10]. As a result, the pseudo-AA and -AB stacking areas periodically appear between the two layers. The periodicity D of the superlattice formed by the moiré pattern between the two adjacent carbon layer planes is estimated by

$$D = \frac{a_0}{2 \sin \phi/2} \quad (1)$$

where a_0 is the two-dimensional lattice constant [10,11]. The number of carbons in a superlattice, N_c , is calculated by

$$N_c = \frac{2D^2}{a_0^2} \quad (2)$$

In the present study, the probability function of ICOKE2000 was estimated by the previous method, and the in-plane ordering of Li-intercalated ICOKE was simulated. If it is postulated that the Li

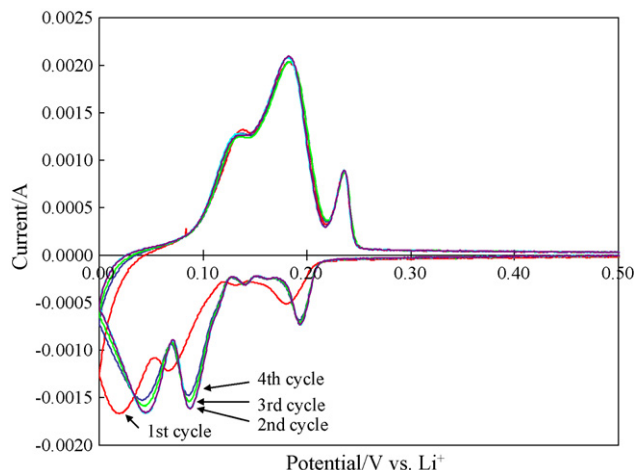


Fig. 6. Cyclic voltammogram of natural graphite.

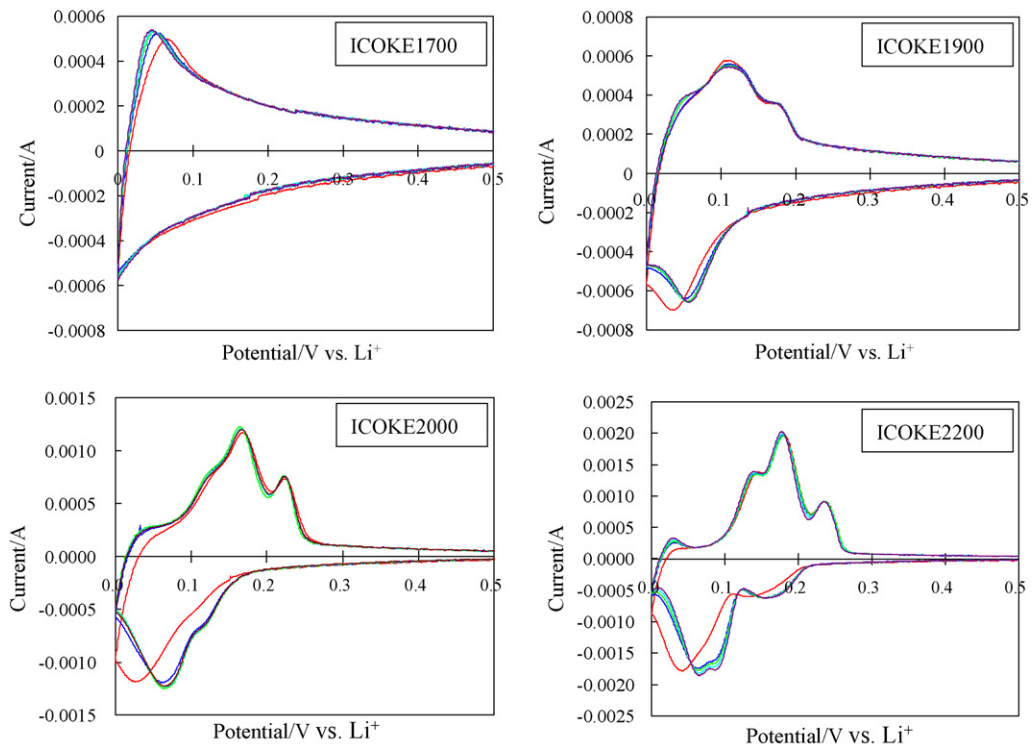


Fig. 7. Cyclic voltammogram of ICOKEs heat-treated at several temperatures.

ion intercalates only in the pseudo-AA stacking site, the in-plane ordering of Li-intercalated ICOKE can be simulated as shown in Fig. 10. The composition in the superlattice is in good agreement with that estimated from the measured discharge capacity. The

reason for the lower discharge capacity than the theoretical value of 372 Ah/kg and the bronze color of the charged electrode can be explained by the peculiar in-plane ordering of Li-intercalated ICOKE.

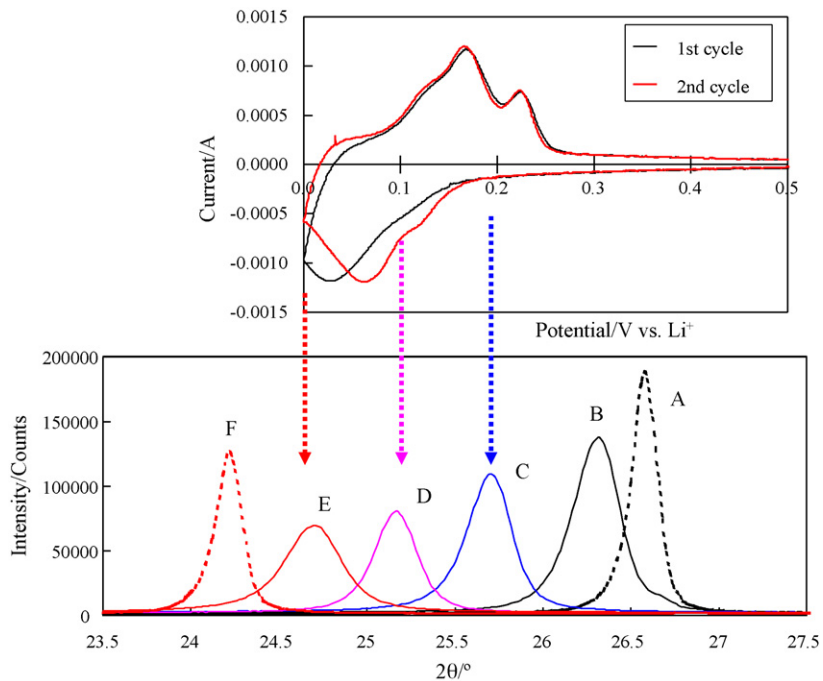


Fig. 8. Cyclic voltammogram of ICOKE2000 and the 002 diffraction profile change by the charge reaction. A: natural graphite before charging; B: ICOKE2000 before charging; C: ICOKE2000 charged down to 0.2V; D: ICOKE2000 charged down to 0.1 V; E: ICOKE2000 charged down to 0.0V; F: natural graphite charged down to 0.0V.

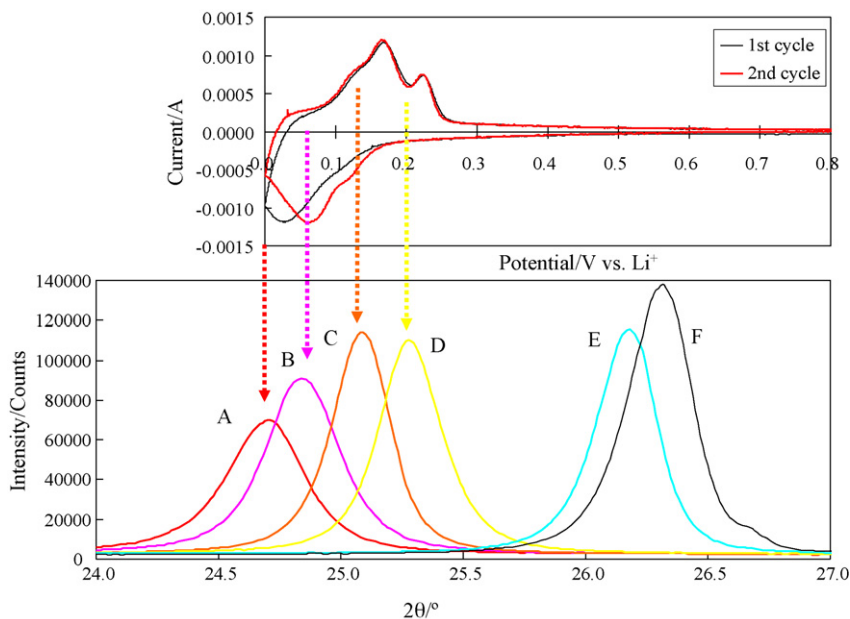


Fig. 9. Cyclic voltammogram of ICOKE2000 and the 002 diffraction profile change by the discharge reaction. A: ICOKE2000 before discharging; B: ICOKE2000 discharged up to 0.075 V; C: ICOKE2000 discharged up to 0.125 V; D: ICOKE2000 discharged up to 0.188 V; E: ICOKE2000 discharged up to 2.000 V; F: raw electrode.

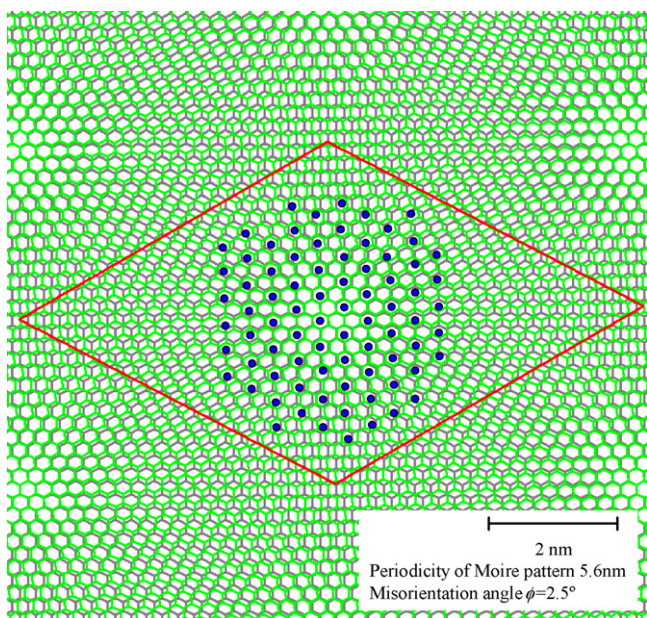


Fig. 10. Simulation of the in-plane ordering of Li-intercalated ICOKE2000.

4. Conclusion

In the present study, the electrochemical input/output power characteristics of ICOKE were examined and the charge/discharge

reaction mechanism was investigated in detail based on the result of cyclic voltammetry and X-ray diffractometry. As a result, it was found that Li-intercalation to ICOKE was somewhat different from the conventional intercalation to graphite. In the latter case, the reaction proceeds from a higher stage compound via the 3rd or 2nd stage to the 1st stage. In the former case, in contrast, the Li-intercalation reaction occurs without forming higher stage compounds and directly forms the 1st and the 2nd stage compound. It was further revealed that the relationship between the capacity and the input/output characteristics was a trade-off.

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