

# Development of Hard Carbon Anode Material from Coal-Tar Pitch

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## Abstract:

*JFE Chemical has been promoting the development of anode materials for lithium-ion batteries, taking advantage of its strength as a manufacturer of coal-based pitch products. As a result of the development of various anode materials, we have succeeded in the development and mass production of hard carbon made from coal-based pitch.*

*JFE Chemical's hard carbon anode material has a small particle size of 3  $\mu\text{m}$  while reducing the specific surface area, which improves high rate charge/discharge properties without reducing the initial efficiency. In addition, the special carbon structure of hard carbon of the material makes it possible to exhibit excellent durability properties. This paper describes the characteristics of the developed hard carbon and its electric characteristics.*

## 1. Introduction

Lithium ion batteries have a high energy density, and are widely used as a power source for mobile devices such as smartphones and laptop personal computers. In recent years, development of various applications has progressed, ranging from vehicle-mounted use in electric vehicles (EVs) and hybrid electric vehicles (HEVs) and applications involving industrial machinery, such as drive power sources and power stabilization power sources for industrial robots, to miniature power sources for heart pacemakers and other healthcare devices. Further growth of demand is also expected in the future, particularly for xEVs<sup>1)</sup>.

JFE Chemical succeeded in mass production of spherulitic graphite, which is a spherical artificial graphite material, using coal-tar pitch obtained by distillation of coal tar produced as a byproduct of the steel manufacturing process, and has marketed this material mainly as an anode material for batteries used in cellphones and mobile personal computers<sup>2)</sup>. On the

other hand, in order to respond to increasingly diverse performance requirements for negative electrode materials accompanying the expansion of battery applications, high performance natural graphite coating materials using coal tar pitch as a coating material and various negative electrode materials in which special heat treatments are applied to coal tar pitch have also been developed. As part of this trend, since hard carbon displays excellent long-term durability and input-output characteristics in the lithium insertion and extraction reactions due to its special carbon structure, hard carbon is being developed as a negative electrode material for applications that require long-term durability and input-output characteristics, such as xEVs, stationary batteries and applications with similar requirements.

## 2. Characteristics of JFE Chemical Hard Carbon Anode Material and Its Performance

### 2.1 Characteristics and Anode Properties of Hard Carbon

Carbonaceous materials used as negative electrode materials can be broadly divided into graphite materials and amorphous carbon materials. The main elements that determine the differences between graphite materials and carbon-based materials are the thermal history and structure of the materials. Graphite materials are obtained through a thermal history which includes a high temperature of around 3 000°C and possess a highly crystalline structure as a result of growth and orientation of the graphene sheet plane. In the carbon type, stacking and orientation of graphene sheets are not fully developed due to the low temperature thermal history (700 to 1 300°C). Carbon-type materials are further classified into soft carbon (graphitizable carbon) and hard carbon (non-graphitizable

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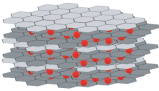
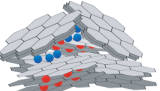


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carbon) depending on the structure. Soft carbon has a structure in which growth and orientation of the graphene sheet planes have already progressed to some degree and easily forms highly crystalline graphite when treated at high temperature. In contrast, hard carbon has a structure in which the small units of the graphene sheets are arranged at random (i.e., “disordered”) and the particle interior contains micropores (interstices), and keeps this structure even when treated at high temperature and does not form graphite crystals<sup>3)</sup>. The special structure of hard carbon is a factor exhibiting the distinctive battery characteristics when hard carbon is used as a negative electrode material for lithium ion batteries.

In lithium ion batteries using graphite as a negative electrode material, the lithium ions transferred from the positive electrode during charging are inserted only between the graphene layers, in a process called intercalation, but when hard carbon is used, lithium ions can be inserted into the microvoids in addition to the spaces between the graphene layers (Fig. 1). This means that a hard carbon electrode can achieve a capacity that exceeds the theoretical capacity of graphite materials (372 mAh/g). Moreover, because expansion and contraction of the hard carbon particles is small, hard carbon has good cycle durability, and its input-output characteristics are also good. As drawbacks, due to the high microporosity of hard carbon, the true density of hard carbon particles is lower than that of graphite, and as a result, its volume energy density is smaller and initial efficiency is lower.

To date, hard carbon negative electrode materials have been developed and commercialized using petroleum-derived<sup>4)</sup>, resin-derived<sup>5)</sup> and bio-derived feedstocks<sup>6)</sup>. Therefore, JFE Chemical developed a high performance hard carbon anode material utilizing the distinctive features of the coal tar pitch owned by this company, with the aim of mass production from coal-derived pitch and commercialization as a negative elec-

	Graphite	Hard carbon
Schematic diagram		
Lithium storage sites	Graphite layers	Graphite layers + microvoids

● Intercalated Li in the graphite layers  
● Inserted Li in the microvoids

Fig. 1 Difference between graphite and hard carbon structures

trode material for use in HEVs.

## 2.2 Manufacturing Process

Figure 2 shows the outline of the hard carbon manufacturing process at JFE Chemical.

First, coal tar pitch is heated until liquid. Air-blown pitch is obtained by inducing an air blowing reaction (oxidation heat treatment) by performing heat-treatment while blowing air into the liquid pitch. The air blowing reaction proceeds with oxidative dehydration as the main reaction, and polymerization occurs due to phenyl-type crosslinking bonding. Based on the fact that there is no significant difference in the oxygen concentration in the pitch before and after the reaction, it has been reported<sup>7)</sup> that bonding of oxygen with the constituent molecules of the pitch is minimal in this process, and JFE Chemical has also confirmed that its air-blown pitch showed no significant difference in the oxygen content before and after the reaction.

The next process is infusibility-imparting treatment, in which oxidizing treatment is performed by heating the air-blown pitch in the solid state in the atmosphere. In this treatment, oxygen in the air is incorporated in the air-blown pitch by the reaction with carbon, which increases the degree of cross-linking, thereby imparting resistance to softening and melting in the subsequent firing process (carbonization), making it possible to maintain the above-mentioned disordered 3-dimensional structure of the graphene units. This is also a key process for removing oxygen in the subsequent firing process and forming the disordered structure of graphene units and microvoids which are distinctive characteristics of hard carbon.

The process following infusibility-imparting treatment is pulverizing treatment, in which the infusibility-imparted pitch is pulverized to the particle size required

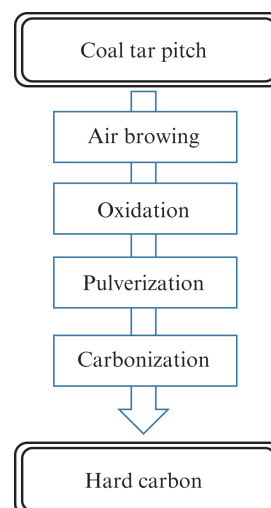


Fig. 2 Manufacturing process of hard carbon

by the intended application. The particle size of a negative electrode material is an important factor which determines battery characteristics. That is, a material with a smaller particle size is suitable for applications which require good input-output characteristics because smaller particles reduce input-output resistance and make it possible to use a thin-film electrode. However, smaller particles also reduce initial efficiency because their larger specific surface area increases reactivity with the electrolyte. As discussed later, JFE Chemical succeeded in producing a hard carbon with a small volume average particle size, while also minimizing the increase in specific surface area and deterioration of initial efficiency, by utilizing the distinctive features of the coal-derived pitch material and innovations in the manufacturing process.

The final process of firing (carbonization) is the critical process which determines the hard carbon structure and battery characteristics. Because the hard carbon structure and battery characteristics change greatly depending on the temperature achieved in firing (firing temperature), the thermal history and other firing conditions, JFE Chemical identified the factors that affect these characteristics and established an original firing process in order to satisfy the requirements of both high performance and mass production.

## 2.3 Basic Characteristics

### 2.3.1 Powder characteristics

Figure 3 shows the particle size distribution and specific surface area of the small-sized hard carbon which is a main product of JFE Chemical. By taking advantage of the distinctive features of coal-derived pitch materials and innovations in the manufacturing process, it was possible to obtain a small volume average particle size of approximately 3  $\mu\text{m}$  while holding the specific surface area to a low level of about 4.7  $\text{m}^2/\text{g}$ . Moreover, the particle shape is also controlled in

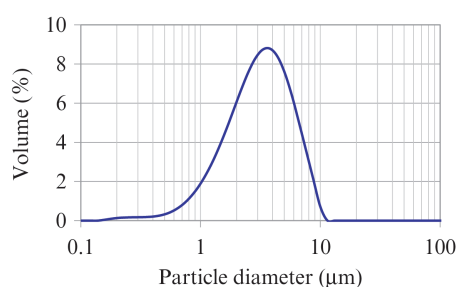


Fig. 3 Particle size distribution and specific surface area of hard carbon

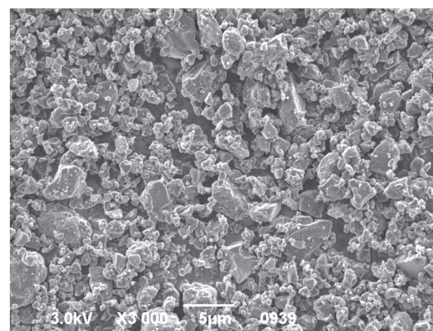


Fig. 4 SEM image of hard carbon

combination with these features.

Because conventional hard carbon has sharp edges, damage of the current collector foil during pressing when manufacturing electrodes for batteries was a concern. However, this company's hard carbon can be expected to reduce pressing damage of the collector foil because the edges are removed and rounded, as shown in the scanning electron microscope (SEM) image in Fig. 4. The effects of this particle shape and the high true density of the powder, as described in the following, have also made it possible to increase an electrode density after pressing to approximately 1.05 to 1.1  $\text{g}/\text{cm}^3$  even with the small particle size of 3  $\mu\text{m}$ . Since the density of petroleum-derived and resin-derived hard carbons is generally no more than 1.0  $\text{g}/\text{cm}^3$ , electrodes with almost 10 % higher density can be produced by using JFE Chemical's hard carbon, thereby realizing higher capacity. This is one important merit of this company's hard carbon.

### 2.3.2 True density and particle carbon structure

In comparison with hard carbon produced from other feedstocks, hard carbon produced from coal-derived raw material has a higher true density (by the pycnometer method using butanol). Figure 5 shows a comparison of the properties of coal-based and oil-

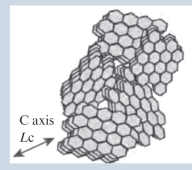
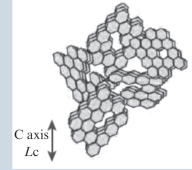
Items	Coal-based HC	Oil-based HC
Schematic diagram		
True density ( $\text{g}/\text{cm}^3$ )	1.63	1.52
$L_c$ (nm)	1.02	0.84
d002 (nm)	0.37	0.38
Pore size (nm)	0.76	0.90

Fig. 5 Comparison of properties between coal-based hard carbon and oil-based hard carbon

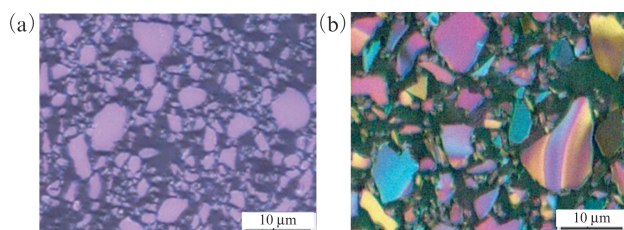


Fig. 6 Polarization microscope images  
(a) Hard carbon, (b) Soft carbon

based hard carbon when prepared by the same method.

The true density of the hard carbon prepared from the coal-based pitch is 1.60 to 1.65 g/cm<sup>3</sup>, which is higher than the 1.52 g/cm<sup>3</sup> of the oil-based material. This difference in the true density is considered to be due to the difference in the carbon structures of the coal-based and oil-based pitches. The results of a comparison of the carbon structures by X-ray diffraction (XRD) showed that the  $L_c$  (crystallite size in the stacking direction ( $c$ -axis)) obtained by wide-angle X-ray diffraction was larger and the void size obtained by small-angle X-ray diffraction was smaller in the coal-based pitch material. Based on these results, it can be inferred that the true density of the hard carbon produced from the coal-derived pitch is higher due to the larger structural unit and smaller pore size.

Techniques for direct observation of the structure of carbon include observation by the polarization microscope and the transmission electron microscope (TEM). In observation using a polarization microscope, an anisotropic organization showing polarization is observed in graphite and soft carbon, both of which have an oriented structure consisting of stacked graphene sheets, but hard carbon displays an isotropic organization without polarization, as it has a turbostratic structure consisting of randomly-oriented disordered graphene sheets<sup>8</sup>. **Figure 6** shows an observation image of the anisotropic organization of soft carbon, which was prepared separately for comparison, with a polarization microscope image of the cross section of JFE Chemical's hard carbon. It can be understood that the hard carbon does not have an anisotropic organization, and has an isotropic organization which does not display polarization.

TEM observation enables visual observation of the local microstructure and orientation at the nm order<sup>9</sup>. **Figure 7** shows the results of observation of JFE Chemical's hard carbon. The distinctive turbostratic structure of hard carbon with disordered graphene sheets can be confirmed.

### 2.3.3 Battery characteristics

Negative electrodes for lithium ion batteries are generally manufactured by mixing the negative elec-

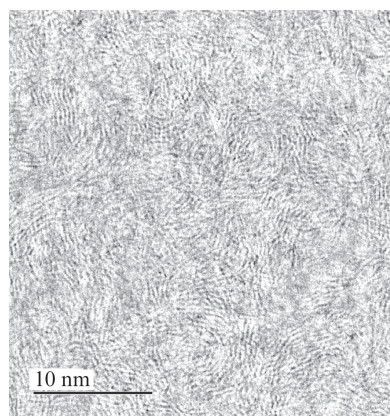


Fig. 7 TEM image of hard carbon

Table 1 Electrochemical Performance of hard carbon

Solvent type	Binder (Binder ratio)	Electrode density (g/cm <sup>3</sup> )	Charge capacity (mAh/g)	Discharge capacity (mAh/g)	Efficiency (%)
Organic solvent	PVDF (4%)	1.06	482	383	80
Water	CMC/SBR (1%/1%)	1.08	474	381	80

trode active material and binder in a dispersion medium (solvent) to obtain a slurry, which is then coated on a copper foil current collector and dried. Two main solvent and binder systems are used in this process, one being an organic system consisting of an organic solvent (NMP: N-methylpyrrolidone) as the dispersion medium and PVDF (polyvinylidene fluoride) as the binder, and the other an aqueous system using water as the solvent and a mixture of CMC (carboxymethyl cellulose) and SBR (styrene butadiene rubber) as the binder. Normally, water-based binders cannot be used with hard carbon, which easily adsorbs moisture, resulting in serious deterioration of properties. However, because JFE Chemical's hard carbon has the characteristics of hardly adsorbing moisture and maintaining the same properties even if adsorption occurs, the initial capacity and initial efficiency of negative electrodes produced using an aqueous solvent are similar to those of electrodes made with an organic solvent (**Table 1**).

**Figure 8** shows the initial charge/discharge profiles of hard carbon measured with a monopolar cell using a metallic lithium counter electrode. Comparing the charge-discharge characteristics of the organic system and the aqueous system, the two systems show almost identical potential profiles. Where charging is concerned, during constant current (CC) charge, the profiles show a characteristic potential curve, in which the potential change vs. the potential of the lithium counter electrode has a gradient, and after switching to con-



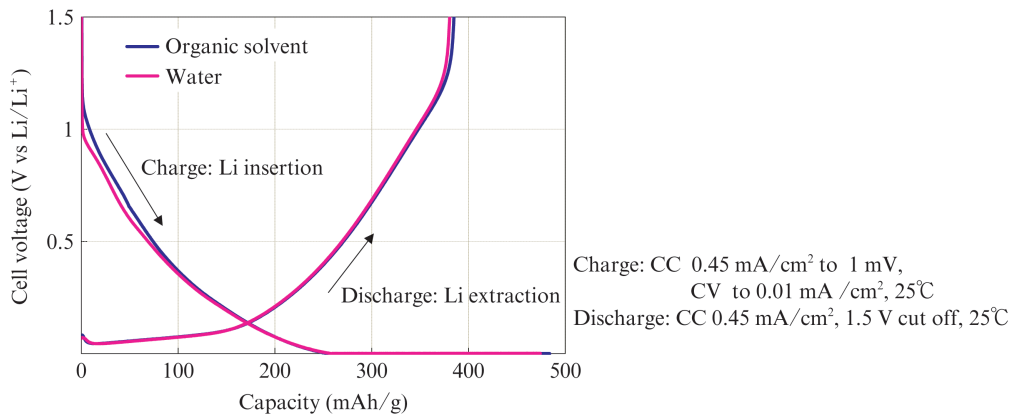


Fig. 8 Charge/discharge profiles of hard carbon

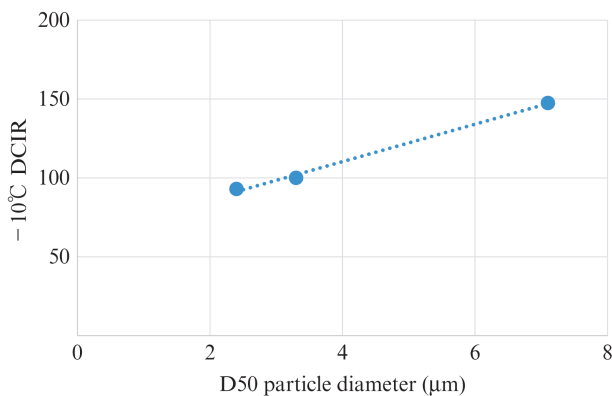


Fig. 9 Correlation between D50 particle diameter and  $-10^{\circ}\text{C}$  DCIR  
(DCIR is the relative value when  $3.3\ \mu\text{m}$  is set to 100.)

stant voltage (CV) charge, the profiles show the characteristic potential curve of hard carbon, which displays a large charging capacity. During discharge, the profiles initially show a plateau potential at low potential, and then show a potential curve with a gradient. In the monopolar cell with the metallic lithium counter electrode, the test electrode (carbon electrode) is the positive electrode (cathode), and the counter electrode (Li electrode) is the negative electrode (anode). However, for convenience, in this paper the direction of Li insertion in the carbon electrode is denoted as “charge,” and the extraction direction is denoted as “discharge.” It is thought that hard carbon displays complex potential changes because the units of the crystal structure are disordered and numerous Li storage states exist, not limited in intercalation between the graphene layers, but also including insertion in voids between units. Although many examples of research on the mechanism of Li storage in hard carbon have been reported to date, many points still remain unclear<sup>10-13</sup>.

Among battery characteristics, input-output characteristics are an extremely important property in xEV applications, and particularly in HEV applications.

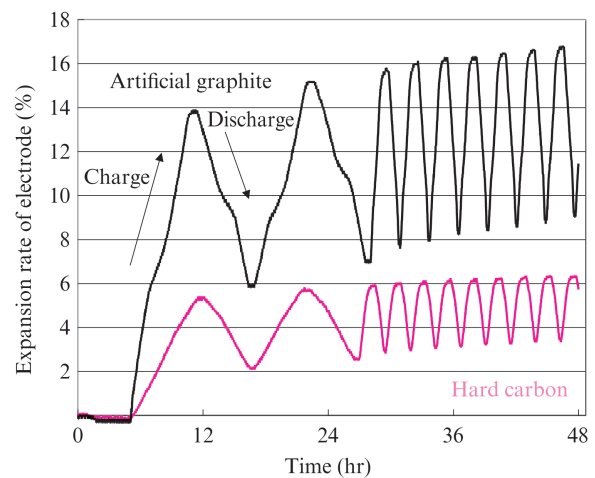


Fig. 10 Expansion rate of anode electrode in charge/discharge cycles

**Figure 9** shows the results of measurement of direct current internal resistance at  $-10^{\circ}\text{C}$  ( $-10^{\circ}\text{C}$  DCIR), which is an index of input-output characteristics, using a coin cell ( $\Phi 20 \times 1.6\ \text{mm}$ ). The fact that DCIR decreases as the particle diameter becomes smaller clearly shows the effectiveness of reducing the particle diameter for obtaining high input-output characteristics for HEV batteries.

### 2.3.4 Electrode expansion property

One distinctive feature of hard carbon is small expansion and contraction during charge/discharge. The expansion and contraction rates of hard carbon and artificial graphite electrodes in charge/discharge cycles were measured by using a special cell which makes it possible to measure electrode expansion and contraction with a displacement gauge, in which LCO (lithium cobalt oxide) is used as the counter electrode. The results are shown in **Fig. 10**. The artificial graphite electrode expanded by nearly 16 % during charging in the 9<sup>th</sup> cycle, and the width of (difference between) expansion and contraction was also about 8 %. In con-

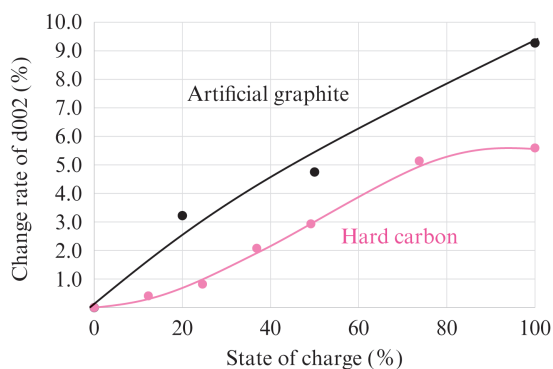


Fig. 11 Change rate of interlayer spacing (d002) at first charge

trast, the expansion of the hard carbon electrode was small, at 6 %, and the width of expansion and contraction was also small, at 4 %. Moreover, while the overall expansion of the artificial graphite increased after the 9<sup>th</sup> cycle, the increase in expansion of the hard carbon electrode was negligible. Because the low expansion and contraction of hard carbon electrodes is considered to be the main factor in their high cycle durability performance, this is an important merit.

Expansion and contraction of electrodes is considered to be caused by expansion and contraction of the carbon particles themselves during charge and discharge. That is, during charging, the particles themselves expand due to widening of the graphene sheet spacing when Li ions are intercalated in the particles, and during discharge, the particles contract as the Li ions are extracted and the graphene sheets return to their original spacing. Since it is not possible to measure the expansion and contraction of artificial graphite and hard carbon independently by the direct displacement measurement method using the battery cell described above, those changes were investigated by measuring the distance between the surfaces of graphene (i.e., the interlayer spacing (d002)) during charge and discharge. As the measurement method, after charging the electrode to the specified SOC (state of charge) with a metallic Li counter electrode half-cell, the target electrode was removed, a special cell with a beryllium (Be) window was assembled, and the interlayer spacing was measured by XRD.

**Figure 11** shows the change rates of the graphene interlayer spacing (d002) of the hard carbon and artificial graphite in the first charge. Since the change in the interlayer spacing of the hard carbon was small in comparison with that of the artificial graphite, it is reasonable to think that its expansion will also be small when used as an electrode because the expansion of the particles themselves is small in hard carbon.

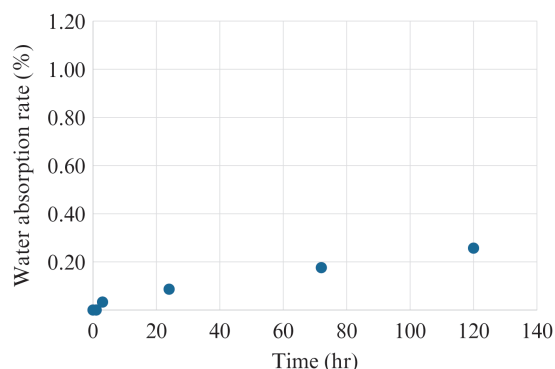


Fig. 12 Correlation between water absorption rate and holding time at 25°C and 50%RH

### 2.3.5 Water absorption and oxidation properties

In lithium ion batteries, the water content of all parts is held to the minimum because water affects battery characteristics, and in particular, affects deterioration due to side reactions in the battery caused by moisture. Conventional hard carbon absorbs water more easily than graphite, and this had caused various problems. In particular, it was difficult to handle the powder and, as described above, it was difficult to use water-based binders. In JFE Chemical's hard carbon, we succeeded in suppressing water absorption by reducing the specific surface area while maintaining a small particle size. To investigate water absorption, an exposure test was conducted by placing hard carbon samples under a 25°C, 50 % RH environment. **Figure 12** shows the water absorption behavior of the samples. In this test, the water absorption rate was calculated by subtracting the sample weight before exposure from that after exposure, and dividing the result by the sample weight after exposure.

The water absorption rate after the samples were left under the above-mentioned environment for 120 h was small, being approximately 0.2 %, and a water content of substantially 0 % was confirmed as a result of drying (120°C × 5 h vacuum drying) during electrode preparation. Among battery characteristics, the decrease in initial efficiency was held to within 1 %, showing that deterioration by water absorption is minimal. Thus, it was also found that hard carbon electrodes prepared using a water-based binder display the same properties as those with an organic-based binder.

Since many lithium ion battery assembly processes are performed in a dry room from which moisture has been removed, the oxidation properties of negative electrode materials in these processes are important. Hard carbon is readily oxidized by reaction with oxygen even under ordinary temperature conditions, and this causes deterioration of battery characteristics. Therefore, the change in the properties of JFE Chemi-

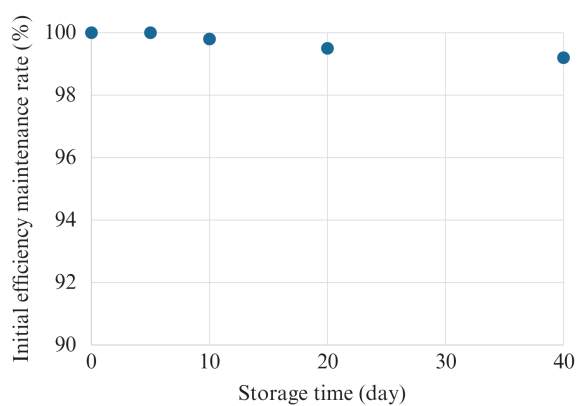


Fig. 13 Correlation between storage time and initial efficiency

cal's hard carbon when stored in powder form under an environment with a dew point of  $-70^{\circ}\text{C}$  and temperature of  $25^{\circ}\text{C}$  was investigated. **Figure 13** shows the results. Since the decrease in initial efficiency was limited to about 1 %, even after 40 days, it can be said that this material has good storage stability in powder form.

### 3. Efforts to Improve Properties of Hard Carbon

Hard carbon has also attracted attention as a negative electrode material for next-generation batteries because of its features of low expansion and contraction and long life. As part of this trend, JFE Chemical's hard carbon has been used in the negative electrodes of all polymer batteries<sup>14)</sup>, in which almost all parts of the battery, including the electrodes, are made from polymers. All polymer batteries have cost advantages as well as high safety and high energy density owing to their unique manufacturing process, and hard carbon is necessary and indispensable in the composition of all polymer batteries because of its small expansion and contraction. As a supplier of hard carbon, JFE Chemical invested in APB Corporation, a startup company which manufactures all polymer batteries and plans to expand its business centering on batteries for energy storage systems (ESS).

It is also possible to customize the particle size distribution, specific surface area and other properties of JFE Chemical's hard carbon to meet the properties requirements of diverse types of batteries, not limited to batteries for HEVs, but also the above-mentioned ESSs and EVs. We are also studying raw materials and manufacturing processes for further improvement of battery characteristics, and especially capacity and initial efficiency. **Figure 14** shows an example of the charge/discharge profiles of developed hard carbon products. At the laboratory level, JFE Chemical has obtained hard carbon with a capacity of 453 mAh/g and efficiency of 83 %. Since one challenge is the balance of performance and cost, how to achieve higher

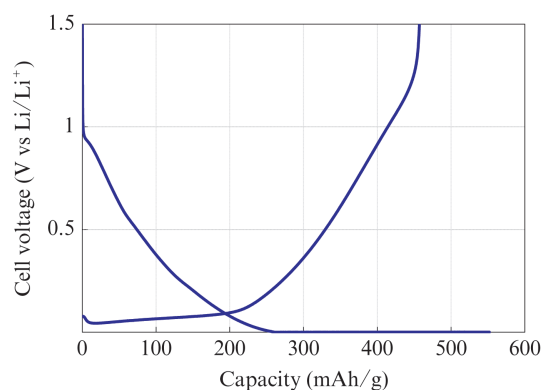


Fig. 14 Charge/discharge profiles of developed materials of hard carbon

Charge: CC 0.45 mA/cm<sup>2</sup> to 1 mV,  
CV to 0.01 mA/cm<sup>2</sup>, 25°C  
Discharge : CC 0.45 mA/cm<sup>2</sup>, 1.5 V cut off, 25°C

performance while holding down costs is important.

In the future, it will be necessary to achieve higher performance and lower cost when considering application of hard carbon as a material for xEVs. From this viewpoint, JFE Chemical is also promoting an approach to high performance from the direction of basic research, including detailed structural analysis of hard carbon, analysis of the charge-discharge mechanism, etc., in cooperation with the Functional Material Research Dept. of JFE Steel's Steel Research Laboratory.

### 4. Conclusion

This paper has described the features and battery characteristics of hard carbon, which was developed by JFE Chemical using coal-derived pitch as a raw material. In addition to the high durability and input-output characteristics which are distinctive features of hard carbon, this material also provides low water absorption and excellent stability against oxidation, and thus is an easy-to-handle material for negative electrodes.

In order to expand the application of hard carbon to EVs and large capacity batteries, it is considered necessary to achieve even higher capacity without sacrificing the distinctive features of hard carbon. Development of a high productivity process with strong cost competitiveness is also essential. JFE Chemical plans to make concerted efforts to solve these issues.

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