

Characterization of Dielectric Energy Storage Mechanism and Achievement of Continuous Production Method for High Capacitance-targeted Ultracapacitors

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ABSTRACT

To achieve high energy density activated carbon for use in ultracapacitors for automobiles, an activated carbon with twice the specific capacitance per unit volume compared to an isotropic activated carbon was developed. The hypothesis was that higher capacitance is related to the space-charge polarization of the inner edge plane. As well, the preparation of graphitizing carbon domains was researched. The high graphitizing activated carbons derived from new aromatic compounds demonstrate higher capacitance. Activated carbons obtained by conventional mass production have batch processing issues, such as contamination by metals generated by etched reactors, variation in capacitance within production batches, and generation of potassium metals. To resolve the above issues, we investigated a continuous mass-production process, and have successfully developed a new KOH activation process.

1. Introduction

The elimination of emission gases, including CO₂, is an important issue from a global warming standpoint, and fuel economy enhancements are required for motor vehicles to meet this goal. One means of enhancing fuel economy would be through the expanded use of electrical powerplants. This increases the importance of an electric power source with peak power buffer that can absorb load fluctuations. Attention is focused at present on the electric double-layer capacitor, which is a low resistance, highly reliable energy storage device. The market for this device has mainly been for small power supplies for backup power in cell phones, etc. In recent years, its use in uninterruptible power supplies

(UPSs) has grown. Expectations for automotive uses include energy storage for fuel cell vehicles (FCVs) and hybrid electric vehicles (HEVs), electrical assist power supplies for electrical auxiliaries, and separated power supplies for electronic devices. Capacitor strengths lie in the ease of energy regeneration due to high input/output density, and high reliability with no limits to cycle life. The most sought after properties in expanding capacitors use are to maintain their high power density characteristics, their main strength, and to increase energy density. In this development project, energy storage theory was verified and an activated carbon was developed as a new high energy density storage material. Mass production techniques were also developed, and a continuously operating plant process was verified. The results are reported below.

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2. Capacitor Features

The electric double-layer capacitor is composed of cathode- and anode-activated carbon electrodes, and a non-aqueous electrolyte. There are 1-2 nm pores inside the activated carbon. The ions are absorbed as charged ions, and desorbed by a discharge. The advantages of a capacitor over a secondary battery are clear. In a secondary battery there exists an active material chemical change, including the thermodynamic losses accompanying chemical energy conversions, and deterioration over time. The discharge power density of batteries is related to electrode reaction speeds, so the amount of power discharged is limited. In addition, the power density is temperature-dependent, thus the batteries can only be used under a limited environment. Because of this it is necessary to control the charge and discharge current of a battery by using a current limiting device. In contrast, a capacitor maintains an electric potential difference that is generated by an externally applied voltage. Therefore, intrinsic high energy efficiency, rapid charge and discharge is possible, strengthening its repetitive charge and discharge characteristics regardless of environmental temperature, in addition to being highly reliable. Figure 1 shows a comparison of power and energy densities for a capacitor and secondary batteries. Although capacitors have many desirable characteristics, including very high power density, they have very low energy density. To make capacitors useful for automotive applications (and use their high reliability and high power density), it is crucial to create capacitors with higher energy densities.

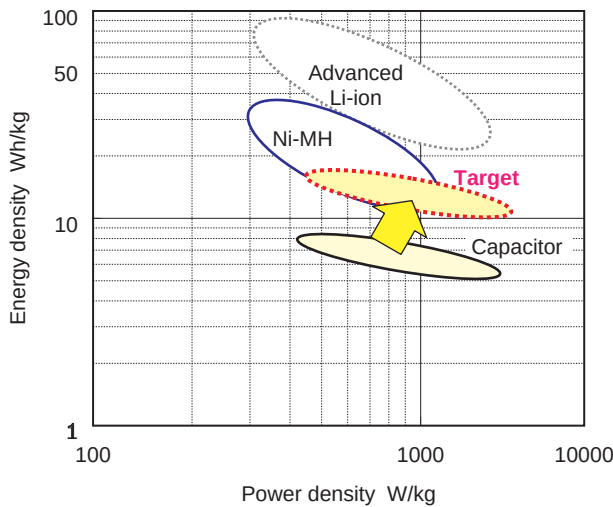


Fig. 1 Ragone plot of capacitor and secondary batteries at 25°C (initial profiles)

3. Development Goals

The development target for the capacitor's energy density was set at 10 Wh/kg, which is approximately three times that of conventional small capacitors. New material technologies were essential to meet this target. The main section explains the technologies that are used to create high capacitance in the activated carbon, as well as the mass production technologies involved.

3.1. Hypothesis of the Theory of New High-Capacitance

Material Methods used to produce high energy density capacitors include raising the rated voltage and raising the capacitance of the activated carbon electrode. The rated voltage for many electric double-layer capacitors is 2.5 V. Though in theory the application

of a higher voltage is possible, this method in practice is restricted, due to a drop in reliability. To raise the rated voltage, a new nonaqueous electrolyte that is unlikely to produce electrochemical degradation is needed. The authors of this study focused on giving the activated carbon a higher capacitance. An electrical charge of electric double-layer is formed between different electrochemical potentials. That is to say, it is formed on the interface between the carbon surface and the electrolyte. Referring to the capacitor's general equation (1), with an electric double-layer capacitor the dielectric existence ϵ or distance between electrical charges d cannot clearly be defined⁽¹⁾. Accordingly, to raise capacitance C , it is important to expand the electric double-layer interface S . It is well known that the capacitance of conventional activated carbon electrodes is extremely large when an electrode's specific surface area is around 2000 m^2g^{-1} . If the area is expanded further, the activated carbon density drops, and the electrode becomes bulky, so raising the capacitance per unit volume is not possible⁽²⁾. However, in 1995 a new activated carbon was discovered that had higher capacitance, despite its smaller specific surface area

$$C = \epsilon_0 \epsilon \frac{S}{d}$$

Eq. 1 General formula of capacitance

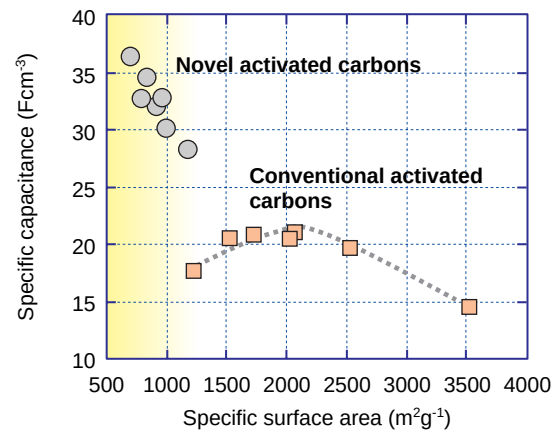


Fig. 2 Relationship between capacitance per unit volume (Fcm^{-3}) and specific surface area (m^2g^{-1}) of activated carbons

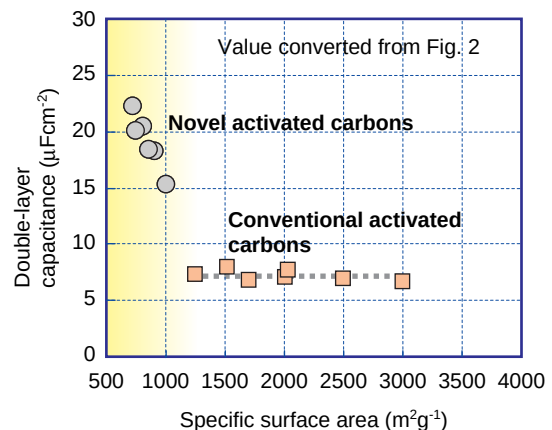


Fig. 3 Relationship between capacitance per unit surface area (μFcm^{-2}) and specific surface area (m^2g^{-1}) of activated carbons

(Fig. 2)⁽³⁾. This activated carbon was obtained by activating a graphitizing carbon to increase its porosity, using potassium hydroxide. Figure 3 shows the results of a cause analysis for increasing material capacitance. The relationship between specific surface area (m^2g^{-1}) and capacitance per unit specific area (μFcm^{-2}) of the newer activated carbon is clearly different from that of conventional activated carbon. As the specific surface area decreases, i.e., the activated carbon density increases, the electric double-layer interface capacity (μFcm^{-2}) also increases. From these results, it was hypothesized that solid dielectrics exist inside of this activated carbon, like those existing in ceramic and aluminum electrolytic capacitors, and capacitance is increased. Specifically, it was assumed that an area of high dielectric constant exists from the edge plane towards the bulk when electric double-layers are formed between the edge surface of the fine graphite crystals, known as the edge plane, and the electrolyte⁽⁴⁾. This reasoning is based on the reports that were published in the 1970s by J. P. Randin and E. Yeager, among others, on their highly oriented graphite electrode research. They studied the differences in graphite fracture surfaces and reported that edge plane capacitance is particularly large, and moreover, that capacitance is voltage-dependent. From these results, they suggest that capacitance was increased due to space charge polarization, and that the increase rate was related to the proportions of edge plane sp^2 - and sp^3 -bonds that were present. They used a semiconductor model to show that capacitance is greater when the sp^2 -bond ratio is higher⁽⁵⁾. The same phenomenon occurs with the porous carbon electrodes, such as those made of activated carbon. To achieve higher capacitance, it was necessary to form an electric double-layer interface with many edge planes with the carbon structure of activated carbon like the structure of graphite.

3.2. Mass Production Issues in Alkaline Activation

The standard activated carbon production method involves carbonizing organic raw materials such as cellulose, and activating them so that the materials become porous by means of oxidation through high temperature water vapor. However, the new material has a graphitizing structure, so gas activation is difficult. Therefore, a production method known as alkaline activation was adopted, which can make the material porous by mixing it with a metal

hydroxide such as potassium hydroxide and creating a reaction at 600 °C or higher.

There are two issues that need to be taken into consideration when using the alkaline activation method for mass production⁽⁶⁾ (Fig. 4-1). The first is that when a reaction involving molten alkaline at high temperatures is used, there is corrosion of the reaction furnace material. Nickel (Ni), with good corrosion resistance, was used, but with continuous operation was found to produce corrosion deterioration. The results of an analysis of this process are shown in Fig. 4-2. The thermal history of furnace causes the grain growth of furnace material (Ni), and molten potassium hydroxide (KOH) permeates the grain boundaries. In the presence of molten KOH, Ni, and activated carbon, electrolytic corrosion accelerates, and Ni particles separate. When these Ni particles become electrodisolution in the activated carbon electrode, as shown in Fig. 5, the electrolytic reduction that occurs at the counter electrode creates a conductive path, leading to a large voltage drop (self-discharge). That is to say, because of the Ni contamination,

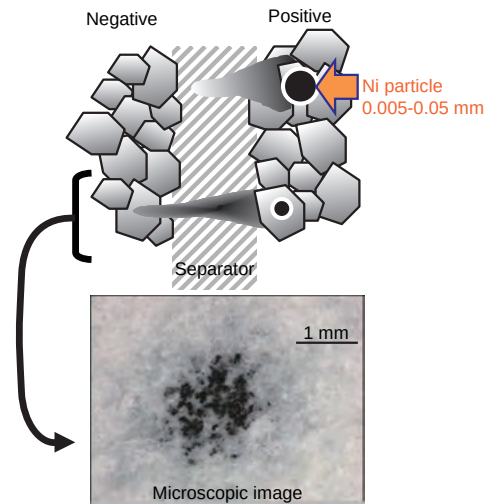


Fig. 5 Model of self-discharge caused by Ni particle and microscopic image of dotted separator

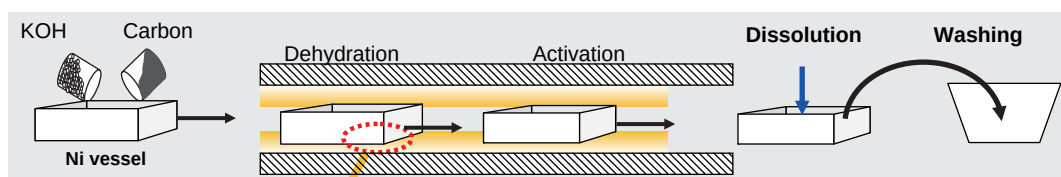


Fig. 4-1 Diagram of conventional process

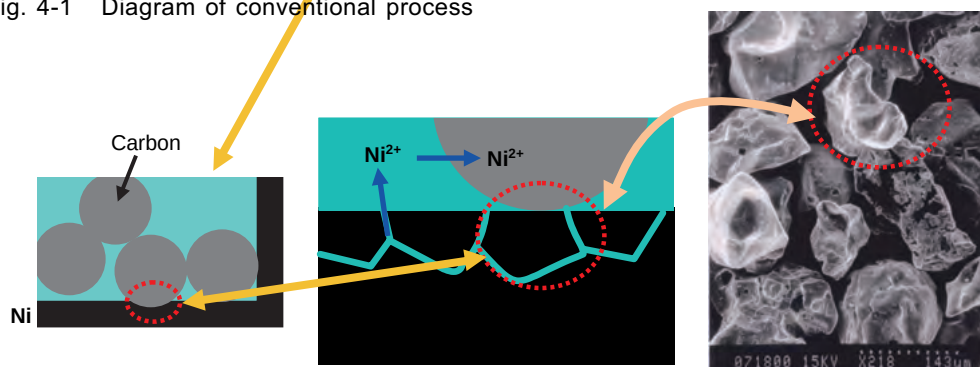


Fig. 4-2 Mechanism of vessel corrosion in conventional KOH activation process

there is a decrease in the capacitor cell yield, producing a reduced lifespan in the production equipment. The second issue is that with high temperature heating, metal potassium is created from the KOH as a by-product, which remains in the reaction system, making it difficult to continue safely operating the system on a long-term basis, and difficult to increase manufacturing quantities. This means batch production is used, which is an impediment to cost reduction efforts. It was necessary to create new mass production methods to address these issues.

4. Means of Resolution

4.1. Technology for Carbocyclic Arrangement for Higher Capacitance

First, the standard graphitizing carbon material production method is explained. When the heavy residues of petroleum or coal are heated, thermal condensation (at approx. 300 °C) multicycles the aromatic compounds, forming condensed polycyclic aromatic compounds. The condensed polycyclic aromatic compounds form stacked aggregates that lead to optical anisotropy (mesophase pitch). This state is the starting point for a graphite structure. The mesophase pitch is further heated at 700 °C for it to be carbonized and pulverized. The resulting graphitizing carbon powder reacts (is activated) with the KOH, creating activated carbon. Mesophase is a molecule group (domain) of condensed polycyclic aromatic compounds, and when the domain grows large, graphene sheets of carbocyclic rings are formed, and graphite material develops. However, if these formations develop too much, the crystallite enlarges, destabilizing KOH impregnation and reaction. As such, since the activation reaction does not occur, activated carbon is not produced. To form more edge planes for higher capacitance, a divided graphite crystalline structure is required. This would necessitate the formation of carbocyclic rings only in the stacked (C axis) direction. However, no carbonaceous production methods like this have been reported, up to now. The authors of this study carbonized various organic materials and characterized their structures. Among them, particularly activated carbon obtained from pitch, which is made from PVC (polyvinyl chloride) resin, showed higher capacitance than that of the activated carbon obtained from mesophase pitch. Focusing on these results, it was assumed that rather than the aromatic rings, which are the main structure of organic raw materials, the adjoining side change

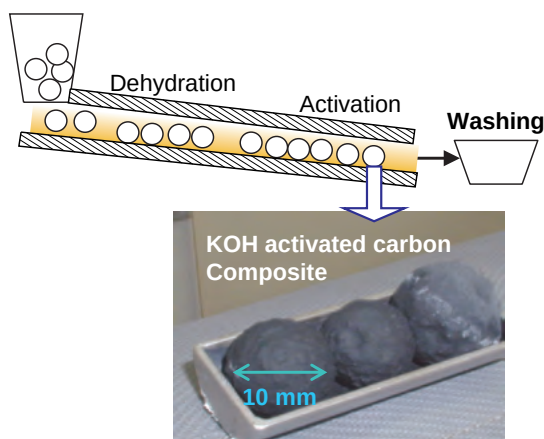


Fig. 6 View of newly developed activation process and picture of activated KOH-carbon composite

molecular structure is more important in developing domain of carbocyclic stack in the C axis direction. A new base organic molecular structure was developed.

4.2. Continuous Alkaline Activation Technology

In addition to addressing the issues in the manufacturing process of furnace material corrosion and by-products such as metal potassium, high quality, low-cost activated carbon for automobile applications must be manufactured. To reduce material characteristic variations, carbon and alkaline should be mixed and heated uniformly. To reduce cost, fast reactions need to occur. As a result of studies, a new continuous production method was created, as shown in Fig. 6⁽⁷⁾. In the conventional activation reaction, an excess amount of solid KOH was mixed in, causing a reaction in the molten KOH. With the new production method, the carbon powder and KOH are mixed in advance in a stoichiometric composition, and after being molded into spherical shapes (composites), they are heat-treated. Changing the composite molding condition and size can change the physical properties of the activated carbon. One feature of this production method is that because the KOH is impregnated with the carbon powder before the high temperature heat-treatment, meltdown of KOH is prevented, thereby avoiding equipment corrosion. Moreover, because the amount of KOH can be reduced, by-products are also reduced. Reaction of the composite on a moving bed, e.g. a rotary kiln, allows a uniform reaction process, enabling activated carbon with a uniform characteristic to be produced.

5. Results

5.1. High-capacitance Activated Carbon Generation Process

We proposed the use of condensed polycyclic aromatic compound pitch (aliphatic pitch: ALP) having a low softening point and plenty of aliphatic groups, which are suitable in obtaining

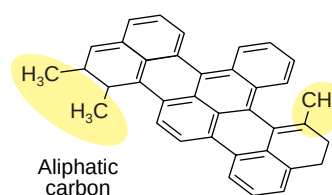


Fig. 7 Design concept of new aromatic compound, ALP

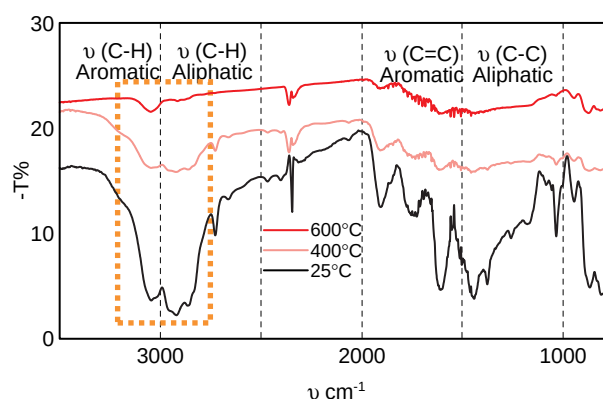


Fig. 8 ALP FT-IR profiles during carbonization process

graphitizing carbon compounds with dispersed fine graphite crystals (Fig. 7)⁽⁸⁾. ALP derived from methylnaphthalene monomer was heat-treated, and the ALP based carbon precursor forming process was analyzed using Fourier transform infrared spectroscopy (FT-IR). Focusing on changes around 3000 cm^{-1} in Fig. 8, the ALP aliphatic -CH peak is greatly reduced due to dehydrogenation, and the formed graphitizing carbon compounds have residual aromatic -CH. These results are shown in the model in Fig. 9. Due to the steric effect of the methyl group, which is an ALP side chain, there is stacking in the layer direction⁽⁹⁾, and because of the presence of naphthene rings, the integral molecular structure is weakened, stacking carbocyclic flat surface structure development in the carbonization process, and at the same time, the aromatic -CH group remains, which is the reactive site. In the scatter plot of Fig. 10, the horizontal axis is the graphitizing carbon atomic ratio H/C, while the vertical axis is the real density of the carbonization. The relationship between the capacitor capacitances obtained is shown. In the carbonization process, dehydrogenation and carbocyclic compound creation and shrinkage occur in turn, so the relationship between the H/C ratio and real density is fixed and the conventional reaction is described by the black line. However, when using ALP, in heat-treatment at comparatively low temperatures, high real density and high H/C (new relationship), new graphitizing carbon compounds can be formed, so activated carbon that used this compound was shown to have a capacitance that is 25% higher, as shown with the dotted line.

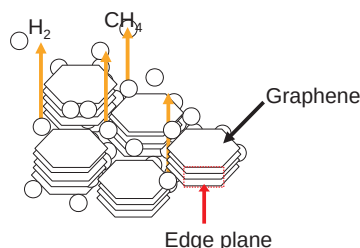


Fig. 9 Model of stacking graphene and graphitizing carbon domain during carbonization

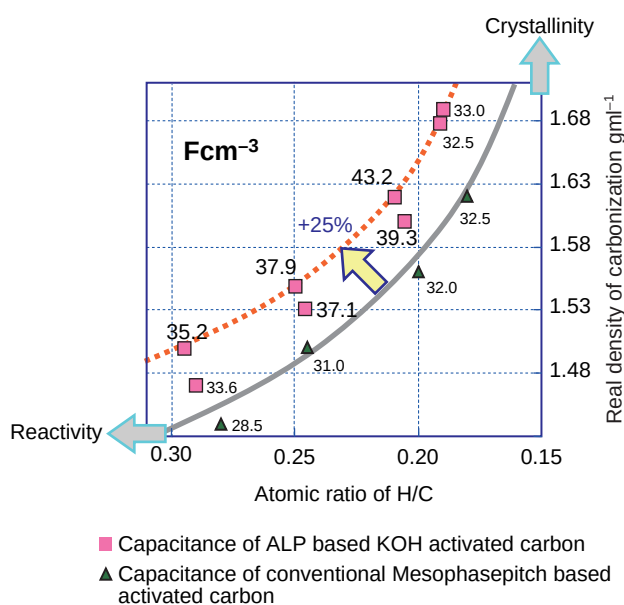


Fig. 10 Scatter plot of capacitances derived from several carbon sources

5.2. Plant Continuous Operation using the New Production Method

The activation furnace (rotary kiln) for the new production method is shown in Fig. 11. The composite is introduced into it from the left side of the diagram, passes through the electrical furnace heating zone, and is discharged after cooling. As shown in the photo in Fig. 6, the activated composite is discharged without any changes to shape. Figure 12 shows the capacitor cell performance results using the activated carbon produced in the activation furnace shown in Fig. 11, and Fig. 13 shows the associated tolerance of self-discharge. Because the heat-treatment process is stabilized and variations in the physical properties of the activated carbon pieces are reduced, the activated carbon capacitance is raised 10% or more, with the accompanying self-discharge yield also enhanced. An advantage of this production method in terms of cost is that it is possible to reduce the amount of KOH used, and thus reduce the metal potassium that is produced as a by-product. This makes it possible to have a continuous manufacturing process. Moreover, Ni, a high-cost metal, is not consumed in the process. With the conventional production method, the activated carbon adheres to the reaction vessel, so it was necessary to have a process where water was poured in and the activated carbon scraped out. However, with the new method, the composite is moved to the washing process in its spherical shape, allowing a continuous process more easily than before. Even if the production quantity expands, the system can be easily adjusted by extending the reaction zone, allowing a reduction in capital expenditures.

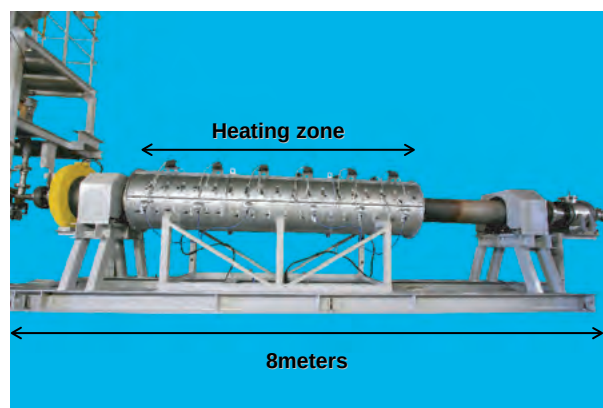


Fig. 11 Picture of newly developed mass production plant

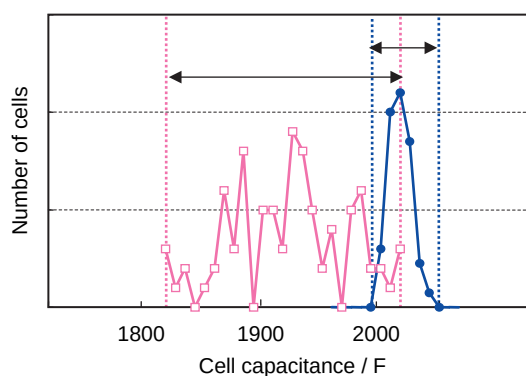


Fig. 12 Histogram of capacitance variation

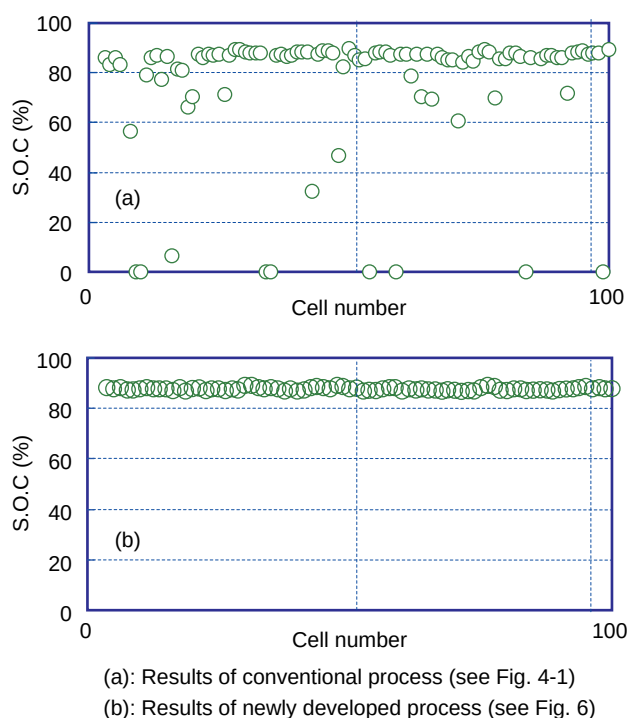


Fig. 13 Comparison of self-discharge characteristics after 72hr at 25°C

6. Considerations

6.1. The Possibilities for Graphitizing Activated Carbon

When designing carbonaceous compounds with a dispersed graphite structure such as ALPs, it is very important to focus on

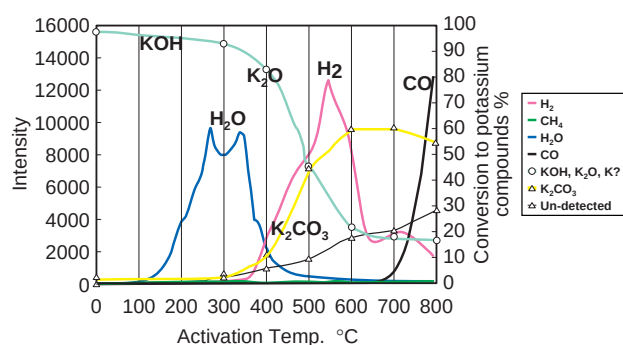
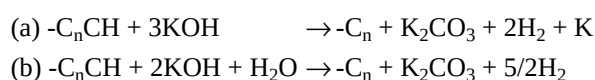


Fig. 14 TDS-MASS and KOH conversion profiles during activation process

the thermal motility of the polycyclic aromatic molecules during the carbon precursor forming process. Specifically, it is possible to suggest that a low-cost organic raw material with a mixed aromatic-aliphatic structure can be searched. In addition, there are additional issues involved when making such compounds with even higher capacitances. If the graphite structure is developed to raise capacitance, this results in a higher carbon bulk density, and pore volume (mlg⁻¹) is reduced. Therefore, the electrolyte ions that would be necessary for charge balance at the electric double-layer interface are in a saturated state at the space, and the activated carbon swells. To overcome this issue in the future, it is important to develop electrolyte ions or an ionic-liquid having high charge balance efficiency properties.

6.2. Proposal of an Alkaline Activation Reaction Mechanism

Until now, few studies had been conducted on the KOH activation reaction mechanism^{(10),(11)}. Therefore, in modifying the procedure for mass production, a detailed analysis of a KOH activation reaction mechanism was carried out, and those results are shown in Fig. 14. From 300 °C KOH dehydration occurs, and at around 400 °C, KOH is consumed and converted to potassium carbonate, at the same time, generating hydrogen. At approximately 600 °C, activation is complete, and at 700 °C or higher, CO desorption on the carbon surface occurs. These results are summarized in Fig. 15. KOH permeates between the graphite crystallite, and reacts with the aromatic -CH, with dehydrogenation, after which the edge plane oxidation occurs. Next, disproportionation of KOH forms potassium oxides, while removing the edge carbon atoms to form K₂CO₃, leading to pore creation. If this reaction is optimized, reaction Eq. 2-(b) is obtained. Conventionally, the reaction is Eq. 2-(a), where hydrogen and metal potassium generation is caused by the excess KOH. However, by introducing a reaction that reduces KOH, the quantity of KOH used is reduced by 15%, thereby reducing by-product metal potassium formation, allowing the formation of an activated carbon continuous manufacturing process.



(a) Conventional KOH activation process
(b) Lower KOH activation

Eq. 2 Comparison of chemical equations

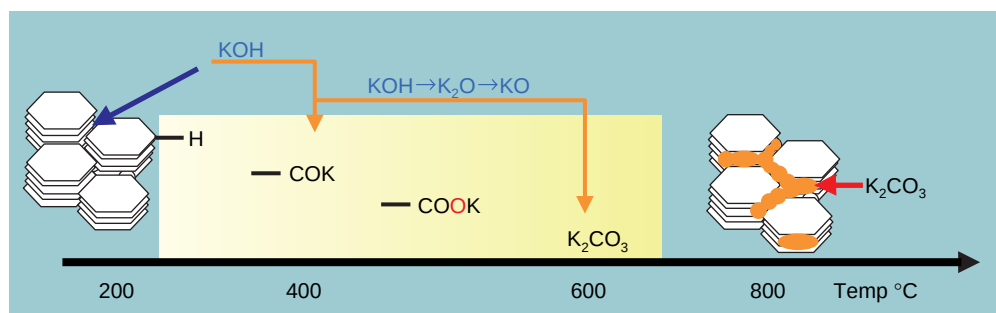


Fig. 15 Mechanism of KOH activation process

7. Conclusion

To increase the energy storage capacity of an electric double-layer capacitor, a high-capacitance activated carbon material was developed, and a mass production process was created.

- (1) A high-capacitance energy storage theory was introduced using activated carbon for the capacitor, and a carbon structure was derived for this purpose.
- (2) As a result of the development of a new organic compound that can produce a high-capacitance carbon structure, capacitor energy storage was increased to twice that of the conventional structure, achieving a practical energy density (wh/kg) equivalent to that of a secondary battery.
- (3) To obtain high quality, low-cost activated carbon, a continuous mass production method was created that resolves the issues associated with conventional alkaline activation production methods. A mass production demonstration plant was built, its operation verified, and its effectiveness confirmed.
- (4) The reaction mechanism of the production method required for this mass production as well as the new reaction mechanism were clarified.

References

- (1) Ue, M.: Denki Kagaku Capacitor you Dennaieki, DENKI KAGAKU (Presently Electrochemistry), Vol. 66, No. 9, p. 904-911 (1998) (in Japanese)
- (2) Morimoto, T., Hiratuka, K., Sawada, Y., Kurihara, K.: Electric double-layer capacitor using organic electrolyte, Journal of Power Sources, Vol. 60, p. 239-247 (1996)
- (3) U. S. 5877935
- (4) Fujino, T., Oyama, S., Oki, N., Noguchi, M., Sato, K., Endo, M., Kim, Y. J.: A characterization of alkaline-activated mesophase-based carbon for electrochemical capacitor, Mol. Cryst. Liq. Cryst., Vol. 388, p. [481]/67-[488]/74 (2002)
- (5) Randin, J. P., Yeager, E.: Differential capacitance study on the edge orientation of pyrolytic graphite and glassy carbon electrodes, Electroanalytical Chemistry and Interfacial Electrochemistry, Vol. 58, p. 313-322 (1975)
- (6) Morimoto, T.: Development and Industrialization of Electric Double-Layer Capacitors, Tanso, No. 214, p. 202-209 (2004)
- (7) JP W2003/089371
- (8) U. S. 6660583
- (9) Mochida, I., Korai, Y., Kun, C. H., Watanabe, F., Sakai, Y.: Chemistry of synthesis, structure, preparation and application of aromatic-derived mesophase pitch, Carbon, Vol. 38, p. 305-328 (2002)
- (10) Maeda, T., Kim, Y. J., Koshiha, K., Ishii, K., Kasai, T., Endo, M., Nishimura, Y., Kawabuchi, Y.: Activation Method of a Mesophase Pitch-based Carbon Fiber, Tanso, No. 201, p. 7-11 (2002)
- (11) Kim, Y. J., Horie, Y., Matsuzawa, Y., Ozaki, S., Endo, M., Dresselhaus, M. S.: Structural features necessary to obtain a high specific capacitance in electric double layer capacitors, Carbon, Vol. 42, p. 2423-2432 (2004)

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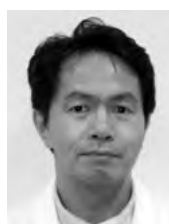
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