

Development of Activated Carbon Electrode for Advanced Electric Double-layer Capacitor

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ABSTRACT

An electrode has been developed for the electric double-layer capacitor utilized in the Honda FCX fuel cell vehicle. Control of the property of the pores of the activated carbon, which is the main material, and efforts to increase electrode density have enabled the achievement of a capacitance per unit volume of 17.6 F/cm^3 , while optimization of the electric conductive adhesive has resulted in a surface resistivity of $6.7 \Omega\cdot\text{cm}^2$. Excellent durability has been achieved by controlling residual organic impurities in the production process. As a result, the capacitor cell in which the electrode is utilized has a capacitance of 1350 F and an internal resistance of $2.5 \text{ m}\Omega$, is highly durable, and was judged suitable for use in the Honda FCX.

1. Introduction

The Honda FCX fuel cell vehicle (referred to as the FCX hereafter), which was first commercially introduced in December 2002, employs an electric double-layer capacitor used as an energy storage device (referred to as the capacitor hereafter). The capacitor has characteristics different from a conventional secondary battery, and in combination with the fuel cell vehicle, much is expected of these new technologies, looking towards the future.

Unlike a secondary battery that involves an electrochemical reaction during charge and discharge, the charge and discharge of a capacitor are carried out through electron movement due to physical absorption of the ions (Fig. 1). Therefore, the capacitor shows superior characteristics in high rate input and output, which is often restricted with a secondary battery, and in charge-discharge cycle life. However, at the same time, capacitor cells on the market (referred to as cells hereafter) are usually small cells of approximately a few F to tens of F. Cells exceeding 1000 F, such as those used in this development project, are still in the prototype stage. Furthermore, because specific capacitance and specific power are low in these cells, their larger size and increased weight would be unavoidable. These cells are not

feasible as the energy storage device for the FCX. This paper reports on the development of an electrode material for a capacitor that achieves both high capacitance and low resistance, for use in the FCX, and on the development of its manufacturing process.

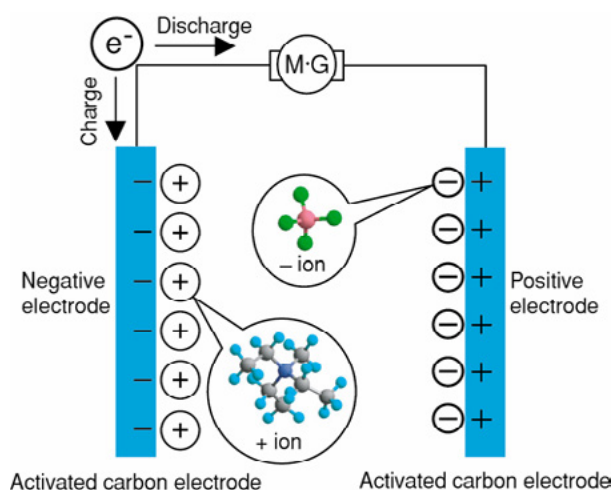


Fig. 1 Model of capacitor

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2. Electrode for Capacitor and its Manufacturing Process

2.1. Electrode for Capacitor

The electrode used in the capacitor is mainly composed of activated carbon formed into electric double layers. In addition, conductive admixture was included to improve electrical conductivity, and a binder material was included to maintain the shape (Fig. 2). The electrode is formed in a sheet shape, and attached to the surface of the aluminum foil current collector by an electric conductive adhesive, creating the electrode (Fig. 3). As is clear from the operation principles outlined above, the capacitor uses the same electrode for the positive and negative poles. This means that it is not necessary to separately manufacture the positive and negative poles, like with a secondary battery, and so is of great benefit in terms of cost and quality control.

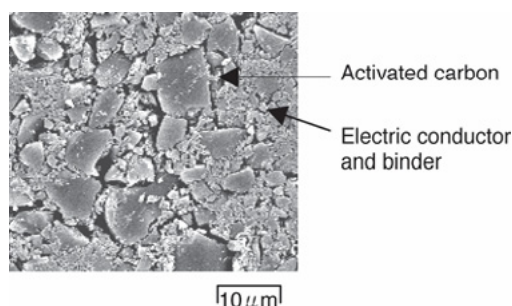


Fig. 2 SEM image of sheet electrode

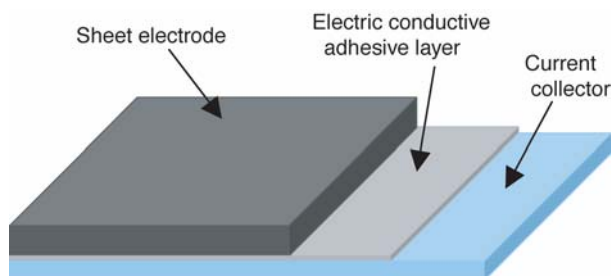


Fig. 3 Structure of electrode

2.2. Electrode Forming Process

Figure 4 shows the electrode forming process in this development process (calender casting method). The details of the process shown in this figure are given below.

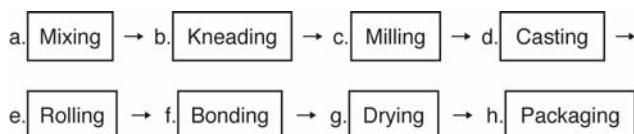


Fig. 4 Production process of electrode for electric double-layer capacitor

(a) Mixing of the raw materials (activated carbon, PTFE binder, conductive admixture)

- (b) Pressing and kneading of the mixture, causing fibrillation of the PTFE binder
- (c) Crushing, grinding, and milling of the kneaded matter
- (d) Adding an organic solvent (referred to as solvent hereafter) to the milled material obtained in step c, and processing into the primary sheet, using a calender casting machine
- (e) Rolling the primary sheet, and processing into a sheet electrode of the specified thickness
- (f) Bonding the sheet electrode and the current collector to each other using an electric conductive adhesive
- (g) Drying, to remove the solvent and water from the electrode
- (h) Packaging the product hermetically after drying

Known methods of electrode forming include the doctor blade method, which makes a slurry of the raw materials mixture and coats it, and the extrusion molding method. In making a capacitor with high-capacity, which was one goal of this development project, calender casting was adopted because high-density electrodes can be expected, and because the amount of solvent added can be kept to a minimum.

The features of this manufacturing method are summarized below.

- (1) The amount of solvent used in forming is small, and so the burden of removing it is small.
- (2) There is plenty of freedom in material combination ratios, and it is possible to raise the amount of the activated carbon, which is the polarizable electrode material.
- (3) There is good control of the electrode density.
- (4) There is good flexibility in changing the electrode thickness dimensions.

In particular, the solvent noted in (1) changes the liquidity during kneading and rolling, and affects the fibrillation of the PTFE binder, which is a binding component. If this fibrillation is not sufficiently carried out, there is a drop in electrode density and a drop in electrode strength, which may cause poor handling. In addition, because the solvent is absorbed by the activated carbon, it can easily remain inside the electrode, and may cause secondary products due to oxidation and thermal denaturation during the removal process. These materials are dissolved during capacitor operation and cause deterioration.

In this development project, in addition to the goals of high capacity and low resistance, a major focus was to create an electrode manufacturing process that actualizes an electrode with superior durability.

2.3. Development Goals

2.3.1. Capacitor cell performance targets

Characteristics required of an energy storage device for the FCX are high energy storage, high output power, and good durability. In order to actualize high energy storage, the target for the cell was a capacitance of 1300 F or more. In addition, to obtain high output power, an internal resistance of the cell of no more than 3.0 mΩ was the target.

To achieve these targets, the goals for the electrode were as given in the next section.

2.3.2. Electrode performance targets

Performance targets for the electrode were set as follows.

- (1) Capacitance per electrode volume (referred to as specific capacitance hereafter): 16.9 F/cm³ or more
- (2) Surface resistivity (referred to as resistivity): 8 Ω·cm² or less
- (3) Durability: same as vehicle life, or longer

3. Electrode Development Concept

The electrode development concept was determined as follows, in light of the targets (1) through (3) above.

- (1) Improve specific capacitance: Optimization of electrode material, and improvement of electrode density.
- (2) Reduce resistivity: Optimization of electrode material, collector material, and electric conductive adhesive.
- (3) Improve durability: Reduction of the amount of impurities remaining in the electrode.

In addition, emphasis was also placed on stability of the quality of the electrode, and full consideration was given to optimization of the manufacturing process.

4. Tackling Performance Improvements

4.1. High Energy Storage

4.1.1. Selection of polarizable electrode material (activated carbon)

Generally, the material of polarizable electrode is a porous carbon, such as activated carbon fiber or activated carbon powder, as shown in Fig. 5. In the development of a high capacity cell, it is necessary to raise the specific capacitance of the electrode, and therefore high electrode density is required of the electrode.

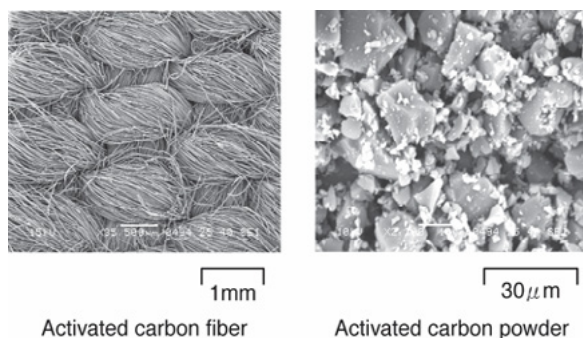


Fig. 5 SEM images of activated carbons

Activated carbon fiber is available as cloth or in a paper form, and it has the benefit of being, in itself, an electrode structure, simplifying the electrode manufacturing processing. However, in terms of its character as a fiber, charging efficiency is low, and it is not possible to expect improvements in electrode density or in specific capacitance. In contrast, it is possible to improve electrode density using activated carbon powder, by controlling grain size and through the electrode forming process. For these reasons, activated carbon powder was adopted for this development project.

Activated carbon powder can be based on natural materials such as coal or coconut shells, etc., or can be based on a synthetic material, such as resin. It is then steam activated. The former is better in terms of cost, but variations in physical properties or residual impurities between manufacturing locations or raw material lots can easily occur. In contrast, the latter is at a slight disadvantage in terms of cost because it is a material chemically synthesized, but in comparison with those based on natural materials, its physical properties are stable and it is superior in terms of control of impurities, making it possible to achieve high specific capacitance.

Figure 6 shows a comparison of specific capacitance of

various common activated carbons. Among these, this development project focused on synthetic activated carbon, and in particular on activated carbon powder that uses phenol resin giving high specific capacitance. Studies were made of its application as a capacitor electrode material.

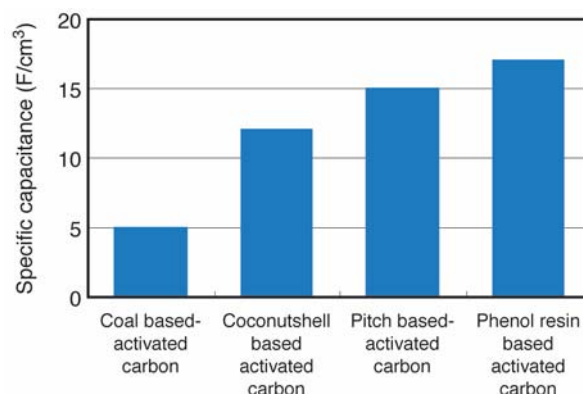


Fig. 6 Specific capacitance of activated carbons

4.1.2. Improvements in specific capacitance

(1) Physical Properties of Activated Carbon

To improve specific capacitance, it is necessary to balance the physical properties of the activated carbon and the electrode forming process. Generally, the physical properties of activated carbon change according to the physical properties of the raw material carbon and according to the steam activation process conditions in the manufacturing process. In particular, the pore forming state not only affects the electrode density incorporating the bulk density of the activated carbon itself, but it also has a close relationship with the specific capacitance and resistivity. In this development project, it was confirmed that the benzene absorption ratio as specified in JIS K1474 is effective as a parameter indicating pore-forming state. With this method, by measuring the benzene vapor absorption ratio against the activated carbon weight, it is possible to specify the raw material's physical properties with higher precision compared to parameters such as specific surface area and pore volume.

Figure 7 shows the relationship between the material's benzene absorption ratio and its specific capacitance. As the material's pore forming progresses, its benzene absorption ratio rises. As this happens, the specific capacitance also changes, becoming largest at 57% and 17.6 F/cm³. At 59% or more, there is a tendency for the specific capacitance to drop due to excessive pore formation.

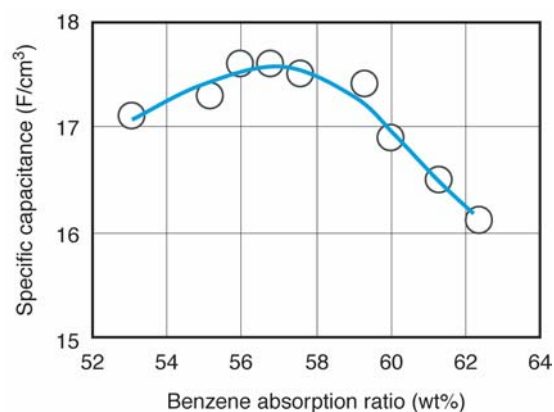


Fig. 7 Relationship between benzene absorption ratio and specific capacitance

(2) Electrode Manufacturing Process

In considering the electrode manufacturing process using this activated carbon, a study was made to raise the electrode density. A solvent is used in this process, to improve formability. A solvent with a low boiling point was used, to reduce the burden of the later elimination process. The solvent is added during (a) mixing, (b) kneading, and (d) the primary sheet forming process using a calender caster (referred to as the calender process hereafter). Among these processes, the most amount of solvent is added in the calender process. Therefore, a study was made of the amount added in this process, and the electrode's physical properties.

In the calender process, the solvent is mixed with the kneaded grain, and machined into a sheet. At this time, the solvent is impregnated with the crushed material, and bonds with the crushed material, improving liquidity. This makes it possible to raise the sheet electrode's density and strength, and also stabilize formability.

Figure 8 shows the relationship between the ratio of solvent added to crushed material weight and the density of the sheet electrode. Figure 9 shows the relationship between the solvent ratio and the tensile strength of the sheet electrode. There is little change in density against the amount of solvent added, but when there is little solvent added there is a tendency for the dispersion to be larger. Concerning tensile strength, too, there is a drop in strength when the additive ratio drops, and there is a tendency for worsening of handling. When the additive ratio exceeds 90 wt%, redundant solvent destroys the shape of the crushed material, causing not only a worsening of formability but also a worsening of mold-releasing from the calender roller. This often leads to forming deviations such as breaking or tearing of the primary sheet. From these results, the solvent additive ratio during the calender process was set at 90 wt% to achieve maximum density and tensile strength.

With this amount of additive, a sheet electrode was manufactured using the actual forming machine, with the set thickness of 150 μm and a length of 150 m. The results of thickness measurements are shown in Fig. 10. Forming deviations during production did not occur, the median thickness was 150 μm , and variation had a standard deviation of $\sigma = 0.18$. The sheet electrode's density was 0.65 g/cm^3 , and the standard deviation was $\sigma = 0.0029$.

From these studies, stable and continuous manufacturing was actualized, maintaining a thickness precision of $\pm 5 \mu\text{m}$, in a state with high sheet electrode density.

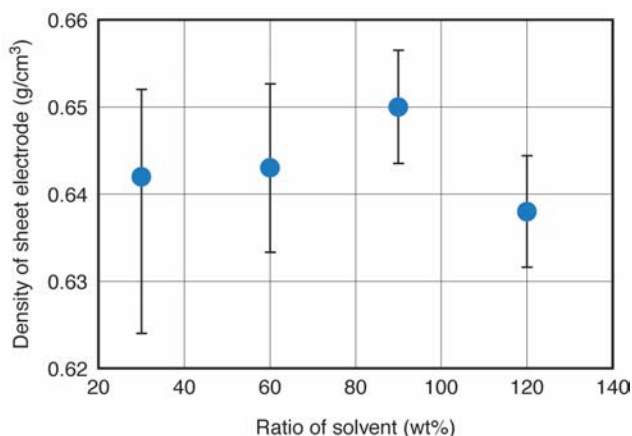


Fig. 8 Sheet electrode density with amount of solvent added

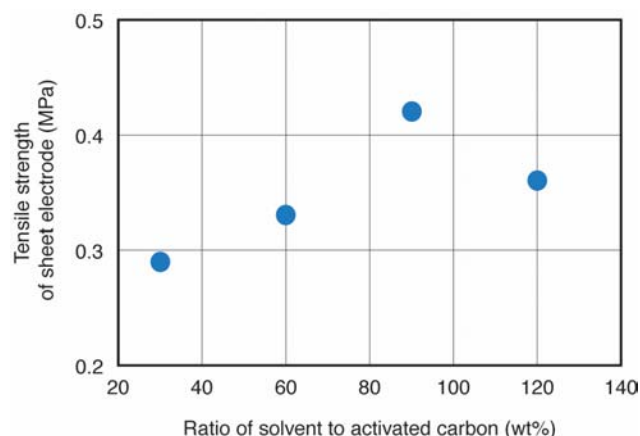


Fig. 9 Tensile strength of sheet electrode with amount of solvent added

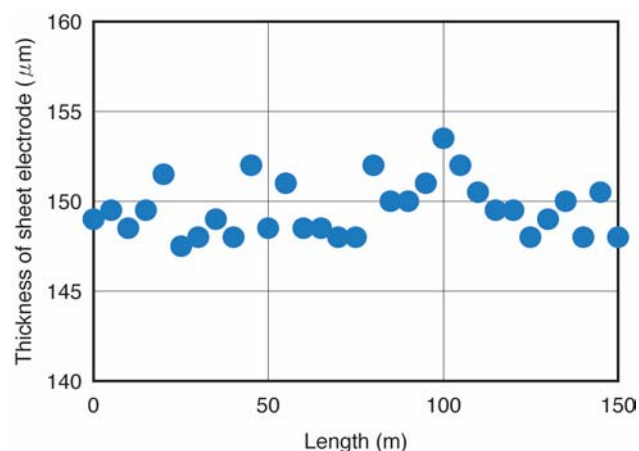


Fig. 10 Thickness distribution of sheet electrode

4.2. High Output Power

4.2.1. Activated carbon's physical properties and internal resistance of capacitor cell

Figure 11 shows the relationship between benzene absorption ratio and surface resistivity. In the range of low benzene absorption, that is to say, the range where pore development is insufficient, there is a rise in resistivity due to inhibition in electrolyte diffusion. Specifically, there is a marked tendency towards this at 55% or less. From the above results, the benzene absorption ratio was stipulated to be between 55.5% and 58% – that being the activated carbon physical property range necessary for specific maximum capacitance and minimum resistivity.

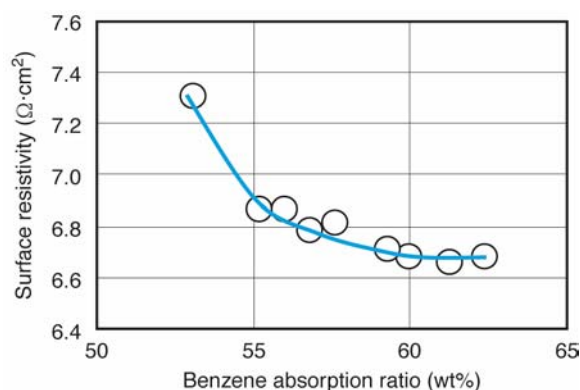


Fig. 11 Relationship between benzene absorption ratio and surface resistivity

4.2.2. Development of an electric conductive adhesive

An electric conductive adhesive is used in the process bonding the sheet electrode and current collector. Generally, a solution of a highly conductive component and an adhesive component distributed in a solvent is used as an electric conductive adhesive. When applied to a capacitor, a mixture of graphite powder and amorphous carbon powder (referred to as carbon black hereafter) is generally used as the conductive admixture, from the point of view of stability and minimization of electrochemical reactions. As for the adhesive component, materials such as those from the poly-imide-amide, silica sol, and polyvinyl alcohol (PVA) groups are used. Table 1 gives a comparison of various adhesive components.

Table 1 Characteristics of adhesive components

Adhesive component	Solvent	Electrolyte resistance	Features
Poly-Imide-amide	N-methyl pyrrolidone	Good	· High adhesive strength · Difficulty of solvent removal · Low durability
Silica sol	water	Good	· Fragile and easy to peel with bending
PVA	water	Good	· Good flexibility · Easy to reduce residual solvent

In terms of adhesion strength, the poly-imide-amides are superior, but giving full consideration to the issue of solvent recovery during manufacturing and to the effect of residue on capacitor performance, a PVA and water solvent adhesive was adopted.

Next, the conductive admixture was optimized, with the purpose of reducing resistance between the sheet electrode and the current collector.

For the conductive admixture, the aforementioned graphite and carbon black were used. The surface of the current collector surface shown in Fig. 12 has indentations and protrusions (pits) of 1 to 10 μm . In order that the conductive admixture sufficiently permeates these pits, the diameter of the graphite grain, which forms scaly particles, was set as 3 μm maximum. In addition, the carbon black grain diameter was set as 0.2 μm or less. The adhesive layer after the sheet electrode has been attached reaches the state shown in Fig. 13 and the carbon black fills in the pits and between the graphite particles. In this state the graphite forms the macro conductive path and reduces the resistance of the adhesive layer itself. On the other hand, the carbon black

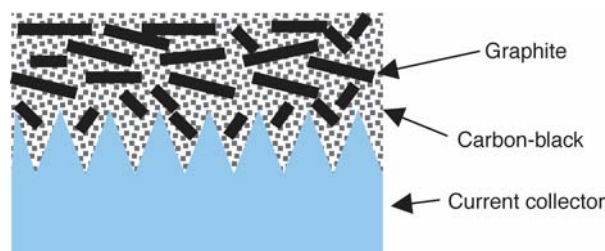


Fig. 13 Image of adhesive layer

serves the function of maintaining conductivity in the space of the graphite particles and with the current collector. Accordingly, the mixture proportions of these two types of carbon material greatly affect contact resistance between the sheet electrode and the current collector.

Figure 14 shows the relationship between the graphite and carbon black weight ratios and the surface resistivity. From these results, it is clear that resistivity is at its smallest when the weight ratio is 1:1. In the range where graphite is rich, conductivity in the space of the graphite particles is insufficient, and resistivity increases. In the range where carbon black is rich, resistivity increases because the macro conductivity paths are insufficient.

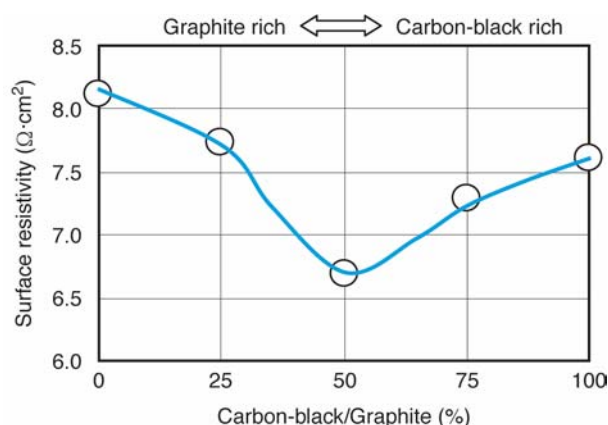


Fig. 14 Effect of carbon-black/graphite composition on surface resistivity behavior

4.3. Durability Improvements

4.3.1. Removal of organic residue inside the electrode

Solvents used during forming, organic matter and water absorbed in the manufacturing process are all causes of performance deterioration during capacitor operation. In order to effectively remove these impurities, drying processes were studied. It is necessary to dry the electrode at no more than 160 $^{\circ}\text{C}$, due to heat resistance constraints of the electric conductive adhesive and the sheet electrode. A possible method for efficient drying in this temperature range is vacuum drying. In this drying process, the long electrode made by bonding current collector and sheet electrode is rolled up and placed inside a drying oven. Then, the air is removed to create a vacuum and the temperature inside is raised to dry. Placing the whole roll in the vacuum drying oven means that it is batch processing, making it easy to put in airtight packaging after removing it from the oven after drying. This has the advantage of reducing the chance of later

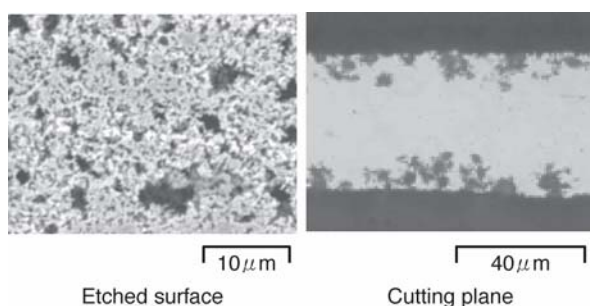


Fig. 12 SEM images of current collector

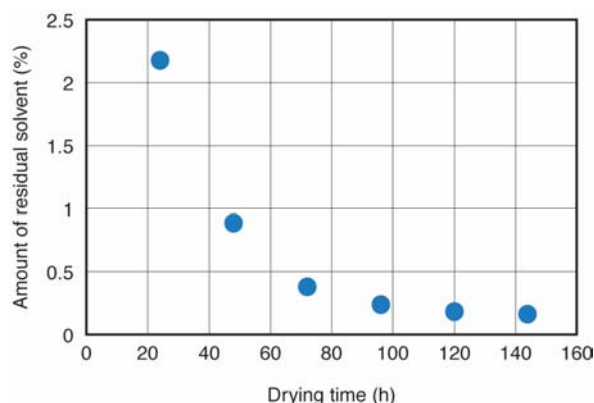


Fig. 15 Relationship between drying time and amount of residual solvent

water absorption or of re-absorption of organic material in outside air. However, it is easy for the temperature inside the vacuum to lose its uniformity, and so it is necessary to establish a sufficient isothermal heating period.

Figure 15 shows vacuum drying time and amount of residual solvent (with the value before drying being 100).

A gas chromatograph was used in quantifying the solvent. A part of the electrode was filled in the test tube of the thermal desorption apparatus, heat was applied while helium gas flowed, and vaporized components were collected in an interior trap. Those components were introduced into the gas chromatograph. The detector uses FID, the quantity is provisionally calibrated from pentene strength, assuming that FID strength is in proportion to the carbon count. Peak qualitative analysis was carried out using mass spectrometry.

From Fig. 15 it is clear that the longer the drying time, the more solvent is removed. However, at the point when vacuum drying is complete, it was confirmed that there were organic impurities, from solvent reactions. These impurities are thought to be organic matter that occur due to oxidation or dehydrate condensation of solvent, which is absorbed or remaining in the pores of the activated carbon. That is to say, when drying is carried out in a rolled state where the concentration of residual solvent is high, impurities are generated secondarily. Accordingly, it is necessary to carry out vacuum drying in the rolled state after the concentration of solvent has been reduced to a certain extent. In order to resolve this issue, prior to vacuum drying in the rolled state, preliminary drying is carried out when the long electrode is still flat. Using this method, the solvent is removed in an open condition.

This has made it possible to reduce the residual solvent and its reaction material, the organic impurities, by 20%.

4.3.2. Control of metallic impurities in the electrode

There are some cases where minute amounts of metal are in the electrode, brought in by the raw material (particularly the activated carbon) or due to contamination during the manufacturing process.

Among these metals, it is known that oxidation-reduction material within the capacitor operation potentially ionizes from the positive electrode, and deposits on the negative electrode. This deposited metal grows on the cathode in the dendrite state, and in the end, penetrates the separator and destroys electrical insulation between the poles. Accordingly, it is necessary to control the raw material manufacturing process and to confirm its content. It is also necessary to avoid metal contamination during the electrode manufacturing process.

5. Confirmation of Electrode Performance

An electrode, produced under the aforementioned conditions, is shown in Fig. 16. When evaluating this electrode, performance such as shown in Table 2 was obtained.

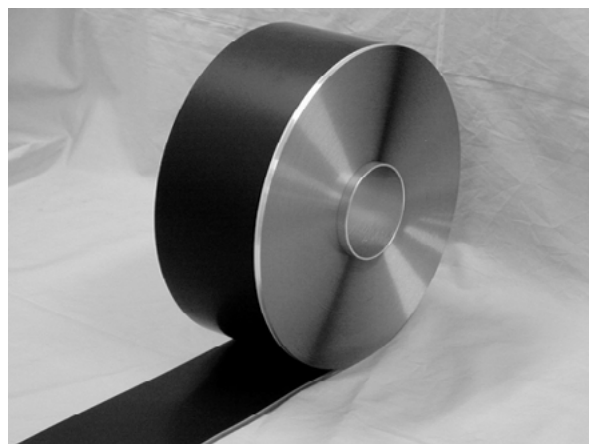


Fig. 16 Electrode coil

Table 2 Electrode performance

Item	Achieved value
Specific capacitance	17.6F/cm ³
Surface resistivity	6.7Ω·cm ² (per single electrode)

In addition, it was possible to achieve the quality shown in Table 3 as sheet electrode, and continuous production with stable quality was made possible.

Table 3 Sheet electrode quality

Item	Achieved value
Thickness accuracy of sheet electrode	±5μm (σ=0.18)
Density accuracy of sheet electrode	±0.01g/cm ³ (σ=0.0029)

6. Confirmation of Capacitor Cell Performance

When cells were produced using this electrode, performance as shown in Table 4 was obtained.

Table 4 Capacitor performance

Item	Achieved value
Capacitance	1 350F
Resistance	2.5mΩ
Durability	longer than FCX life

By improving electrode performance and quality, and by reducing organic impurities, it is possible to manufacture a high output power, high energy storage, high durability cell that can be used in the FCX.

7. Summary

As an energy storage device for the FCX, an electrode was developed for use in a capacitor making possible the actualization of high output power and high energy storage. The results of this project are summarized below.

- (1) By controlling the pores of the activated carbon, which is the major material of the electrode, and by improving electrode density, a specific capacitance per electrode volume of 17.6 F/cm^3 was achieved.
- (2) By optimizing the electric conductive adhesive composition, surface resistivity of $6.7 \text{ } \Omega \cdot \text{cm}^2$ was achieved. Full consideration was given to the environment, with the use of a water-based solvent.
- (3) By minimizing the residual organic impurities, which affect capacitor durability, in the electrode manufacturing process, an electrode was actualized that surpasses the durability required of an actual vehicle.
- (4) A process was established that makes it possible to continuously manufacture large, 1000 F cell grade electrode, with stable quality.

Thanks to these measures, a capacitor cell with a capacitance of 1350 F and an internal resistance of $2.5 \text{ m}\Omega$ was achieved, making possible the manufacture of a cell with excellent durability, which can be used for the Honda FCX fuel cell vehicle.

8. Acknowledgements

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