

## Feature Article

# High Power Electric Double Layer Capacitor (EDLC's); from Operating Principle to Pore Size Control in Advanced Activated Carbons

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## 1. Introduction

An electric double layer capacitor (EDLC) is defined as a device using induced ions between an electronic conductor such as activated carbon and an ionic conductor like as organic or aqueous electrolyte. The current commercial electric double layer capacitor (EDLC) is a small, battery-like device which can provide power during the temporary failures of primary power sources [1-4]. The most common applications for these small size EDLC, named as button cell, are as a semiconductor memory back-up, for electronic equipment, which contains CMOS, RAM or microprocessor. They are also used as auxiliary power sources for mechanical operations in small appliances like laptop computers, alarms, VCRs, telephones and camcorders. EDLC's are well suited as a back-up source because of their energy storage density, low cost and maintenance-free long life operation. On the other hand, extensive studies for high energy density EDLCs for use in electric vehicles or hybrid vehicles drive-lines have been performed eagerly [5-6].

EDLC's with a packaged energy density as high as 3 to 5 Wh/kg have been manufactured using activated carbon electrodes [7-8]. Present energy density depends on the basic electrochemical properties of the activated carbons and on the specific manufacturing technology that is employed. The capacitance of EDLC is strongly affected by the surface properties of activated carbon materials such as the specific surface area ( $\text{m}^2/\text{g}$ ) and pore structure. Thus, the specific capacitance ( $\text{F}/\text{g}$ ) of an EDLC electrode is linked to the physical surface area, to the pore size and the ionic accessibility from electrolyte to the electrode material, and of course to the electrolyte properties. In particular, the pore size distribution (PSD) has been considered to be the most important parameter, because the accessibility from electrolyte to the pore sites of activated carbon strongly depends on the microstructure. Image analysis of TEM pictures on activated carbons has developed as a powerful method for analyzing the PSD [9-10], especially to evaluate the pore size for EDLC uses.

In the present paper, we are willing to present the relationship between specific surface areas, pore size distribution and specific capacitance ( $\text{F}/\text{g}$ ) for various carbon materials in

aqueous as well as non-aqueous electrolytes. Moreover, the size effect of the electrolyte ion is also discussed, and also future prospect of EDLC as a high power applications and related key concepts are demonstrated.

## 2. Historical Overview

The discovery of the possibility of storing an electrical charge on surface arose from phenomena associated with the rubbing of amber in ancient times. Of course, the origin of such effects was not understood until the mid-eighteenth century in the period when the physics of so-called "static electricity" was established. In relation to such historic investigations, the development of the Leyden jar, and the discovery of the principle of charge separation and charge storage on the two surfaces in the Leyden jar, separated by a layer of glass, were of major significance for the physics of electricity and later for electrical technology, electronics, and electrochemical engineering. The utilization of this principle to store the electrical energy for practical purposes, as in a cell or battery in an aqueous solution, have been first proposed and claimed as an original development in the patent granted by Becker in 1957 [11]. Commercial double layer capacitors originated in the Standard Oil of Ohio Research Center (Cleveland) in 1961 and 1962 [12]. Development work continued and the first advertising brochure was released in 1969. Sohio also utilized the double-layer capacitance of high surface area carbon materials, but in a non-aqueous solvent containing a dissolved tetraalkylammonium salt electrolyte. Due to a lack of sales, in 1971, Sohio halted their development efforts and later licensed the technology to Nippon Electric Company (NEC) who developed and marketed commercial double layer products. Carborundum (formerly Sohio) currently sells double layer capacitor products under the name MAXCAP. Several series providing low ESR, high temperature, small diameter or low height packages are offered. Product brochures describing the Carborundum MAXCAP products show a similar construction to the NEC capacitors and are another source of illustrated information on the double layer effect.

During the 1980s, Matsushita Electric Industrial Co.,

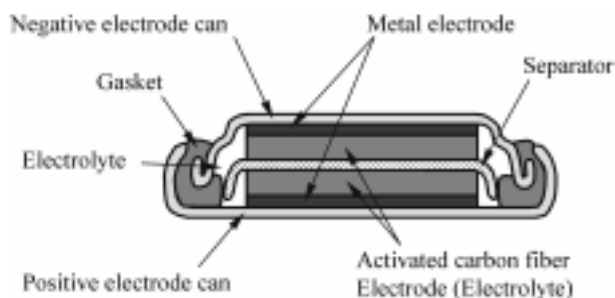


Fig. 1. Practical coin cell with activated carbon electrode made by Matsushita industrial Company [14].

Japan, patented [13] methods for producing double layer capacitors containing improved electrodes. One, made from activated carbon fibers woven into a fabric, was the initial basis for the line of electric double layer capacitor called Gold capacitors. Fig. 1 shows the cross-sectional view of a practical button cell using an activated carbon fiber as a polarizable electrode [14].

At present, the market of electric double layer capacitor has been drastically developing due to the increasing demand such as a mobile phone and a lap top computer, electric vehicle and so on. Moreover, it has been interested as a clean energy technology with increasing the consideration for the environmental pollution.

### 3. Operating Principle

#### 3.1. EDLC principle and structure

In general, positive and negative charges are arrayed at counter position with an extremely short distance, such as atomic distance, between both at the contact interface of two different phases (e.g., solid electrode and liquid). This charge distribution layer is called the electric double layer. There are various explanations for this interfacial charge distribution. Fig. 2 presents the behavior of electrolyte ion and the pore with and without electric field.

EDLC is made from a pair of polarizable electrodes (activated carbon fiber cloth) and electrolyte solution. The capacitance,  $C$ , accumulated in the electric double layer formed at the interface between the polarizable electrodes and electrolyte solution is defined by Eq. (1)

$$C = \frac{\epsilon}{4\pi\delta} \int dS. \quad (1)$$

where  $\epsilon$  is the dielectric constant of the electrolyte,  $\delta$  is the distance from the electrode interface to the center of the ion,  $S$  the surface area of the electrode interface.

#### 3.2. Model for electric double layer

The concept of the energy associated with the electrode's charge distribution in the interfacial region is shown here. The charge distribution depends on the electrode material as well as on its crystalline structure and exposed crystallographic face. However, it is interesting to see the historical

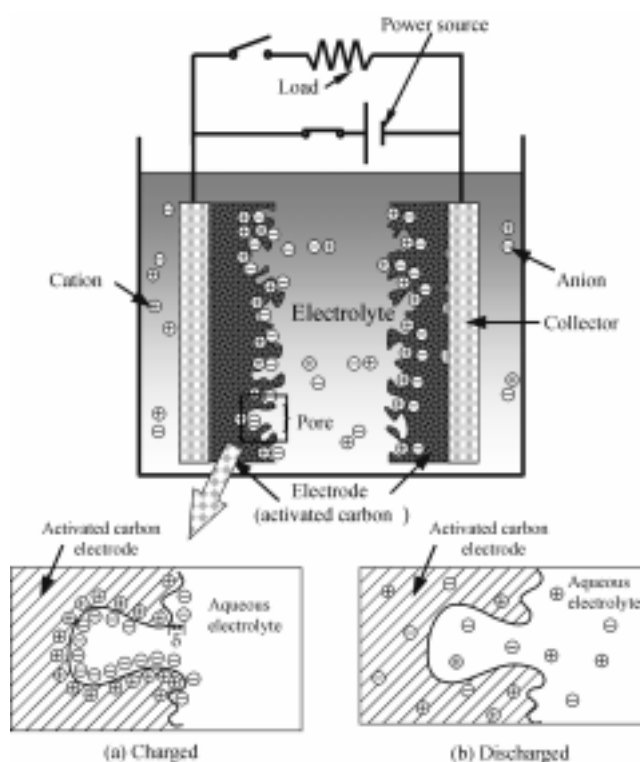


Fig. 2. Behavior of electrolyte ion in the pore when charge and discharge performed.

evolution of the reflecting the structure of induced ions.

The first double layer model considered the ordering of positive and negative charges in a rigid fashion on the two sides of the interface, giving rise to the designation of double layer (or compact layer) and no interactions stretching any more into the solution. Fig. 3(a) illustrates the Helmholtz [15] model. This model of the interface is comparable to the classic problem of a parallel-plate capacitor. One plate would be on the contact surface metal/solution. The other, formed by the ions of opposite charge from solution rigidly linked to the electrode, would pass through the centers of these ions, that is, ionic radius. But in this model, two principal defects were found. The first is that it neglects interactions occurring further from the electrode than the first layer of adsorbed species, and second is that it takes into account no dependence on electrolyte concentration.

At the beginning of this century Gouy [16] and Chapman [17] independently developed a double layer model in which the applied potential and electrolyte concentration were considered, both influencing the value of the double layer capacity. Thus, the double layer would not be compact as in Helmholtz's description but of variable thickness and the ions being free to move (Fig. 3(b)). This is called the diffuse double layer. In this theory, we should pay attention to the approximation in which ions are considered as point charges but real ion can not enter into the inside of the plane of closet approach, because of its specific size. Stern [18] combined the Helmholtz model and the Gouy-Chapman model. He considered that the layer was formed by a compact layer

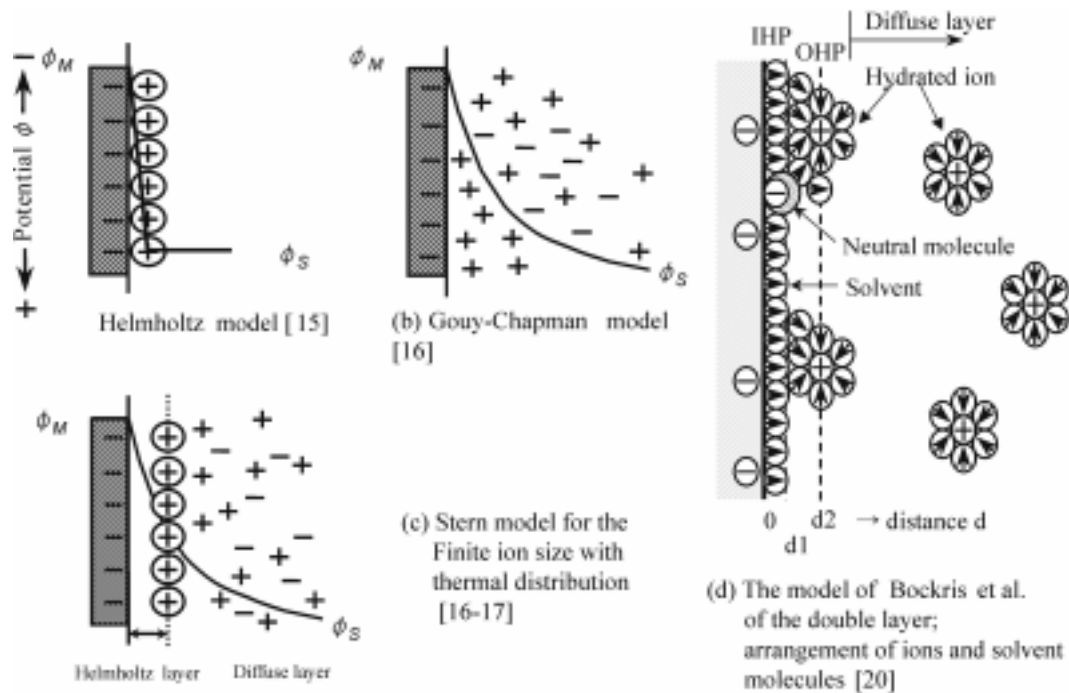


Fig. 3. Models of the double layer: (a) Helmholtz model [15], (b) Gouy-chapman model (point charge model) [16-17], (c) Stern model [18], (d) BDM (Bockris, Devanathan, Muller) model [20].

of ions next to the electrode followed by a diffuse layer extending into bulk solution (Fig. 3(c)).

Grahame [19] developed a model constituted by three regions of inner Helmholtz plane (IHP), outer Helmholtz plane (OHP) and the diffuse region. The difference between this and the Stern model is the existence of specific adsorption. A specifically adsorbed ion loses its solvation, approaching closer to the electrode surface. Besides this have the same charge as the electrode or the opposite charge, the bonding is strong. More recent models of the double layer have taken into account the physical nature of the interfacial region. In dipolar solvents, such as water, it is clear that an interaction between the electrode and the dipoles must exist. This is reinforced by the fact that solvent concentration is always much higher than solute concentration. The Bockris, Devanathan and Muller model [20] recognizes this situation and show the predominance of solvent molecules near the interface as shown in Fig. 3(d). Present model could be acceptable in the following discussion on high power EDLC.

#### 4. Capacitor Types and Their Major Characteristics

A capacitor is classified into three types as follows; 1) electrostatic capacitor, 2) electrolytic capacitor, 3) electrochemical capacitor. At the first, electrostatic capacitor has a small capacitance compare with that of another capacitors. However, it is possible to charge/discharge at a high voltage, especially, used in a high voltage short pulse power system due to the high discharge time of about mili-seconds. The type of electrostatic capacitor assorted like ceramic capaci-

tor, glass capacitor, mica capacitor, and plastic/metalized film capacitor by the electrode material. Electrolytic capacitor has been used most generally up to now, because it has a large specific capacitance. But, Electrochemical capacitors is a new type of capacitor offering new features by means of characteristics between those of a battery and a simple capacitor [21-22]. The specific capacitance of electrochemical capacitor is much larger (over 10-1000 times) than that of conventional capacitor as mentioned before.

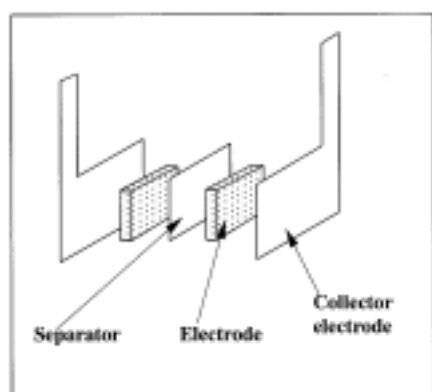
And, the capacitor also separated as a non-aqueous electrolyte system and an aqueous electrolyte system by the solvent for the dissociation of electrolyte. Table 1 presents the characteristics of the organic solvent system and aqueous EDLCs.

The former has the advantage of high working voltage, so that it proper to perform the charge and discharge at high voltage. High decomposition voltage is profitable to get the energy, because the capacitance is proportion to the square of voltage. And, organic solvent can be used in wider extent of temperatures. On the other hand, internal resistance is high and it needs a seal hermetically to avoid moisture absorption, because moisture existed in the atmosphere cause the extreme degradation of the cell. Therefore, the cost for a production is expensive.

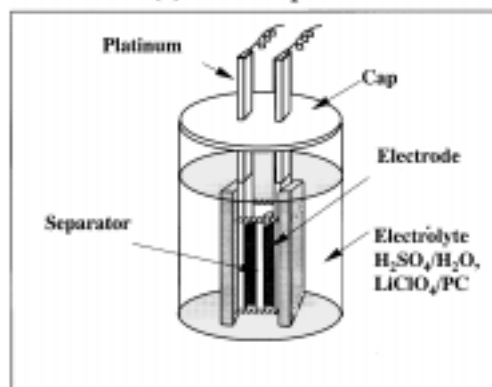
The latter, aqueous solvent system capacitor has a high ion mobility and high dielectric constant so that the internal resistance is very small. Moreover, it is non-flammable (safety excellent), and stable in an ambient condition. Production cost per unit cell is relatively low. But, there is also a disadvantage such a low decomposition voltage around 1.3V and the limited working temperature for depending on the properties of water. In this study we use the electric double

Table 1. Characteristics for non-aqueous and aqueous electrolyte capacitors

Electrolyte	Merit	Demerit
Organic system	High working voltage, compact, high energy density Metal can be used in a cell construction Wide working temperature	High internal resistance Need a seal hermetically to avoid moisture absorption (Moisture cause the degradation) Expensive production costs
Aqueous system	Low electrical resistance High ion mobility High dielectric constant Stable in ambient condition Non-flammable Low unit cost of production	Low decomposition voltage; 1.23 V Limited available temperature



(a) Cell composition



(b) Experimental cell for the capacitance measurement

Fig. 4. Experimental cell for the capacitance measurement.

layer capacitors (EDLCs) in the category of the electrochemical capacitor based on the activated carbon electrode. And, at first, we discuss the specific capacitance in both systems.

### 5. Relationships Between Specific Capacitance and Pore Size Distribution of Activated Carbons in Aqueous and Non-aqueous Electrolytes [23]

Fig. 4 illustrates the experimental cell used for the experiments, in which the same electrodes for cathode and anode were adopted for the cell configuration. Various kinds of activated carbon (AC) and carbon fiber (ACF) electrodes

Table 2. Fundamental properties of activated carbon fiber (ACF) and activated carbon (AC) used in this study

Sample No.	Specific surface area (m <sup>2</sup> /g)	Average moisture content (%)	Adsorption ability of Chloroform (unit)	Precursor material
①	1016	1.81	1.3	Pitch
②	1026	5.54	1.1	Pitch
③	1076	–	1.6	Pitch
④	1100	2.3	1.75	Pitch
⑤	1182	3.1	2.9	Pitch
⑥	1221	0.37	3.3	Pitch
⑦	1350	2.3	1.06	Pitch
⑧	1450	4.7	0.84	Pitch
⑨	1521	0.1	1.1	Pitch
⑩	1634	1.45	0.3	Pitch
⑪	1965	0.25	0.8	Pitch
⑫	1232	2.32	–	Phenol resin
⑬	1542	0.99	2.3	Phenol resin
⑭	1864	0.61	2.1	Phenol resin
⑮	2300	–	–	Phenol resin
⑯	713	12.29	0.0	PAN
⑰	1692	–	1.0	Coconut shell
⑱	86	0.43	–	Pitch-based CF
A	1000	–	–	Pitch
B	1500	–	–	Pitch
C	2000	–	–	Pitch
D	3000	–	–	Pitch

were set up in a glass beaker as an anode and cathode, with a 30wt% sulfuric acid aqueous solution or 1M of LiClO<sub>4</sub>/PC. Before the capacitance measurement, each electrode was treated under primary vacuum conditions at room temperature, for more than 14 hours to remove the residual air remaining in the electrode and for the impregnation of the electrolyte. Platinum plates were attached mechanically to the electrodes samples for the output terminal. Glass paper (Oribest) was used as a separator. The specific capacitance (F/g) was measured as a function of SSA at 0.9V and 2.5 V charge voltage and 1mA discharge current for aqueous and organic electrolyte, respectively. Here, to prepare a typical sample, 40 mg of AC/ACF material were mounted on a Pt plate and then pressed to make enough electric contact to

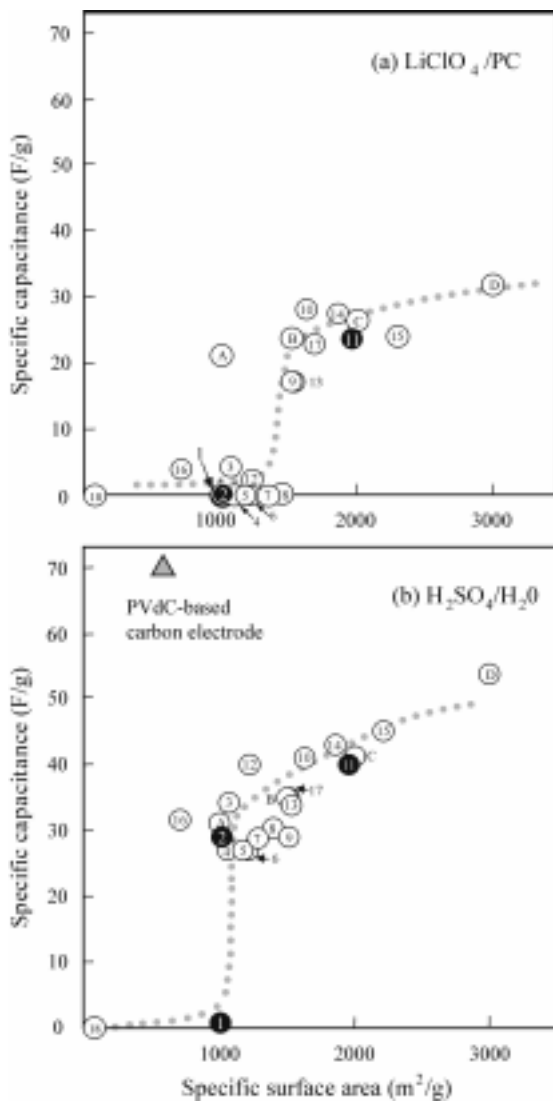


Fig. 5. Distribution of the specific capacitance vs. specific surface area for various samples in (a) a non-aqueous electrolyte (LiClO<sub>4</sub>/PC), (b) an aqueous electrolyte (H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O).

measure the capacitance. The capacitance measurements were carried out using a constant voltage charge – constant current discharge method.

LiClO<sub>4</sub>/PC organic electrolyte system were taken as electrolytes under argon atmosphere at room temperature in the glove box. The capacitance was measured by constant current charge-discharge method. The fundamental properties of samples used in this study were summarized in Table 2.

Fig. 5(a) and (b) show the distribution of capacitance for various samples in aqueous and non-aqueous electrolytes, respectively. It is clear that there is some threshold for EDLC operation is specific surface area in the range of 1000 m<sup>2</sup>/g, which is much larger as 1400 m<sup>2</sup>/g for organic system than aqueous one. Even though there is no definite difference depending on types of starting materials, it is worthwhile to note that the aqueous system shows relatively higher specific capacitance as compared with those of non-aqueous system. For the case of ACFs with surface area

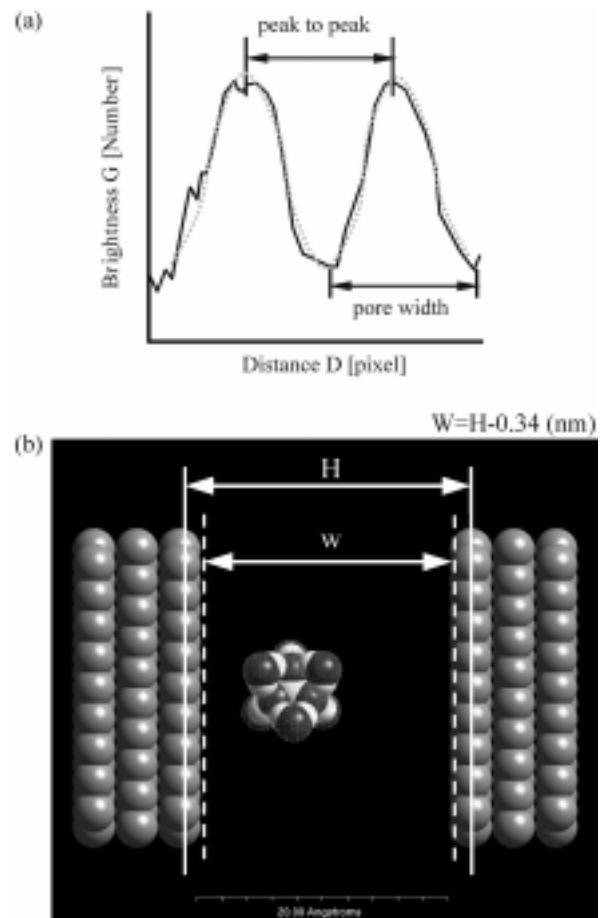


Fig. 6. Recognition of the pore size in an image processing: (a) Pore width by the variation of tone wedge, (b) Pore width by the molecular simulation.

lower than 1400 m<sup>2</sup>/g, the non-aqueous system shows very lower capacitance whereas the aqueous system exhibits higher value of capacitance from 25 to 40 F/g. Based on this data, we classified samples into three groups as followings; the first group (sample ⑪) shows good capacitance for both types of electrolytes, the second group (sample ②) shows only capacitance for the aqueous system, and the third group (sample ①) shows no capacitance for both types of electrolytes.

Fig. 6 presents the importance to evaluate the pore size of activated carbon especially for use in EDLC by pore size consideration of the solvated ion size. Fig. 6(a) is the brightness variation across the pore in the TEM picture. A white place in the picture means the pore and in reverse, a black zone means the part existing the carbon atom. So, the variation of brightness in the original TEM picture could correspond to the amount of the existing carbon atom. Hence, it is considered that the variation of brightness is respecting the pores. X-axis is the variation of brightness and Y-axis means the some place existing in a TEM picture [24]. Fig. 6(b) presents the model of the pore width and adsorbed solvated ion.

Fig. 7 shows the morphology observed by transmission electron microscope (TEM). Using the binary image analysis method, size of white area for sample ⑪ is relatively larger

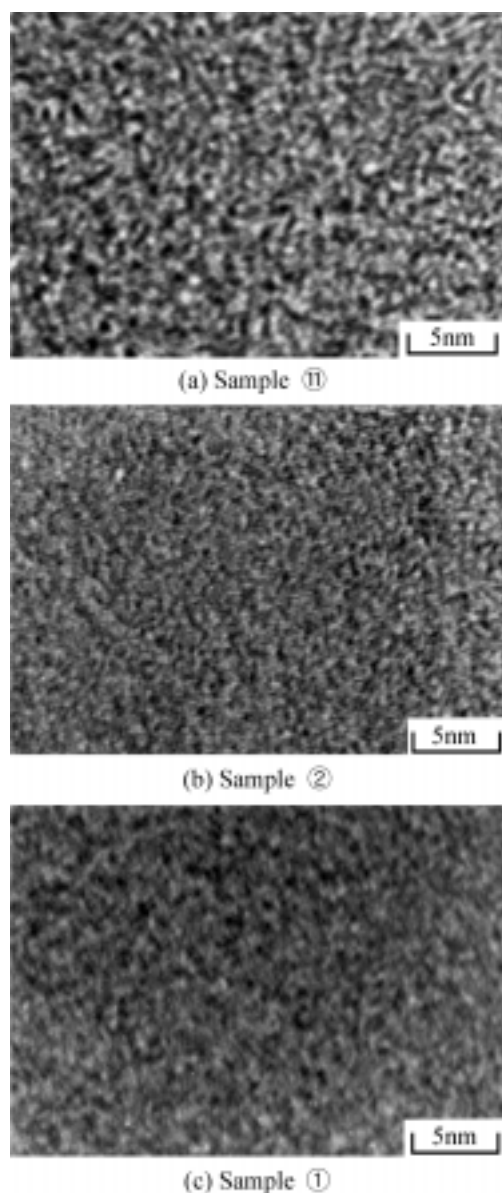


Fig. 7 Morphology of three representative samples obtained by TEM observation; (a) sample ①, (b) sample ②, (c) sample ③.

as compared than those of other samples. And also, it is clarified the result of the pore size distribution (PSD) through image analysis (Fig. 8) [28]. In particular, main pore sizes for sample ①, ②, ③ are observed to be 30Å, 20Å, and 15Å, respectively. As a result, it is confirmed that the pore size distribution have strong relation with specific capacitance, and also, the relationship between pore size and ion diameter of electrolyte affect greatly on the capacitance.

Fig. 9 shows the models for pore structure on basis of the fractal simulation, conventional pore model and TEM picture of activated carbon fiber. As shown in this result, the model of pores existing in the porous material can be expressed using a simulation device, and it consistent with the result obtained from TEM observation.

Fig. 10 presents the electrolyte ion model obtained by molecular simulation using also the software Cerius2 (ver.

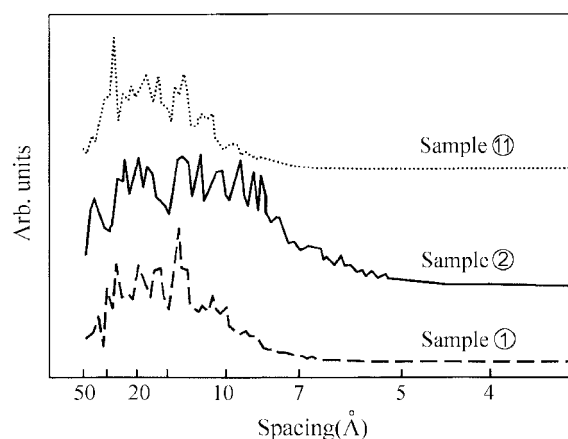


Fig. 8. Pore size distribution obtained by the image analyses of TEM photographs.

3.8). We performed the calculation about the radius of the ions that can exist with a solvent. Moreover, we calculated the diameter of huge complex produced with the hauling force between ion and a solvent molecule, and it can explain the relation between the pore size of porous carbon material and EDLC performances.

We evaluated the performance of EDLCs using various ACFs as the electrode in aqueous and non-aqueous organic electrolytes. The AC and ACF used in this study were distinguished into three groups based on the relationship between PSD and capacitance. Finally, it is possible to that the reciprocal relation between solvated ion diameter in electrolyte and pore size of carbon materials affects greatly on the capacitance of EDLCs.

## 6. A New Type of Electrode Material Obtained from PVDC [25]

It is well known that the capacitance of EDLCs is strongly affected by surface properties of carbon materials, for example the specific surface area and pore structure when carbon materials are used as the polarized electrode. Generally, activated carbon materials have been prepared by activating process, which includes the oxidizing process with steam or CO<sub>2</sub> after the stabilization or carbonization step. But we found that a well-defined pore size distribution in polymer-based carbon material could be obtained by only carbonization step without any activation. This material was named as VESC (Very Early Stage of Carbonization), and has been applied in aqueous EDLC. They showed a high specific capacitance as compared with those of conventional activated carbons such as carbon char.

Fig. 11 shows the specific capacitance per unit weight (F/g) as a function of the output current density for various VESC bulk electrodes. The specific capacitance for each sample is observed to decrease with increasing current density. It is worth while to note, in particular, that the VESC-1000°C sample shows an extremely high efficiency for vari-

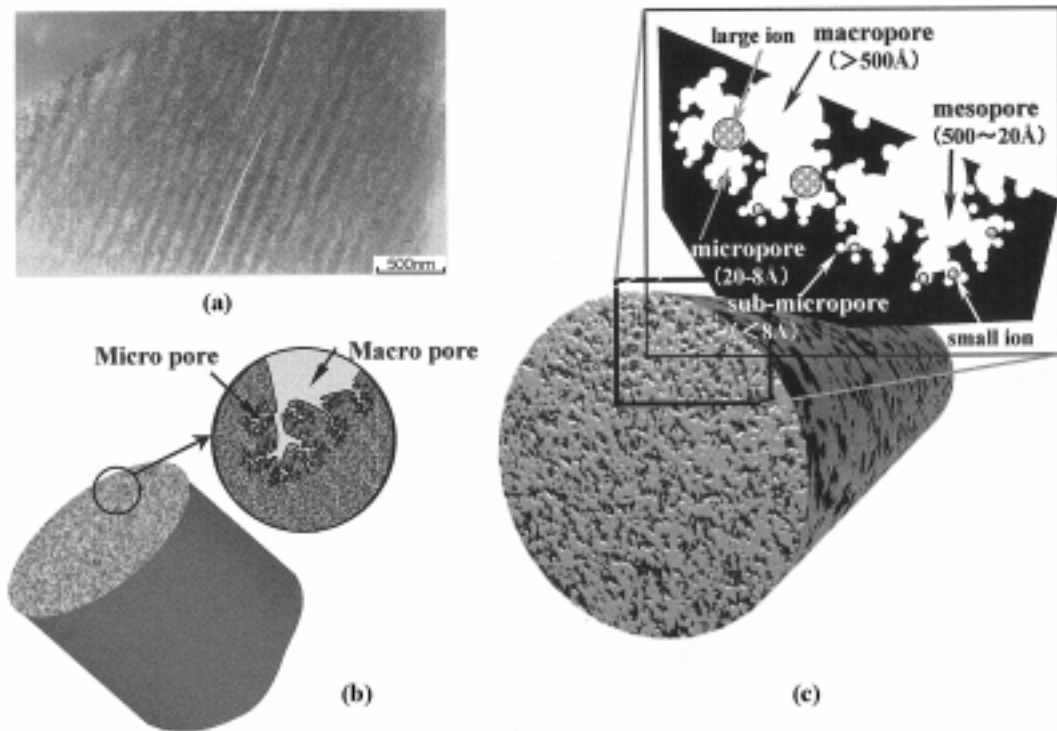


Fig. 9. Pore model for porous carbon materials; (a) TEM image of the transverse thin section sample of an ACF, (b) Conventional model for activated carbons, (c) on the basis of the fractal simulation using the software Cerius2.

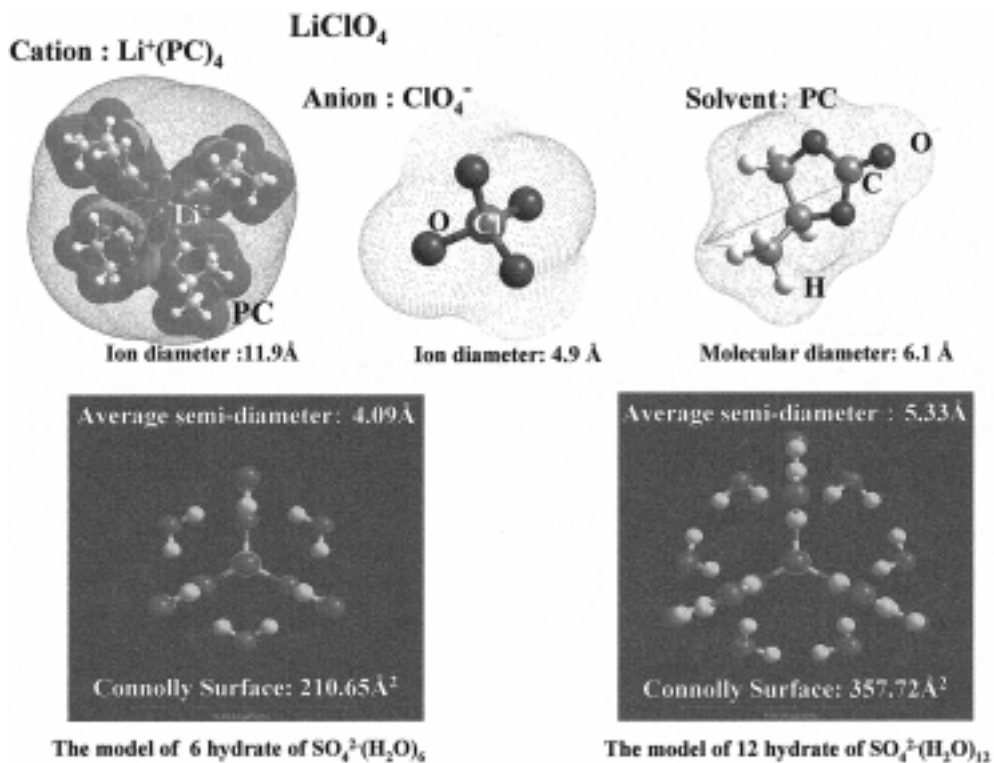


Fig. 10. Electrolyte ion model resulted from molecular simulation using the software Cerius2.

ation of the current density. The Fig. shows that the VESC-700°C obtained the largest capacitance of 64 F/g at a low current density of 1 mA/cm<sup>2</sup>, although the VESC-800°C sample had a larger specific surface area than that of VESC-

700°C. The higher the heat treatment temperature, the better is the maintenance of the specific capacitance with increasing current density. The EDLC test was discharged at 1 mA of constant current, and charged at 0.9V of constant voltage

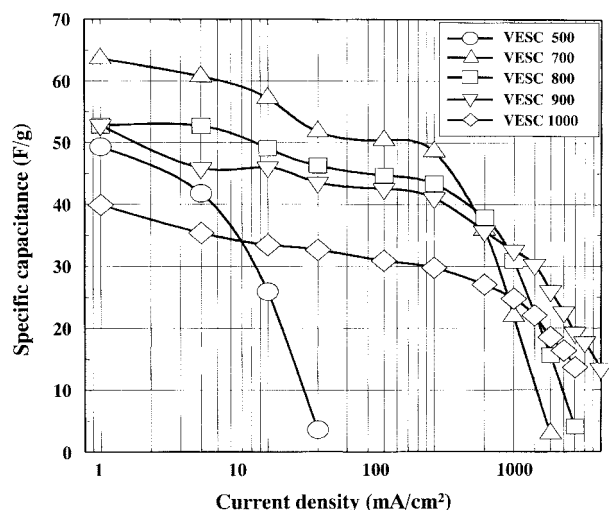


Fig. 11. Specific capacitance per unit weight (F/g) as a function of the output current density for various VESC bulk electrodes.

Table 3. Fundamental characteristics of commercial VGCF used in this study [30-31]

Characteristic	Units	Value
Fiber diameter	$\mu\text{m}$	0.15
Fiber length	$\mu\text{m}$	10-20
Specific surface area	$\text{m}^2/\text{g}$	13
Density	$\text{g}/\text{cm}^3$	2
Bulk resistance	$\Omega \cdot \text{cm}$	0.012
Mono filament resistance	$\Omega \cdot \text{cm}$	0.0004
Ash	%	0.1

for 5 min. It is worth while to note that relatively high capacitance as high as 30 F/g is obtained at higher out-put current of 1000  $\text{mA}/\text{cm}^2$ . The present performance is very much promising as a high power capacitor applicable for HEV or EV.

SEM picture of the PVDC-based carbon electrode was shown in Fig. 12. The sample was heat treated at 700°C for 1hour. It is worthwhile to note the electrode formed huge bulk-like morphology. Owing to the peculiar method for preparation of electrode, the cell has a bulk-like structure all over the electrode.

In order to investigate the relation between the pore size distribution (PSD) and the specific capacitance, novel method by image analysis was used. Transmittance Electron Microscope (TEM) is one of the most powerful apparatus to investigate the morphology of nano-scale. Moreover, it was confirmed that TEM is of use apparatus to observe the pore dimension by J. R. Fryer in 1980 [26]. Fig. 13(a), (c), (e) shows high-resolution TEM image and the corresponding pore size distributions of PVDC-base carbon samples, VESC, in comparison to the PSD obtained from the adsorption isotherms. The results show the existence of large numbers of nano-pores with diameters less than 1nm. Fig. 13(b), (d), (f) show the PSDs obtained by image analysis of the TEM pictures, using the corresponding FFT patterns for each

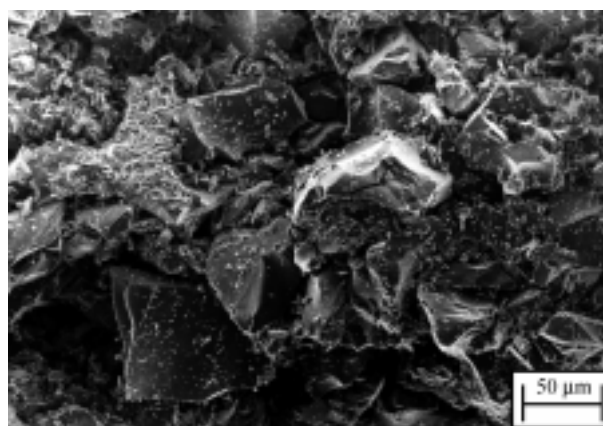


Fig. 12. SEM photograph of PVDC capacitor electrode heat-treated at 700°C for 1hr.

photographs [27-28]. The x-axis denotes the spatial wavelength, and the y-axis denotes the intensity of the power spectrum. In this Fig., it is shown that the pore size is shifted toward larger sizes with increasing HTT, and that the dominant pore sizes are less than 1.5 nm for all three cases. The pore size distributions obtained by image analysis are quite consistent with those of the  $\text{N}_2$  adsorption isotherms. PVDC-based carbon has a porous structure with a proper pore-size distribution, which could be more suitable for EDLC applications. The results for capacitance measurements as a function of SSA for various AC/ACFs and carbonized PVDCs was shown in Fig. 5(b). It measured under 1  $\text{mA}/\text{cm}^2$  discharge current. At this point, it is concluded that the PVDC-based electrodes show a higher capacitance than those of commercial AC/ACFs materials, which is reflected in the suitable pore size for the  $\text{H}_2\text{SO}_4$  aqueous electrolyte, by investigating the relation between the capacitance and the PSD (pore size distribution) of the host material. These PVDC-based carbon electrode samples, having a much smaller specific surface area than those of typical ACF/AC ( $\sim 2000 \text{ m}^2/\text{g}$ ), but nevertheless show a two times higher specific capacitance. This result can be related to the relative size difference between the pore and the electrolyte ion. As observed in Fig. 10, the capacitance for this sample is dominated by ultra micro pores of less than 10 Å size.

The  $\text{H}_2\text{SO}_4$  electrolyte separates into a  $\text{H}^+$  ion and a  $\text{SO}_4^{4-}$  ion in the aqueous solution. The  $\text{H}^+$  ion, with a very small size can easily participate in a repeated insertion and exciting process many times. For the case of the  $\text{SO}_4^{4-}$  ion, it was considered as a possible structure of a hydrated sulfide. There could be various kinds of solvated sulfide water molecules, such as  $6(\text{SO}_4^{2-} \cdot (\text{H}_2\text{O})_6)$  and  $12(\text{SO}_4^{2-} \cdot (\text{H}_2\text{O})_{12})$  as shown in Fig. 8. According to a simulation by a semi-experimental calculation, these species have ion sizes of around  $\sim 10 \text{ \AA}$ , indicating that these sulfide ions can be filled into a pore having a typical size of around 10 Å. Such a relative range in size between the pore and the inserted ion into the pore seems to be best for getting a high specific capacitance.



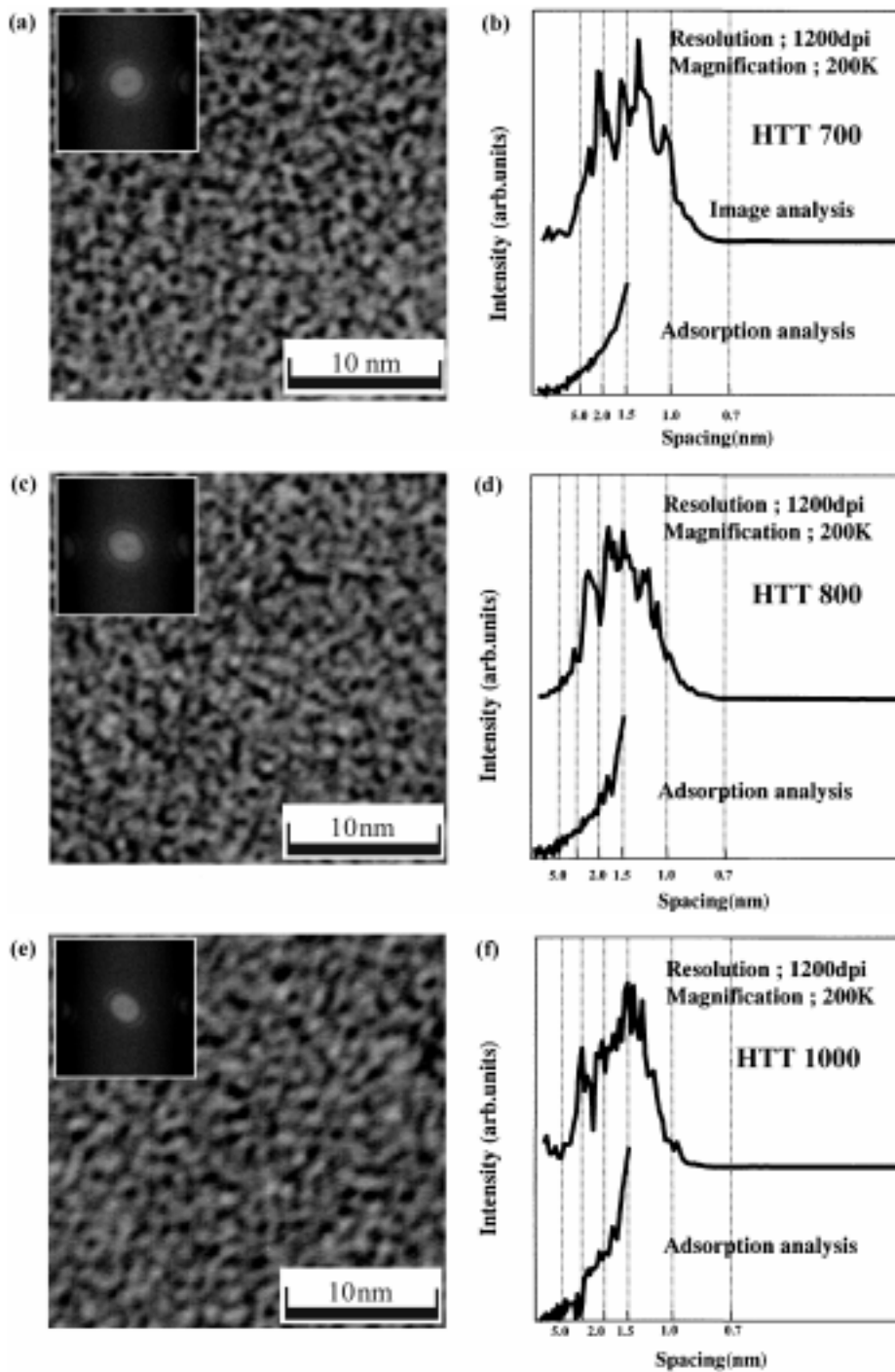


Fig. 13 Transmission electron microscopy (TEM) photographs and pore size distribution (PSD) curves obtained by image analysis.; (a), (b): PVdC-700°C, (c), (d): PVdC-800°C, (e), (f): PVdC-1000°C.

## 7. The Improvement for EDLC Electrode by VGCF Addition [29]

Resistance component of electrode in EDLC is very important as a requisite for high power electric double layer capacitor applications. In particular, it is more important for capacitor use in HEV, because the charge/discharge performed at the high current density. In this section, the increment of conductivity was taken into the consideration and

the enhancement of a large current-capacity property was tried by mixing with Vapor Grown Carbon Fiber (VGCF, Showa Denko, G grade) as an additive [30-31]. The preparation of sheet-type electrode was performed after mixing 10-30wt% VGCF to an activated-carbon weight. The host material used as an activated electrode is a coconut shell. The particle size of activated carbon could be 20  $\mu\text{m}$  or less, and much smaller than VGCF fiber length. VGCF is uniformly dispersed around activated carbon as shown in Fig. 14. On

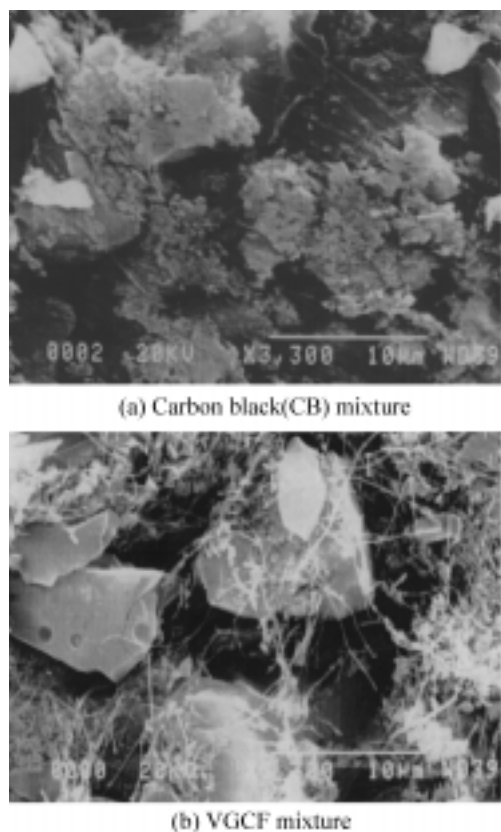


Fig. 14. SEM photographs of double layer electrode mixed with an additive: (a) carbon black (CB) mixture, (b) Vapor grown carbon fiber (VGCF) mixture.

the other hand, mixed carbon black has confirmed growth of an aggregated particle, even though carrying out to the mull of carbon black with an alcohol (IPA) as a dispersant. In Table 3, the properties of commercial VGCF used in this study were summarized. VGCF used in this study is G grade made from Showadenko Co. (Japan). The valuation of electrostatic capacitance was performed by the constant-current method and it performed by the discharge of the fixed electric current after retention for 30 minutes in the charge to 2.3V.

Fig. 15 shows the electrical series resistance (ESR) of capacitor electrode when carbon black and VGCF were used as an additive. ESR value becomes low with the addition of VGCF, and it was reduced 20% compared with that of carbon black (CB) addition at the same amount. VGCF has a fiber like morphology, large L/D, and it has the excellent conductivity along the fiber axis. The improvement in ESR by the mixing with VGCF originated from the entanglement among the additives. That is, VGCF used in electrode as an additive contact among them due to fiber-like morphology so that it may become entangled with an activated-carbon grain arises. The reduction of contact resistant by the VGCF addition is considered the reason why the improvement of activated carbon electrode.

Fig. 16 presents the capacitance improvement at the high-current density by mixing with an additive. For the case of

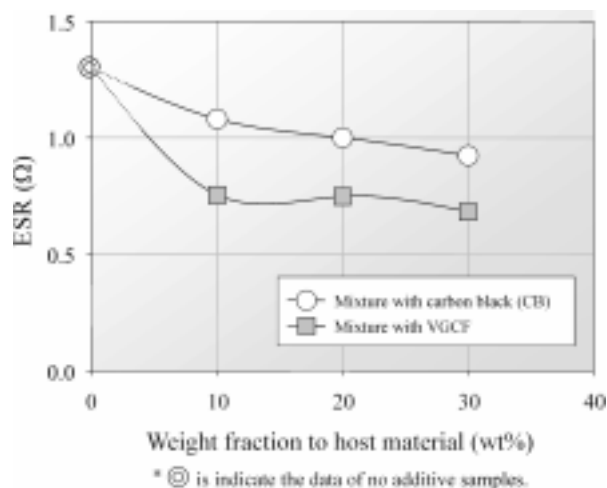


Fig. 15. Electrical series resistance (ESR) of capacitor electrode using a CB and a VGCF as an additive.

VGCF addition, the capacitance in a high electric-current superior to that of the CB addition. It is thought that the internal-resistance reduction effect by the VGCF addition, thus it holds down a capacity depreciation in a high electric-current region compared with that of CB.

The mixing with the materials having a good conductivity, such a VGCF, which can improve further the electrode performances. This is just same as in Li ion battery in which VGCF is contribution to provide high cyclability, high current out-put and long life of the cell.

## 8. Future Prospect for Capacitors

New concepts on electric double layer capacitors applicable in the fields of energy recycling hybrid and fuel cell based vehicles have been stimulating the related research for developing the new type of activated carbons and cell technologies of EDLC. Some use of the conventional second battery, such as NiCd and Pb acid batteries which have been required to solve the environmental problems, can be replaced by the high performance capacitors. And they are

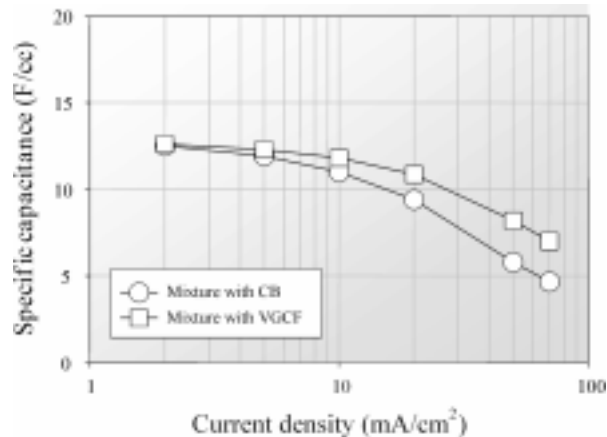


Fig. 16. Capacitance improvement at the high-current density by mixing with an additive.

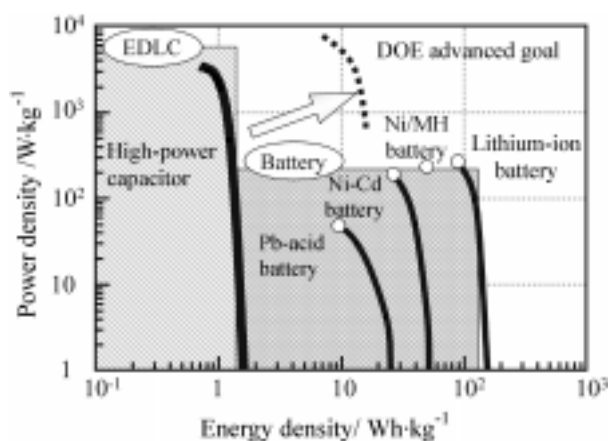


Fig. 17. Comparison of the energy density for various energy devices [31].

recyclable and fit well to the environmental age of 21st century.

Fig. 17 shows the comparison of the energy density for various energy devices [32]. High power capacitors for an EV or a hybrid electric vehicle (HEV) was required a high working voltage of 100~300 V with low resistance and a high energy density [33] by the series and parallel connections of elemental capacitors, in which also very homogeneous performances in each EDLC unit are essential in such a system. Furthermore, a continuous trial to Fig. out the problems in the energy density would improve the capacitor performance much more. Consequently, the EDLC having an energy density as high as a secondary battery should be realized, in very near future.

Fig. 18 suggests that the direction to the high power capacitor. At present, it has been realized the commercialization for Hybrid Electric Vehicle (HEV) application. In Japan, HEV started to sale as goods, e.g. "PRIUS with Ni-H battery", which started to sale from October 1997 by Toyota. According to the further investigation for high power energy source, the complete electric vehicle will be come true in future.

Fig. 19 shows the high power capacitor prepared for motor vehicle application in our laboratory with capacitance of 1,500~4,000 F/2.5V with a non-aqueous electrolyte (left side of the picture) and 25~90 F/0.9 V in an aqueous electrolyte (right side of the picture), respectively. A 100 and a 500 ¥ coin was placed by the cell as the standard of the cell dimension. These experimental cells show the sufficient performances for EV/HEV applications in performances and life cycle.

## 9. Conclusion

Lots of efforts have already been done to develop various kinds of carbonaceous materials for use as polarized electrode materials in electric double-layer capacitors. Of course, the capacitance property is originated from the sum of whole

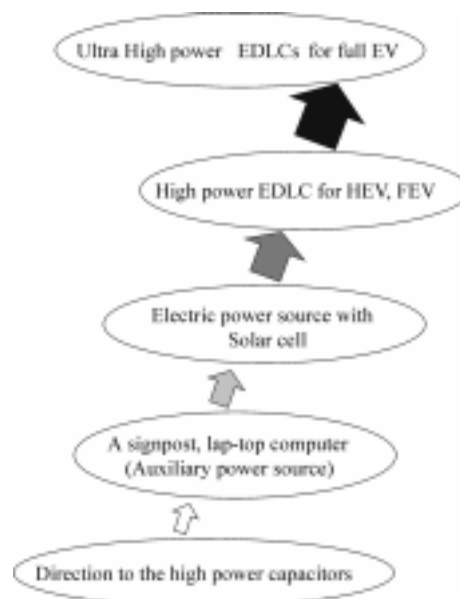


Fig. 18. The final goal for the high power EDLCs.



Fig. 19. High power capacitor of (left side of picture, cylindrical type) 1,500~4000F, working voltage is 2.5 V with non-aqueous solvent, (right side of picture, box type) and 25~90F, working voltage is 0.9V with aqueous electrolyte.

parameter such as an electrolyte (i.e., dielectric constant, dipole momentum, viscosity of solvent, etc), material (i.e., pore size distribution, functional group, conductivity, etc) and so on, but is not from one. If it is systematically associated each together, the promising capacitor age will be soon realized. We suggest the PVDC-based carbon material as an EDLC electrode for a practical application in a sulfuric acid aqueous solution. A carbonized PVDC electrode dominated by ultra micro-pores less than 10 Å in size without using any activation process. The present PVDC-based carbons exhibit an especially suitable pore size and pore size distribution with a higher bulk density that induces a high specific capacitance. These also can afford various technical merits in device applications. It is further possible to develop large-scale capacitor production using present PVDC-based polar-

izable carbons, and the homogeneous structure and properties attainable in these electrodes configuration could contribute to large-scale series and parallel connections of such as unit cells. The main keys in porous carbon as a polarizable capacitor electrode are elucidation of the relation between the pore size distribution and the ion size. The contribution of carbon science has been enormous until now, and further achievement of scientific study on new forms of carbons, such as activated carbon, could afford larger success of electric double layer capacitor, which are required as an important greening technology in 21 century for environmental and energy problem, including EV or HEV, and mobile IT. Optical Network Unit (ONU) is also considered as a very important application area of EDLCs in the age of IT based on high capacity optical fiber network.

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