Highly-Durable Carbon Electrode for Electrochemical Capacitors
Electrodos de Carbón de Alta Duración para Condensadores Electroquímicos

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Abstract

The electric double layer capacitor (EDLC) is an electrochemical capacitor storing electric energy by charging the electric double layer on the micropores of a nanoporous carbon electrode such as activated carbon. The EDLC has a fast charge-discharge property and excellent cycle life, but its energy density is lower than other electrochemical energy storage devices such as the rechargeable battery. The energy density of the EDLC can be improved by increasing the double layer capacitance and the maximum charging voltage. In this review, the author describes the activated carbon electrodes for use in a durable EDLC for high voltage charging.

Resumen

Un condensador de doble capa eléctrica (EDLC) es un condensador electroquímico que almacena energía eléctrica por la carga de la doble capa eléctrica en los microporos de un electrodo de carbón nanoporoso, como puede ser un carbón activado. El EDLC tiene propiedades de carga-descarga rápida y un excelente tiempo de vida al ciclado, pero su densidad de energía es más baja que la de otros dispositivos de almacenamiento de energía electroquímicos, tales como las baterías recargables. La densidad de energía de los EDLC se puede mejorar mediante el aumento de la capacidad de doble capa y del voltaje de carga. En esta revisión, el autor describe las características de electrodos de carbón activado para su uso en EDLC de gran durabilidad en condiciones de elevado voltaje de carga.

1. Introduction

In recent years, electrochemical capacitors, which have a higher capacitance than conventional dielectric capacitors (e.g., film capacitor, ceramic capacitor, and electrolytic capacitor) have been the focus as an electric energy storage device with a rapid charge-discharge performance [1]. The EDLC is an electrochemical capacitor based on the dielectric property of the electric double layer at the interface between the electrolyte and a nanoporous carbon electrode, such as activated carbon, as shown in **Fig.1**. EDLC has been widely used as a power source for electric devices since its commercialization in the 1970s. However, the energy density of the EDLC is lower than that of rechargeable batteries, such as the lithium ion battery, therefore, it should be further improved for energy storage applications. According to the $E = CV^2 / 2$ correlation, the energy density (E) of the EDLC depends on the double layer capacitance (C) of the activated carbon electrode and the maximum applied voltage (V). Many scientists and industries have already made significant efforts to find the optimized pore structure of the activated carbons [2-4], but the approach for improving the energy density of the EDLC only by pore structure design has met some limitations. The typical maximum charging voltage of the commercialized EDLC using an organic electrolyte (e.g., propylene carbonate solution containing an alkylammonium salt) is about 2.5 ~ 2.7 V. The higher voltage charging of the EDLC, such as above 3.0 V, is required to improve the energy density, but it is known to cause a capacitance decline and cycling deterioration due to electrochemical decomposition at the electrode interface [5-7]. There are only a few research examples concerning the improvement of the maximum charge voltage for the EDLC compared to those relating to the change in the capacitance. This review addresses some techniques for carbon electrode enhancement for improving of the maximum voltage of the EDLC.
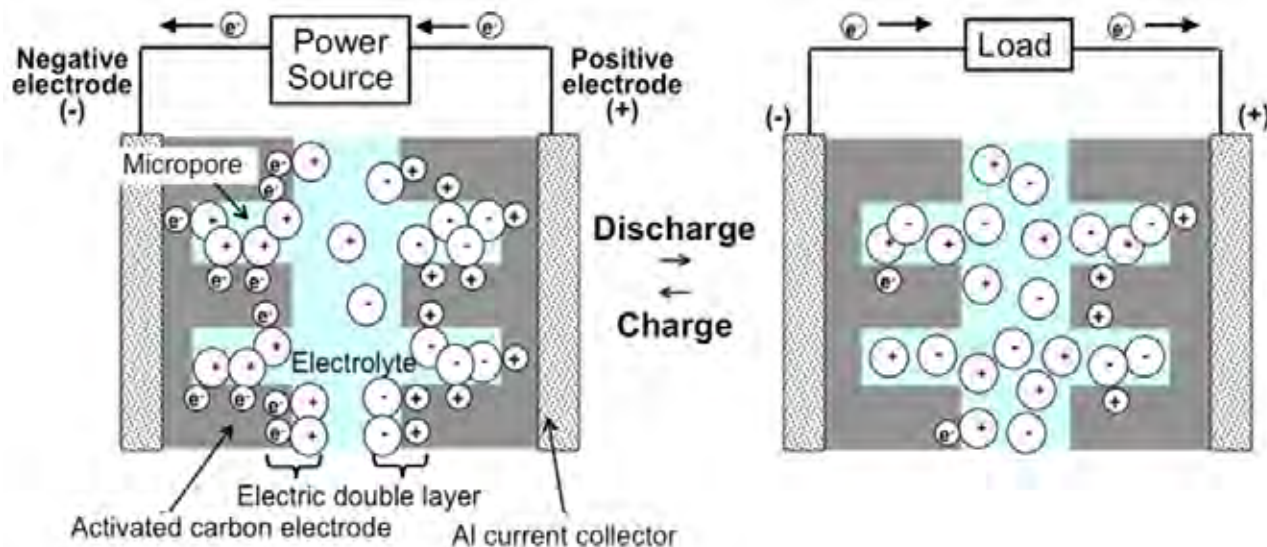

Fig.1 Schematic illustration of electric double layer capacitor (EDLC)
Fig.1 Esquema de un condensador de doble capa eléctrica (EDLC)

2. Heat-treatment of Activated Carbon [8]

The origins of the capacitance decline by high voltage charging are thought to be the electrochemically active sites such as the oxygen-containing functionalities or the defect points (e.g., edge plane) on the activated carbon electrode. The heat-treatment above 1000°C can remove the oxygen-containing functionalities and improve the carbon crystallinity of the micropore walls. Raman spectra (**Fig.2**) of the heated-activated carbons (phenolic resin based, steam activated) in an inert atmosphere revealed that narrowing of the band width of the G band or D band by increasing the heat-treatment temperature, suggesting a crystallinity improvement. The BET specific surface area, micropore volume, mean micropore width, amount of the oxygen surface functionalities, initial capacitance, and capacitance retention after the durability test (floating condition, 3V/70°C/100 h or 3.5V/60°C/200 h) are summarized in **Table 1**. The capacitance retention after 3.0V at 70°C for 100h was improved by the heat-treatment, and the maximum retention was obtained at 1500°C. Additionally, the heat-treatment effect is very prominent under the more aggressive condition (3.5V/60°C/200 h). Since most of the oxygen surface functionalities were removed by the heat-treatment, the durable property is due to the deactivation of the electrochemically active site of the oxygen surface functionalities and the crystal defects. However, the higher temperature during the heat-treatment lowered the specific surface area and the micropore volume. This is due to the shrinkage and blocking of the micropores. The initial capacitance, which is related to the specific surface area, also decreased with the increasing heat-treatment temperature. Thus, the heat-treatment of activated carbons, which is very simple and a cheap method, produces the undesired trade-off relationship between the initial capacitance and the capacitance retention.
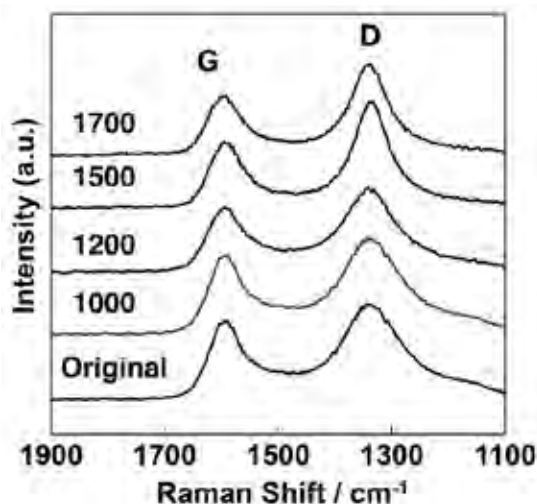

Fig.2 Raman spectra (532 nm) of original activated carbon (AC) and heated AC (1000 ~ 1700 °C) in inert gas.

Fig. 2 Espectros Raman (532 nm) del carbón activado original (AC) y AC tratado (1000 ~ 1700 ° C) en gas inerte.

The effect of the heat-treatment at a higher temperature, such above 2000°C, has attracted interest, but the activated carbons heated above 2000°C show very low capacitances due to complete micropore shrinkage. The author confirmed the heat-treatment effect at high temperature using multi-walled carbon nanotubes (MWCNT) as the electrode active material for the EDLC. The BET specific surface area, the initial capacitance, and the capacitance retention after the durability test (floating condition, 3V/70°C/100 h or 3.5V/60°C/200 h) are summarized in **Table 2**.

The MWCNT used for the test (it is the same material as reported in the literature [9]) was thermally stable against the heat-treatment at 2800°C and maintained the tube structure as shown in **Fig.3**. The MWCNT heated at 2800°C exhibited the perfect capacitance-retention even under the more aggressive conditions (3.5V/60°C/200 h). The capacitance of the MWCNT is not high, but this result should be noted such that the elimination of the active sites is significant for realizing a durable EDLC against high voltage operation.
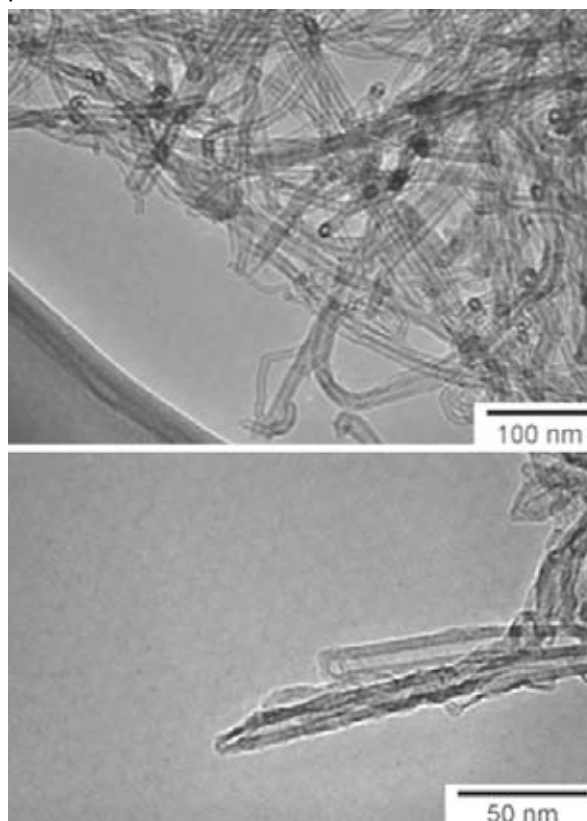

Fig.3 Transmission electron microscopic (TEM) image of MWCNT heated at 2800 °C

Fig.3 Imagen de microscopía electrónica de transmisión (TEM) de MWCNT calentados a 2800°C

Nitrogen Doping of Activated Carbon [8]

Nitrogen-doped nanoporous carbons, namely, nanoporous carbons containing nitrogen atoms or nitrogen-enriched nanoporous carbons are known to have a higher capacitance compared to the nitrogen-free conventional activated carbons [10-12]. The origin of the high capacitance is still under investigation, but the contribution of the redox (pseudo) capacitance by the nitrogen surface functionalities, the electronic modification of the electrode interface (carrier concentration increase), and the high wettability of the pore walls have been proposed. Thus, the nitrogen-doping of an activated carbon is an attractive technique for increasing the capacitance. The author's group also focused on the nitrogen doping and determined that it is also effective for improving the durability of the EDLC for the high voltage charging [8]. The nitrogen-doped activated carbons are easily prepared by the heat-treatment

Table 1. Pore structure of heated activated carbon (AC) and the durability of EDLC against high voltage charging.
Tabla 1. Estructura porosa del carbón activado tratado (AC) y durabilidad de los EDLC para un voltaje de carga elevado.

Sample	HTT [°C]	S_{BET} [m²g⁻¹]	V_{micro} [mlg⁻¹]	w_{micro} [nm]	A_{CO} [mmolg⁻¹]	A_{CO_2} [mmolg⁻¹]	C_0 [Fg⁻¹]	$C_d(1) / C_0$ [%]	$C_d(2)/ C_0$ [%]
AC-original	-	2050	0.78	0.98	1.2	0.2	26	81	2
AC-1000	1000	1830	0.70	1.00	0.12	0.05	21	84	-
AC-1200	1200	1780	0.70	0.94	-	-	21	87	-
AC-1500	1500	1660	0.63	0.91	0.07	0.02	17	89	58
AC-1700	1700	1360	0.52	0.91	-	-	13	82	-

Original activated carbon was prepared by carbonization and steam activation of phenolic resin

HTT: Heat-treatment temperature in nitrogen (1000~1200°C, 1 hour) or argon gas (1500~1700°C, 1hour)

S_{BET}: BET specific surface area

V_{micro}: Micropore volume

w_{micro}: Average micropore width

A_{CO}: Desorption amount of CO by TPD analysis (up to 1000°C in He)

A_{CO2}: Desorption amount of CO_2 by TPD analysis (up to 1000°C in He)

C_0: Initial capacitance (two-electrode system, 1M $(C_2H_5)_3CH_3NBF_4$/propylene carbonate, 80mAg⁻¹, 0 ~ 2.5V, 40°C)

$C_d(1) / C_0$: Capacitance retention by durability test (3V/70°C/100 h)

$C_d(2) / C_0$: Capacitance retention by durability test (3.5V/60°C/200 h)

Table 2. Specific surface area of heated multi-walled carbon nanotube (MWCNT) and the durability of EDLC against high voltage charging
Tabla 2. Superficie específica de nanotubos de carbón de pared múltiple tratados (MWCNT) y durabilidad de los EDLC para un voltaje de carga elevado

Sample	HTT [°C]	S_{BET} [m²g⁻¹]	C_0 [Fg⁻¹]	$C_d(1) / C_0$ [%]	$C_d(2)/ C_0$ [%]
MWCNT (cup-open)	-	370	5.1	80	0
MWCNT -2800	2800	190	2.7	102	103

MWCNT was prepared by CVD method and oxidized/washed by acid to remove metal catalyst and open the end cup.

HTT: Heat-treatment temperature (1hour) in argon gas

S_{BET}: BET specific surface area

C_0: Initial capacitance (two-electrode system, 1M $(C_2H_5)_3CH_3NBF_4$/propylene carbonate, 40°C)

$C_d(1) / C_0$: Capacitance retention by durability test (3V/70°C/100 h)

$C_d(2) / C_0$: Capacitance retention by durability test (3.5V/60°C/200 h)

Table 3 Pore structure of NO-treated activated carbon (AC)
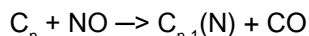**Tabla 3** Estructura porosa del carbón activado tratado con NO

Sample	S_{BET} [m²g⁻¹]	V_{meso} [mlg⁻¹]	V_{micro} [mlg⁻¹]	w_{micro} [nm]
AC-original	2040	0.43	0.85	1.18
NO-AC	1970	0.43	0.82	1.20

Original activated carbon was prepared by carbonization and steam activation of phenolic resin.

Nitrogen atom was doped to the original AC by heat treatment in He gas containing 2000ppm NO gas at 800°C for 1 hour to prepare NO-AC.

S_{BET}: BET specific surface area

V_{micro}: Micropore volume

w_{micro}: Average micropore width

(around 800°C) with nitrogen monoxide (NO). NO is known to react with carbonaceous materials to produce nitrogen-containing carbons, which can be described by the following reaction [13].

$$C_n + NO \longrightarrow C_{n-1}(N) + CO$$

where C_n is the carbon surface and $C_{n-1}(N)$ is the nitrogen-containing carbon surface. This reaction can be applied to activated carbons and the NO method is productive because of the simple dry-process. The typical N1s XPS spectrum of the NO-treated activated carbon (phenolic resin, steam activated) is shown in **Fig. 4**.
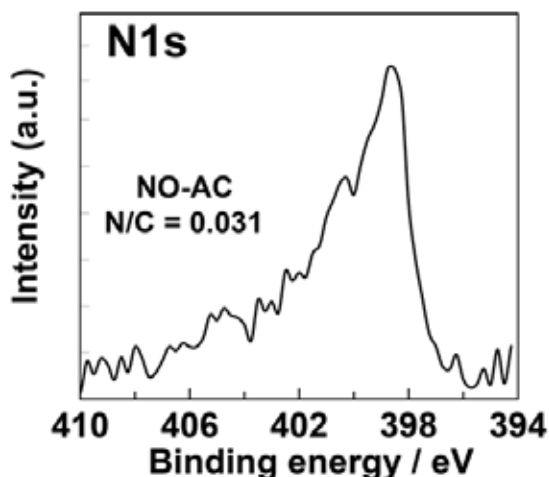

Fig.4 N1s XPS spectrum of NO-AC.
Fig. 4 Espectro XPS N1s de NO-AC.

The main peak attributed to the pyridine-like nitrogen was observed around 399 eV. The peak shoulder around 400 eV can be assigned to the pyrrole-like or quaternary-like nitrogen. The atomic ratio (N/C) was around 0.03. The nitrogen atom is doped in the internal part of the activated carbons since the N/C ratio by XPS corresponds to that by a combustion elemental analysis. **Table 3** shows the pore structure of the NO-treated activated carbons characterized by the nitrogen adsorption isotherms. A comparison of the pore structure before and after the NO reaction showed no significant difference in the surface area, pore volume, and mean micropore width. This means that the NO method is a mild modification to easily provide the nitrogen-doped activated carbon having an optimized pore structure for EDLC use.

Fig. 5 shows the dependence of the capacitance on the charge-discharge cycle. The discharge capacitance of the original activated carbon decreased with the increasing cycle numbers. Especially, the capacitance decline was critical under the most severe condition (3V, 70°C). The data of the simply heated sample at 800°C in an inert gas was plotted for comparison with the NO-treated one to check the influence of the heat history. The heated sample indicated only a slight improvement in the cycle durability, while the NO-treated one at 800°C showed a very stable cycle-performance with a higher capacitance. The durability of the capacitor using the NO-treated activated carbon electrode originates from the electrochemical stability of the nitrogen surface functionalities and the suppression of the electrochemical oxidation. For the heated-activated carbon electrode, the observed improvement is due to the reduction of the oxygen surface functionalities as the electrochemically active sites, but the effect is limited under the heat-treatment condition around 800°C. Therefore, it can be concluded that the nitrogen-doping of the activated carbon electrode is better than the simple heat-treatment for realizing the high voltage operation of the EDLC. Moreover, the author's group has recently developed a safer technique for the nitrogen doping of an activated carbon electrode using ammonium carbamate or carbonate and revealed a durable performance similar to the NO method [14]. The easy and safe dry-process for the nitrogen doping is expected to add value to activated carbons for mass production.

3. Electrode Design of Three-Dimensional Structure

Breakdown of the electric network in an activated carbon electrode is also a critical cause of the capacitance decline by the electrochemical decomposition in addition to the micropore blocking by decomposition products and gas evolution. The conventional EDLC electrode is fabricated as a composite consisting of the activated carbon powder, conductor (carbon black), and binder (**Fig.6**(a)). The electric network was constructed by many electric point contacts by the activated carbon, carbon black, and current collector. It suggests that the electric
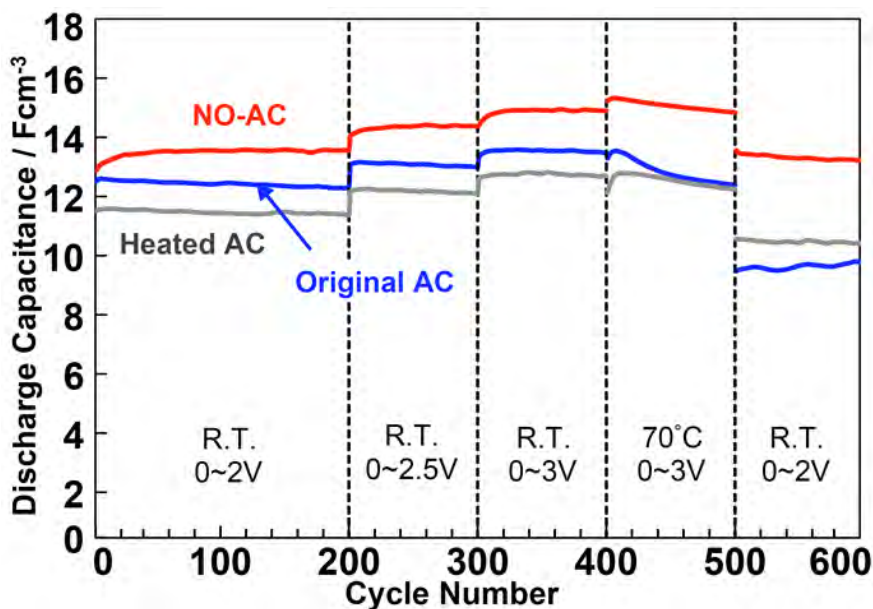

Fig. 5 Capacitance-dependence (two-electrode cell, galvanostatic, 80 mAg^{-1}) on charge-discharge cycle for original AC, heated AC at 800°C in N$_2$ for 2h, NO-AC in 0.5 M TEABF$_4$/PC. The charging voltage and temperature : 0 ~ 2V at room temperature (R.T.) (1 ~ 200 cycle No.), 0~2.5V at R.T. (201~300 cycle No.), 0~3V at R.T. (301~400 cycle No.), 0 ~ 3V at 70°C (401~500 cycle No.), and 0 ~ 2V at R.T. (501 ~ 600 cycle No.).

Fig. 5 Dependencia de la capacidad (célula de dos electrodos, medida galvanostática, 80 mAg^{-1}) con los ciclos de carga-descarga para el AC original, el AC tratado a 800ºC en N$_2$ durante 2 h, y tratado con NO (NO-AC) en 0.5 M TEABF$_4$/PC. El voltaje de carga y la temperatura son: 0 ~ 2 V a temperatura ambiente (RT) (N º ciclo 1 ~ 200), 0 ~ 2,5 V a RT (N º ciclo 201 ~ 300), 0 ~ 3 V a temperatura ambiente (N º ciclo 301 ~ 400), 0 ~ 3 V a 70ºC (N º ciclo 401 ~ 500) y 0 ~ 2 V a temperatura ambiente (N º ciclo 501 ~ 600).

network is easily collapsed since the electrical contact at the particle boundary and the interface between the active material layer and the current collector are not mechanically and chemically inert to electrochemical decomposition reactions. Thus, a novel electrode structure unrelated to this problem should be developed. Recently, the author's group found that a particle-boundary free (seamless) electrode structure [15] and a porous current collector [16] are very effective for improving the durability against high voltage charging. In this section, the author provides an outline of the EDLC performances using the seamless activated carbon electrode (**Fig.6**(b)) and the foamed aluminum current collector (**Fig.6**(c)) focusing on the durability against high voltage charging (>3V).
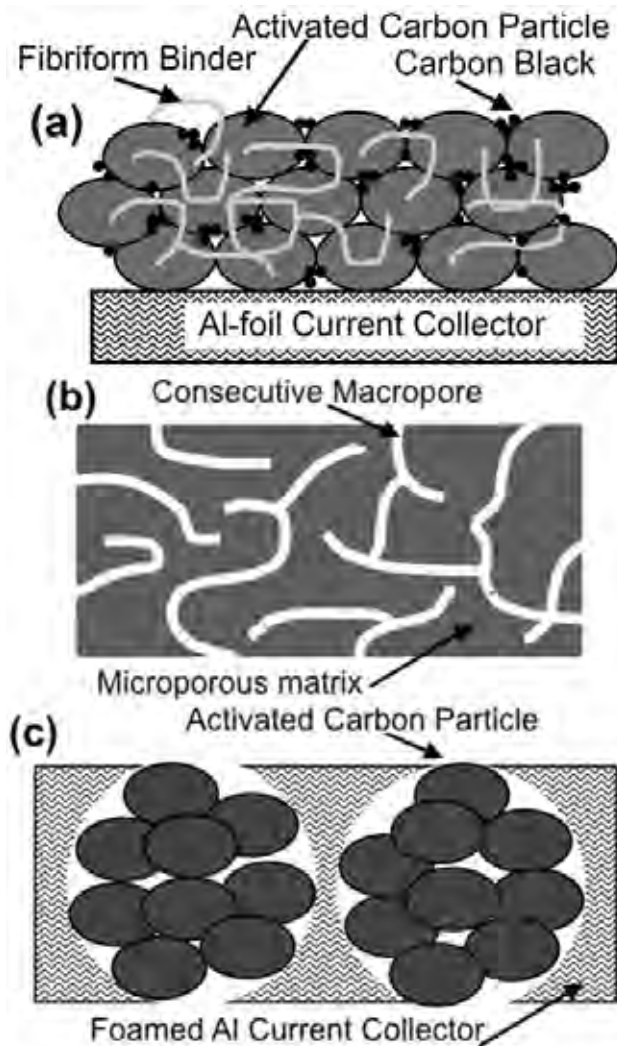

Fig. 6 Schematic model of (a) conventional electrode, (b) seamless activated carbon electrode, and (c) activated carbon electrode using foamed Al as current collector for EDLC

Fig. 6 Modelo esquemático de (a) electrodo convencional, (b) electrodo de carbón activado sin aglomerante, y (c) electrodo de carbón activado usando espuma de Al como colector de corriente para EDLC.

The seamless activated carbon electrode (16mm diameter disk) was prepared by the carbonization (800 °C) and CO_2 activation (850 °C) of the consecutively macroporous phenolic resin matrix called "MICROLIGHT" (mean pore size: 7 μm, commercial product of AION Co., Japan). **Fig.7** shows the scanning electron microscopic (SEM) images of the conventional composite electrode, the original MICROLIGHT, and its carbonization/

activation product (seamless activated carbon electrode, carbonization yield: 40%, activation yield: 57%). The typical composite structure consisting of activated carbon grains and carbon black particles was observed in the conventional composite electrode. The SEM image of the MICROLIGHT and its activation product indicated the macroporous structure without particle boundaries and that the macroporous structure was maintained after the CO_2 activation process. This seamless activated carbon electrode has the BET specific surface area of 1960 m^2g^{-1}, the micropore volume of 0.76 mlg^{-1}, and the mean micropore width of 0.93 nm. This means that the micropores in the seamless electrode are highly developed as well as the conventional activated carbon.
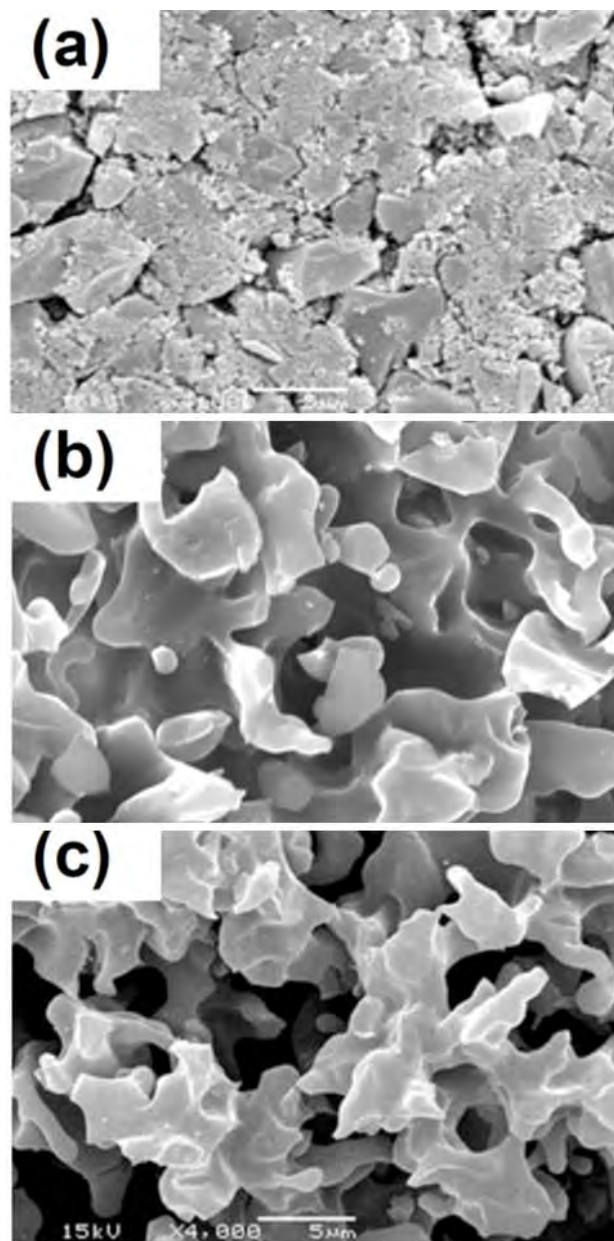

Fig. 7 SEM images (×4000) of (a) conventional activated carbon electrode, (b) original MICROLIGHT (consecutively macroporous phenolic resin), and (c) seamless activated carbon electrode

Fig. 7 Imágenes de SEM (× 4000) de (a) electrodo de carbón activado convencional, (b) MICROLIGHT original (resina fenólica macroporosa), y (c) electrodo de carbón activado sin aglomerante.

The foamed Al current collector (mean pore size: 600 μm, commercial product of Mitsubishi Materials Co., Japan) was filled with the activated carbon powder

(containing a small amount of carbon black and PTFE binder) to prepare the capacitor test electrode (16mm diameter disk). YP50F (Kuraray Chemical. Co., Japan), which is a typical steam-activated carbon powder for the EDLC, was used as the active material for the foamed Al current collector. YP50F has the BET specific surface area of 1550 m^{2}g^{-1}, micropore volume of 0.60 mlg^{-1}, and mean micropore width of 0.97 nm. The SEM image of the foamed Al and the backscattered electron microscopic (BSE) image of the test electrode are shown in **Fig.8**.
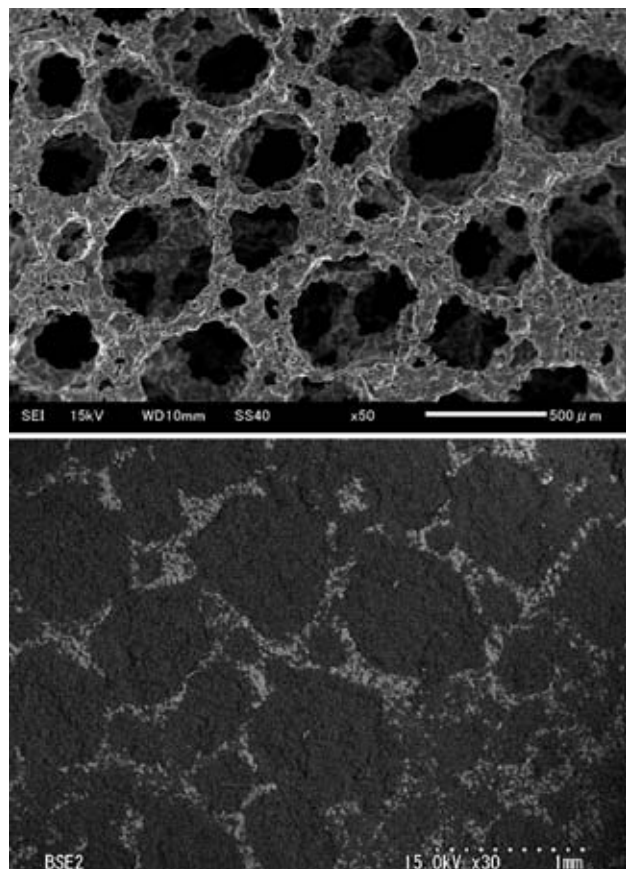

Fig. 8 (a) SEM image of foamed Al current collector (average pore size: 600 mm) and (b) BSE image of YP50F-filled foamed Al electrode

Fig. 8 (a) Imagen de SEM del colector de corriente de espuma de Al (tamaño de poro promedio: 600 mm) y (b) la imagen de BSE del electrodo de espuma de Al relleno de YP50F

The test capacitor cell (two-electrode system) was fabricated by these electrodes, paper-type separator, and organic electrolyte (1.0 M (C$_2$H$_5$)$_3$CH$_3$NBF$_4$ / propylene carbonate). The capacitance was measured by the galvanostatic method (80mAg^{-1}, 0~2.5 V) at 40°C. The durability test was conducted by the floating condition (3.5 V charging, 100h, 70 °C). The results of the durability test are summarized in **Table 4**. Both the seamless activated carbon electrode and the YP50F-filled foamed Al electrode indicated very high capacitance retentions (>80%) and only a small increase in the internal resistance during the 3.5 V durability test. The conventional composite activated carbon electrode using YP50F and etched Al foil current collector showed a very low capacitance retention (~10%) and significant change in the internal resistance during the same durability test, therefore it was revealed that the seamless structure or the foamed current collector is very effective in improving the durability of the EDLC against high voltage charging. For the seamless electrode, the excellent durability is postulated to result from alleviating the electrical contact problem caused by the electrochemical decomposition. It is considered that the foamed current collector has the function that the activated carbon particles inside the pores maintain strong contacts to each other to form a stable electric network.

4. Conclusion

Some techniques for the activated carbon electrode are reviewed from the viewpoint of the high voltage EDLC operation. The surface modification of the activated carbon electrode (e.g., heat treatment, nitrogen doping) and the three-dimensional electrode structure with a strong electric network (e.g., seamless electrode, formed current collector) are effective for developing a durable electrode against high voltage charging. The former technique is related to the suppression of the electrochemical decomposition and the latter is concerned with the construction of the strong electric network. The combination of these two techniques is also expected to have a synergistic effect. In any case, the important issue is that establishment of a simple and mass-productive method like the methods presented in this review should be necessary for practical use and commercialization.

5. Acknowledgement

Table 4 Capacitance and internal resistance of EDLC before and after durability test (floating condition: 3.5V, 100h, 70°C)

Tabla 4 Capacidad y resistencia interna del EDLC antes y después del test de durabilidad (condiciones de flotación: 3.5V, 100h, 70°C)

Activated Carbon	Al Current Collector	C_0 [Fg^{-1}]	C_d/C_0 [%]	R_0 [Ω]	ΔR [Ω]
Seamless	Etched foil	30	80	3	8
Powder composite (YP50F)	Foamed	26	87	5	15
Powder composite (YP50F)	Etched foil	25	12	5	38

C0: initial capacitance (two-electrode system, 1M (C$_2$H$_5$)$_3$CH$_3$NBF$_4$/propylene carbonate, 80 mAg^{-1}, 0 ~ 2.5V, 40°C)

C_d/C_0: capacitance retention

R_0: initial internal resistance

R: increase of internal resistance

6. References

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