Development of Novel Carbon Electrode for Electrochemical Energy Storage. Nano-sized Carbon and Classic Carbon Electrodes for Capacitors

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ABSTRACT
Electrochemical capacitors are energy storage devices characterized by high power and long cycle life for charging/discharging. Carbon materials play a very key role as electrode active materials for the electrochemical capacitors. This comprehensive paper mainly covers the author’s research regarding the carbon materials as electrodes for the electric double layer capacitor used as an electrochemical capacitor. The importance of focusing on the pore structure, the surface chemistry, and the three-dimensional structure of the electrodes is stated from the viewpoint of improving the energy density and reliability, and the characteristic carbon materials that have a high capacitance even with a low microporosity are also reported. These research results indicate the potential of nano-sized carbons and classic carbons, such as activated carbon and graphite-related materials, to further develop the technologies of the capacitor electrodes.

Keywords : Electrochemical Capacitors, Nitrogen Doping, Seamless Structure, Graphite Intercalation Compound

1. Introduction
Electrochemical energy storage devices, such as electrochemical capacitors and rechargeable batteries, are necessary to save fossil fuels and suppress CO₂ emission. The electrochemical capacitors involve electric double layer capacitor (EDLC), redox capacitor using oxide or conductive polymers, and hybrid capacitors as shown in Fig. 1. Carbon materials are very important as the electrode for these electrochemical energy storage devices. The EDLC (Fig. 2), which is an electrochemical capacitor with the longest commercial history, store the electric charge in the dielectric layer (electric double layer) formed at the interface between the electrode and electrolyte by a non-faradaic process.4–3 The EDLC has a variety of applications because of its high capacitance, high power density, and excellent charge-discharge cycle life, which cannot be achieved with conventional electrolytic capacitors. The EDLC has the disadvantage of a low energy density compared to rechargeable batteries, but based on the technology of the EDLC, the hybrid capacitors (e.g., lithium-ion capacitor) using the electrodes of the EDLC and rechargeable battery have been developed to successfully improve the energy density of the commercialized electrochemical capacitors.4 For both the EDLC and hybrid capacitors, carbon is the key material. The author has investigated the carbon electrode for use in electrochemical capacitors for more than 20 years. This paper addresses the ideas and research results related to the carbon electrode for electrochemical capacitors.

2. Requirements of Electrode Materials for EDLC
The energy (E) stored in a capacitor is in proportion to the...
The pores of activated carbon are developed under about 800 °C by the gasification of the carbon matrix with steam, CO₂, chemical reagent, such as KOH or H₃PO₄, etc. The pore formation process by the gasification of carbon is referred to as "activation". Activated carbon is strictly defined as nanoporous carbon that is produced by the gasification process (activation process). In general, the micropore is selectively generated through the activation process, resulting in a high surface area. The micropores of the activated carbon are considered as a nanospace with a distorted slit-like nanospace formed between small fractions of the hexagonal carbon planes (microporaphite).

In the case of the organic electrolyte for the EDLC, the ion size is around 1 nm, so it is close to that of the micropore. For tetraethylammonium tetrafluoroborate ((C₂H₅)₄NBF₄) as typical electrolyte salt, the ion diameter of the cation ((C₂H₅)₄N⁺) is around 0.7 nm and that of the anion (BF₄⁻) is around 0.5 nm. This suggested that electrolyte ion cannot be smoothly adsorbed in the narrow micropores, thus promoted the research focusing on the mesopores, which is related to direction (a) (Enlargement of the pore width of the activated carbon). In fact, it was observed that the double layer capacitance is very low when the micropores are smaller than the electrolyte ion. This phenomenon is referred to as "ion sieving". The nanoporous carbon with developed mesopores, which is referred to as "mesoporous carbon", is effective for suppression of the ion sieving by the micropores.

The author revealed that the mesoporous carbons prepared by catalytic activation or defluorination of polytetrafluoroethylene (PTFE) show suppression of the ion sieving and a high rate performance as shown in Fig. 3. The volumetric capacitance, which is the specific capacitance normalized by the electrode volume, of the mesoporous carbons is not high because the mesopores decrease the bulk density of the electrode. The volumetric capacitance is more important than the gravimetric capacitance (the specific capacitance normalized by the electrode weight) from the viewpoint of energy storage. Similarly, the volumetric energy density is more significant than the gravimetric energy density for the electrochemical capacitors. Therefore, the mesoporous carbon is not the only way to improve the volumetric capacitance of the EDLC.

Direction (b), the increase in the specific surface area of the activated carbon, is also a difficult way to increase the volumetric capacitance and energy. Figure 4 shows the correlation between the specific surface area and the double layer capacitance that the author previously evaluated. The specific surface area is approximately proportional to the gravimetric capacitance except in the region of the low specific surface area influenced by the ion sieving effect. This indicates that the gravimetric capacitance of the activated carbon electrode basically follows Eq. (1). However, the volumetric capacitance shows a convex curve with a maximum value. The development of the pore structure by the activation process increases not only the specific surface area but also the pore width to decrease the bulk density. The convex curve in Fig. 4(b) is due to the trade-off of the increase in the gravimetric capacitance and the decrease in the bulk density with an increasing specific surface area. This is the reason for the difficulty of direction (b).

The volumetric capacitance estimated from an ideal nanoporous carbon, in which a single carbon hexagonal sheet (graphene) is stacked with a minimum distance for the ion adsorption, is suggestive of limitation to improve the volumetric capacitance by the pore-structure optimization. When the proportionality constant (ε₀є₂/δ) in Eq. (1), which is the specific capacitance normalized by the surface area, is the same (7–8 mF cm⁻²) as that of the activated carbons, the ideal nanoporous carbon with a 0.8 nm slit-like pore...
width is expected to have the volumetric capacitance of 120–140 F cm\(^{-3}\). (Fig. 5)\(^{8,27}\) This is only about twice that of the typical coconut-shell based activated carbon for the EDLC. This suggests that the volumetric capacitance and energy density cannot be essentially improved by the control of the pore structure of the activated carbon electrode.

4. Research Direction other than Optimization of the Pore Structure

Based on the described background, the author is presently investigating a different direction of carbon research for the capacitor from the optimization of the pore structure. This review addresses the following examples.

- Nano-sized carbons (carbon nanotube, carbon nanofiber, fullerenel-related material, graphene, etc.)
- Approach for high voltage charge (Heteroatom doping, Seamless structure)
- Low porous carbons

The hybridization of a redox material with a porous carbon electrode is also a way to increase the volumetric capacitance, but the author focuses on enhancing the potential of the carbon materials, (a) Schematic illustration for formation of porous carbon from fluorocarbon by chemical defluorination (pore structure can be controlled by the reaction condition), (b) pore size distribution curves (1–100 nm) of PTFE-based carbons (meso-PTFE) and activated carbon fiber (ACF) calculated by non-localized density functional theory method. (c) capacitance dependence on current density for meso-PTFE and ACF. Capacitance was measured in 0.5 M R\(_4\)NBF\(_4\)/propylene carbonate (R = C\(_2\)H\(_5\), C\(_4\)H\(_9\), or C\(_6\)H\(_{13}\)) by galvanostatic method (1.7–3.7 V vs. Li/Li\(^+\)) using three-electrode cell. Influence of IR-drop on capacitance was eliminated by using chronopotentiograms between 2.1–3.3 V vs. Li/Li\(^+\).23,24

Figure 3. (a) Schematic illustration for formation of porous carbon from fluorocarbon by chemical defluorination (pore structure can be controlled by the reaction condition), (b) pore size distribution curves (1–100 nm) of PTFE-based carbons (meso-PTFE) and activated carbon fiber (ACF) calculated by non-localized density functional theory method. (c) capacitance dependence on current density for meso-PTFE and ACF. Capacitance was measured in 0.5 M R\(_4\)NBF\(_4\)/propylene carbonate (R = C\(_2\)H\(_5\), C\(_4\)H\(_9\), or C\(_6\)H\(_{13}\)) by galvanostatic method (1.7–3.7 V vs. Li/Li\(^+\)) using three-electrode cell. Influence of IR-drop on capacitance was eliminated by using chronopotentiograms between 2.1–3.3 V vs. Li/Li\(^+\).23,24

Figure 4. Correlation between BET-specific surface area (S\(_{BET}\)) and (a) gravimetric capacitance or (b) volumetric capacitance of various activated carbons in 0.5 M (C\(_2\)H\(_5\))\(_4\)NBF\(_4\)/propylene carbonate solution. Dotted line in (a) corresponds to specific capacitance per surface area of 7 \(\mu\)F cm\(^{-2}\). The capacitance was evaluated by the galvanostatic method (40 mA g\(^{-1}\)) using three-electrode cell. ACF: activated carbon fiber. KOH-PTFE: KOH-activated porous carbon derived from polytetrafluoroethylene, KOH-MCMB: KOH-activated mesophase carbon microbeads. Reprinted from Ref. 8 with permission from Springer Nature.

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Assumption

- Layered graphene sheets with interlayer of 0.8 nm width (slit-like micropore).
- Graphene sheet density: 2.2 g cm\(^{-3}\) as graphite.
- Specific surface area (both sides) of 2630 m\(^2\) g\(^{-1}\).
- Capacitance per unit of surface area is 7-8 μF cm\(^{-2}\).

Figure 5. Gravimetric capacitance and volumetric capacitance of nanoporous carbon with ideal micropore structure.\(^{8,27}\)

Figure 6. (a) Correlation between total specific surface area and double layer capacitance in 1.0 M LiClO\(_4\)/propylene carbonate (galvanostatic method using three-electrode cell: 40 mA g\(^{-1}\), positive process, 2–4 V vs. Li/Li\(^+\)) for various HiPco\(^{\text{®}}\)-SWCNTs and activated carbon electrodes (Ref-ACFs). (b) Rate performance (dependence of capacitance on current density) of HiPco\(^{\text{®}}\)-SWCNTs electrode and Ref-ACFs. Reprinted from Ref. 30 with permission from Elsevier.

4.1 Nano-sized carbons

The carbon nanotube (CNT) is the first nano-sized carbon\(^{38}\) evaluated as the EDLC electrode material. The CNT is an ideal nanoporous carbon with cylinder-like pores. During the initial research stage before the author started evaluating the capacitance properties of the CNT, it had been already reported that the CNT shows a greater capacitance than the activated carbons.\(^{29}\) However, the CNT usually used in those days was not well purified, so the electrochemical property of the CNT was not clear. Therefore, the author carefully evaluated the capacitance property of the pure CNT and the conventional activated carbon under the same measurement conditions.\(^{30,31}\) Figure 6(a) shows the correlation of the capacitance and the specific surface area of the single-walled carbon nanotube (SWCNT) synthesized by HiPco\(^{\text{®}}\) and the activated carbon fiber in a propylene carbonate electrolyte.\(^{30}\) The HiPco\(^{\text{®}}\)-SWCNT, which has very few carbon particles (e.g., graphite and soot) other than the CNTs in spite of a lot of Fe catalysts, was one of highest quality available at that time. The theoretical specific surface area of the SWCNT is 2630 m\(^2\) g\(^{-1}\), but the actual value is often less than 1000 m\(^2\) g\(^{-1}\) because of the bundle structure and the closed inner space of the tube. The gravimetric capacitance of the HiPco\(^{\text{®}}\)-SWCNT is not high, however, the specific capacitance per surface area is higher than that of activated carbon. It is a characteristic property of the SWCNT electrode for the EDLC. Furthermore, the SWCNT electrode shows the higher rate property versus the activated carbon as shown in Fig. 6(b). The good rate performance of the SWCNT is due to the smooth adsorption/desorption path of the electrolyte ions, which is different from the case of the activated carbon with a complicated pore structure. After the author’s research using the HiPco\(^{\text{®}}\)-SWCNT, the EDLC using SWCNT electrodes has been further developed with the advent of the “Super-growth method” that can synthesize ultra-pure SWCNTs.\(^{32}\) Recently, the
the electrolyte, but also the electrode material. The withstand voltage
However, the actual electrochemical window depends not only on
to design the electrolyte with a wide electrochemical window.
4.2 Approach for high voltage charge
metal catalysts and low-crystalline carbons, should not be ignored.
4.2.1 Nitrogen-doping
In general, a surface treatment can modify the electrochemical
properties of the carbon electrode. For the EDLC, the surface
modification of the nanoporous carbon electrode has been inves-
tigated in order to increase the capacitance. Especially, nitrogen
doping, which corresponds to forming nitrogen-containing surface
functional groups, is the focus of the technique for the electrode
modification of the EDLC. However, nitrogen doping is not always
effective in increasing the capacitance, particularly, when using an
organic electrolyte. The author fortunately determined that the
nitrogen doping can stabilize the activated carbon electrode for the
high voltage charging,7,8,34,36,38 while oxygen-containing surface
functionalities degrades the electrode.39 Figure 8 shows the change
in the capacitance of the EDLC cell using the nitrogen-doped
activated carbon electrode during the galvanostatic charge-discharge
cycle test.7,9,34 The capacitance of the pristine activated carbon
electrode is still almost unchanged in the voltage region of 0–2 or
2.5 V at room temperature, but that deceased under aggressive
conditions (0–3 V at 70 °C). The durability against a high voltage
charging at high temperature around 70°C is significant for the energy
density and reliability of the EDLC. The EDLC using activated
carbon-nitrogen-doped by the heat-treatment with nitrogen-mon-
oxide (NO) has a better durability compared to those of the pristine
and simply heated (in inert gas) activated carbons. The nitrogen-
doping by NO is the substitution reaction of carbon atom with
nitrogen atom.40 Figure 9 is the N1s X-ray photoelectron spectra
(XPS) of the nitrogen-doped carbon.7 This indicates that the
nitrogen atom is mainly doped as a pyridine-like functionality41
and the nitrogen functionality is relatively stable to the high voltage
charging. Recently, another research group also reported that the
surface modification with NO is effective for the improvement of the
durability and the rate performance.42 The electrochemical stability
is the key to finding the effective surface modification for the
improvement of the operating voltage of the nanoporous carbon
electrode.
4.2.2 Seamless electrode
Charging the EDLC beyond the withstand voltage causes
electrochemical decomposition at the electrode interface that
markedly decreases the capacitance, thereby leading to decrease in
the energy density. The mechanism of the capacitance decline is
complicated, but the possible factors are shown as follows.43,44
(a) Pore blockage by decomposition deposits and gas43,45–47
(b) Destruction and deformation of capacitor cell by the
decomposition gas46
(c) Breakdown of electric network of electrode (decrease in
electronic conductivity of electrode by binder decomposition
and deposition of decomposition product)47,48
Factor (a) is the reason for the decreasing effective electrode
surface area available for the ion adsorption/desorption. Factor (b)
is a critical problem for commercial EDLCs, which is realistically
protected by a safety valve. The suppression of the electrolyte

Figure 7. Dependence of capacitance (0–2.5 V, 40 °C) of the
EDLC cell using various SWCNT self-standing membrane electrode
(SG: super-growth, A-SG: activated SG, HP: HiPcoSP, P-HP: purified HiPcoSP, ED: cDIPS) and commercial activated carbon
composite electrode (YP50F) on current density (a) before and (b)
after the durability test (3.4 V, 100 h, 70 °C).33

Figure 8. Capacitance-dependence (two-electrode cell, galvano-
static, 80 mA g⁻¹) on charge-discharge cycle for original activated
carbon (AC), heated AC at 800 °C in N₂ for 2 h, NO-AC (nitrogen-
doped AC) in 0.5 M (C₂H₅)₄NBF₄/propylene carbonate.7 The
charging voltage and temperature: 0–2 V at room temperature
(R.T.) (1–200 cycle No.), 0–2.5 V at R.T. (201–300 cycle No.), 0–
3 V at R.T. (301–400 cycle No.), 0–3 V at 70 °C (401–500 cycle
No.), and 0–2 V at R.T. (501–600 cycle No.).

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the conductive additive. Therefore, the degradation related to the electrodes are free of the interface between the particles, including consisting of activated carbon particles, the seamless activated carbon electrode. Unlike conventional composite electrodes concluding that the three-dimensional structure of the electrode reduces the power output. Based on the above drawbacks of the conventional composite electrode, the author concluded that the three-dimensional structure of the electrode is important for strengthening the electric network of the electrode, and developed a “seamless activated carbon electrode” with excellent durability against high-voltage charging as shown in Fig. 12. The rate of the EDLC after the durability with the floating condition (3.5 V, 10 h, 70 °C) is improved by using the seamless structure compared to that using the composite electrode and its improvement is further enhanced by the nitrogen doping of the seamless activated carbon electrode. This is due to the suppression of the micropore blockage and contact-resistance increase caused by electrochemical decomposition during high-voltage charging as shown in Fig. 12.

Other groups also reported that binder-free electrodes of the SWCNT or graphene show excellent high-voltage charging as shown in Fig. 12.
4.3 Non-porous carbons

Low porous carbons were originally unsuitable as an electrode active material for the EDLC. As shown in Fig. 4, the double layer capacitance is almost linear to the specific surface area of the electrode, so a highly-porous carbon with a high specific surface area is advantageous for the EDLC. However, some low porous carbons,55,56 which have a relatively high bulk density, show a comparable gravimetric capacitance and higher volumetric capacitance compared to the highly porous carbons. The author reported that the carbon product derived from the chemical de fluorination of graphite-fluoride (GF) with a charge-transfer complex (e.g., a lithium naphthalenide) has a high capacitance regardless of its low microporosity (< 100 m² g⁻¹).23,24 The GF is a covalent-type graphite intercalation compound (GIC)57 and used as a lubricant and electrode material of primary lithium batteries.58 The GF-Li primary ([(CF)n/Li]) battery has been commercially used due to its high energy density and low self-discharge property. The battery reaction is as follows.59

\[
\text{(Cathode)} \quad (\text{CF})_n + n\text{Li}^+ + ne^- \rightarrow n\text{C} + n\text{LiF}
\]

\[
\text{(Anode)} \quad \text{Li} \rightarrow \text{Li}^+ + e^-
\]

The cathode of the discharged GF-Li battery is known to be composed of a nano-composite of carbon and LiF.60 Several years ago, the author noticed that this cathode discharge-product of the GF-Li battery is analogous to the carbon product derived from the defluorination of the GF as already mentioned. This leads to the author’s idea that the cathode discharge-product of the GF-Li battery can also work as the active material of an electrochemical capacitor. Thus, it was revealed that the discharged GF-Li battery can be recharged as a new hybrid electrochemical capacitor.61 The discharge-charge curves of the GF-Li battery are shown in Fig. 13. The first discharge-curve has a plateau around 2.5 V, which is a characteristic of the GF-Li battery. The successive charge-discharge curves show a triangle shape, which means a capacitive performance. This suggests that the carbon/LiF nano-composite is as the discharge-product of the cathode operates as the positive electrode of the capacitor and that the Li metal is electrochemically deposited/dissolved at the negative electrode (Fig. 14). The author terms this new hybrid capacitor system as the “Graphite-Fluoride Lithium (GF-Li) Capacitor”. The GF-Li capacitor has a higher energy density and power density than...
the EDLC and the performance is comparable to that of the Li-ion capacitor as shown in Fig. 15. The charge-discharge mechanism of the discharged GF electrode was analyzed by the inductively coupled plasma optical emission spectroscopy, ion chromatography, and electrochemical quartz crystal microbalance. As a result, it was revealed that the Li\(^{+}\) cation is doped/undoped into the nanocomposite of carbon and LiF. This analytical result and the low microporosity of the electrode suggest the Li\(^{+}\) adsorption/desorption on the surface of the small-sized carbon crystallite with wide interspace by the diffusion between the LiF nano-particles.

Recently, the author also determined that the primary Li battery using graphite-oxide (GO) as a covalent-type GIC also functions as a hybrid electrochemical capacitor as well as the GF-Li battery. The volumetric capacitance and the energy density of the hybrid capacitor derived from the GO-Li battery is better than those of the GF-Li capacitor. Thus, the less porous carbons derived from the covalent-type GIC are interesting as the electrode materials for electrochemical capacitors.

5. Conclusion

The author has reviewed the idea of using the carbon electrode for electrochemical capacitors. Presently, only optimization of the pore structure of the carbon electrode is difficult to improve the volumetric capacitance and energy density of the carbon-based capacitor including the EDLC. The author believes that not only...
nano-sized carbons but also classic carbons, such as activated carbon and GIC, have a great potential to successfully bring technological innovation of electrochemical capacitors.

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