

Electrode Properties of Double Layer Capacitor on Nano-Structured Graphite by Ball Milling under Hydrogen Atmosphere

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ABSTRACT

Nano-structural graphite prepared by ball milling under H₂ or Ar atmosphere was studied as an electrode for electric double layer capacitors (EDLCs) by means of a conventional 2-electrode galvanostatic method. Especially, the product prepared under H₂ atmosphere using zirconia balls revealed 500 m²g⁻¹ surface area and showed 12 Fg⁻¹ specific capacitance, which was comparable to that of an activated carbon with large specific surface area of 3000 m²g⁻¹ examined as a reference. A proper condition of the milling time is rather a shorter time than ~8 h, where the graphitic feature is remained in the ball milled product. On the other hand, for the sample prepared by using steel balls, the specific capacitance per surface area was several hundreds times smaller than the others, indicating that the small amount of Fe contamination during milling played a negative role for the EDLC properties.

**Keywords: graphite, activation, grinding, thermodynamic analysis,
electrochemical properties**

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1. Introduction

Electric double layer capacitors (EDLCs) have been expected as a candidate substituting for secondary batteries in near future [1]. So far, various types of the EDLCs have been investigated by many researchers [2-8]. As one of the candidates for electrode materials, activated carbons synthesized by some chemical methods have been widely investigated, because its specific surface area is very large and it is easy to design the electrode of the capacitors into various forms [2, 3]. At present, the EDLCs made of activated carbons are commercialized. However, the activated carbon was usually contaminated by some elements like oxygen due to its synthesis method, which disturb the ingress of ions to the micropore of the activated carbons and sometimes lead to deterioration by electrolysis [7, 8].

On the contrary, the electrode properties of mechanically synthesized carbon materials have been investigated as well [9, 10]. In their reports, the properties were affected by the atmosphere in the milling treatments. Especially, the capacitance of the electrode synthesized from a carbon powder by ball milling for 80 h under 1 MPa oxygen atmosphere could reach 57 Fg^{-1} in a Et_4NBF_4 electrolyte between 0 and 1.2V with two electrode system [9], suggesting that the mechanically milled graphite are one of the candidates for electrodes materials of EDLCs.

Until now, our group has reported that nano-structural graphite prepared by

mechanical milling method under 1 MPa hydrogen atmosphere using steel balls for 80 h could absorb ~ 7 mass% hydrogen [11, 12]. The absorbed hydrogen seemed to occupy two different sites; one was the C-H covalent bonding site located at the edges of the graphene sheets, and another was the hydrogen atom located at the defective sites in the nano-structured graphite [13]. After the milling, the specific surface area was estimated to be about $300 \text{ m}^2\text{g}^{-1}$ by the BET method. Therefore, we have considered the application of mechanically milled graphite under the H_2 atmosphere to the EDLC electrodes because the material has a relatively high surface area and does not contain impurities based on the oxygen element.

In this paper, we report the experimental results on the electrode properties of four types of activated graphites as EDLCs, which were prepared by the mechanical ball milling under different conditions, like using steel balls or zirconia balls under hydrogen or argon gas atmosphere. Furthermore, we describe the effect of a heat treatment at $450 \text{ }^\circ\text{C}$ under a high vacuum condition as well.

2. Experimental details

Graphite powder with 99.997 % purity and $\sim 200 \text{ }\mu\text{m}$ diameter was purchased from Rare Metallic. The samples for electrodes were prepared from the graphite by a ball milling under hydrogen or argon atmosphere using a planetary type apparatus (Fritsch P7). 300 mg of graphite powder and 20 balls made of steel (7 mm in diameter, 2.7 g; carbon content ~ 1.0 at.%, chromium content ~ 1.5 at.%) or zirconia (8 mm, 3.1 g) were set into the Cr steel vessel (the inner volume of 30 cm^3 ; carbon content ~ 1.5 at.%, chromium content ~ 12 at.%) in a glovebox (Miwa MFG) under a purified argon atmosphere, and then, the milling vessel was degassed below $1 \times 10^{-4} \text{ Pa}$ using a turbo

molecular pump. After that, a hydrogen or argon gas was introduced up to 1.0 MPa into the milling vessel through a ‘quick connect’ (SS-QC4-D-2PM, Swagelok company), which is guaranteed as a gastight connector up to 1.72 MPa at the disconnection. The ball milling treatments were performed for 80 h with 400 rpm at room temperature (~ 25 °C) under a 1.0 MPa gas pressure of hydrogen or argon, where the hydrogen pressure should decrease during milling process down to about 0.1 MPa due to the hydrogen absorption. To avoid the increase in temperature during milling process, the milling treatment was interrupted every 1 h and rested for 30 min. Finally, we prepared four samples under four different milling treatments, which were named S-H (by steel balls under hydrogen atmosphere), Z-H (zirconia under hydrogen), S-A (steel under argon) and Z-A (zirconia under argon) as shown in Table 1. Afterwards, we performed the heat treatment for each sample at 450 °C under a high vacuum condition, which was indicated by “-450” in the end of sample names.

In order to characterize the above samples, three experiments were performed in this work. The structural properties were examined by X-ray diffraction measurement (XRD, RINT-2100 Rigaku, Cu-K α radiation). Measurements of specific surface area were performed by the nitrogen adsorption method, which was analyzed by the BET method (BET, GEMINI 2375 Shimadzu). The elemental analysis was performed by oxygen combustion elementary analysis (OCEA, 2400 α CHN Perkin Elmer), which provides the amount of carbon, nitrogen and hydrogen within $\pm 0.3\%$ accuracy and the amount of impurities as the residue of the carbon and hydrogen estimations. Especially, with respect to the hydrogenated samples, thermal desorption mass-spectroscopic analysis (TDMS, M-QA200TS Anelva) was performed by using a high-purity helium (purity > 99.9999%) as a carrier gas with a heating rate of 10 °Cmin⁻¹. All the samples were

handled in the glovebox filled with purified argon to minimize oxidation and water adsorption.

The eight samples shown in Table 1 were used for the examination of the EDLC properties, which were mixed with 5 mass% of poly-tetrafluoroethylene (PTFE) as a binder to form coin type electrodes ($\phi 10\text{mm}$, $\sim 500\ \mu\text{m}$ thickness). In addition, the activated carbon (Maxsorb, Kansai Coke and Chemicals) synthesized by the chemical method with $3000\ \text{m}^2\text{g}^{-1}$ was employed as reference for comparing with the electrode properties obtained in this work. The electrolyte was prepared to be 1.0 M tetraethylammonium-tetrafluoroborate (Et_4NBF_4) in an organic solvent propylene carbonate (PC). Finally, the EDLC cell was assembled as schematically drawn in Figure 1, in which the cell is symmetric with two identical electrodes.

The cell was put in the programmed thermostat (IN602, Yamato Scientific), keeping at the temperature of $25\ ^\circ\text{C}$. The electrodes were charged by a constant current method (HJ1001SM8, Hokuto denko) at 1 mA in the potential range from 0.0 to 3.0 V. The specific double layer capacitance, C , was defined by the equation, $C=(i\times\Delta t)/(\Delta V\times m)$, where i and m are, respectively, the constant current and total weight of both electrodes, and ΔV was adopted in the potential range from 1.2 to 1.8 V, and the corresponding time is Δt . The specific capacitance can be determined as the average corresponding to the five times examinations of the charge and discharge cycles.

3 Results and discussions

3.1 Characterization of ball milled graphite

As shown in Table 1, we synthesized four samples under various conditions, that is, S-H, Z-H, S-A and Z-A. Afterwards, the above samples were heat-treated at $450\ ^\circ\text{C}$

under a high vacuum condition. The specific surface areas of the samples S-H ($300 \text{ m}^2\text{g}^{-1}$) and Z-H ($530 \text{ m}^2\text{g}^{-1}$) synthesized under hydrogen atmosphere are higher than those for S-A ($170 \text{ m}^2\text{g}^{-1}$) and Z-A ($28 \text{ m}^2\text{g}^{-1}$) prepared under argon atmosphere. This phenomenon indicates that dissociative gas H_2 can terminate the dangling bond of graphene edges which are produced during ball milling and can prevent to agglomerate the nano-crystalline graphite[14]. On the other hand, since argon gas can not be chemisorbed at the graphene edges, the nano-crystalline graphite itself could be agglomerated, leading to much smaller surface area [15, 16].

The amount of impurities was estimated as the residue except for carbon, nitrogen and hydrogen in the host carbon materials analyzed by the OCEA experiment. The results are also listed in the Table 1, indicating that the amount of impurities for the S-H, Z-H, S-A and Z-A are, respectively, 25, 6.6, 0.7 and 41 mass%. Actually, the samples prepared under argon atmosphere were highly stuck on the surface of steel vessels and steel balls except for zirconia balls, leading to much less contamination of the S-A sample than Z-A. In other words, the sticking samples can prevent the iron contamination of samples. On the other hand, the samples prepared under hydrogen atmosphere were scarcely stuck on the surface of balls and vessels because the graphene edge of the samples could be terminated by hydrogen atoms, leading to much more contamination of the S-H sample than Z-H. As a result, we notice that the iron scraps can be easily generated during ball milling under these conditions due to their hardness and the Z-H and Z-A samples are mainly contaminated by, respectively, small amount of iron scraps and large amount of zirconia ones.

Reflecting the difference of the milling balls, the Z-H sample milled by using zirconia balls under hydrogen atmosphere has much larger surface area than S-H milled

by steel balls, while the Z-A surface area is much smaller than S-A, corresponding to a quite small value of about $30 \text{ m}^2\text{g}^{-1}$. Furthermore, before and after the heat treatments, no clear difference was recognized in the surface area as shown in Table 1. These results suggest that scraps from steel balls with a nanometer size contaminate the graphite powder during ball milling and the scraps instead of hydrogen atoms might terminate the dangling bond, suppressing the agglomerations of the nano-structured graphite. In fact, this small value could not be presented by quite high amount of impurity, because the surface area per carbon content was also quite small as shown in Table 1.

Accordingly, it could be deduced that the terminating effect of dissociative hydrogen should be stronger than that of the iron scraps.

Figure 2 shows the XRD profiles of the above eight samples. Those profiles indicate that all the samples reveal a nano-structural feature because the (002) diffraction peak originated in the graphite structure disappears like amorphous. It is to be noted that the contamination of the scraps in the graphite was confirmed to be smaller than several ten nanometer size, where the XRD profile does not show any structural feature like amorphous, indicating that the sizes of the contaminating iron scraps as well as graphite crystallites are of nanometer scale. Furthermore, the effect of the heat treatment does not appear in almost all the XRD profiles as well as specific surface area. However, only in the S-H-450 sample, the crystal growth of cementite (Fe_3C) phase is recognized. This phenomenon is a common characteristics in the hydrogenated nano-structured graphite, in which the nano-crystalline iron crystallizes to form the Fe_3C phase with a large grain size [14, 17].

In Figure 3, the hydrogen TDS spectra for the samples S-H and Z-H are shown and the corresponding hydrogen contents are listed in Table 1. Of course, the samples milled

in argon atmosphere did not show any noticeable desorption spectra. In the sample S-H, two peaks of hydrogen desorption were found around 450 and 700 °C. On the contrary, we notice that a very broad peak of hydrogen desorption reveals in the sample Z-H. The difference between both the phenomena is thought to be originated in the contamination of the iron scraps from steel balls. In other words, the hydrogen absorption ability in carbon materials can be enhanced when the suitable amount (~ 2 at%) of iron contaminate the nano-structured graphite during ball milling [14]. In addition, it is noticed that the hydrogen which is unable to be released by the heat treatment at 450 °C has existed in the ball milled graphite.

3.2 Electrode properties of ball milled graphite as EDLC

In Table 2 are listed the specific capacitances per weight and per surface area of the above eight samples. As reference, the specific capacitances of the activated carbon electrode with a high surface area of $3000 \text{ m}^2\text{g}^{-1}$ are also listed in the Table 2. The charge-discharge behaviors for all trials showed typical EDLC characters on the constant-current examinations. Surprisingly, only the sample S-H possesses much lower capacitance than the others in spite of having its high surface area. However, although the heat treatment at 450 °C did not lead to any increases of the surface area in the sample S-H, the capacitance in this sample is strongly enhanced. In the structural feature described in the section 3.1, a considerable amount of iron contamination was recognized by the OCEA experiment only in the sample S-H, and the sample S-H-450 possessed the cementite phase after heat treatment at 450 °C. Therefore, we can conclude that the iron scraps as contaminations of the nano-structured graphite lead to lower capacity in the EDLC properties.

With respect to the other as-milled samples Z-H, S-A and Z-A, the specific capacitances per surface area are estimated to be about $2 \mu\text{Fcm}^{-2}$, irrespective of milling conditions. Especially, the sample Z-H revealed the highest capacitance per weight among those trial samples, which is a little bit smaller than that in activated carbon with a high surface area of $3000 \text{ m}^2\text{g}^{-1}$. However, it is noteworthy that mechanochemical methods like ball milling are valid for the activation of the carbon based electrode materials, which are performed under some dissociative gases like hydrogen with less-contamination of the iron scraps.

3.3 Milling time dependence of specific capacitance in EDLC

In order to optimize the milling condition for synthesizing the sample Z-H, the graphite powder was mechanically milled under hydrogen atmosphere by zirconia balls with changing the milling time from 2 to 112 hours. Figure 4 shows the XRD profiles of the six samples with different milling times. We can notice that a nano-structural extent from the initial graphite progresses with an increase in the milling time and the longer milling time than 32 h leads to disappearance of the (002) diffraction peak originated in the graphite structure, indicating the complete nano-structural feature by means of XRD measurement.

The time dependences of specific capacitances and specific surface area are shown in Figure 5. In the initial 8 h milling, the specific surface area drastically increases with an increase in the milling time. After that, the surface area is saturated around $500 \text{ m}^2\text{g}^{-1}$. On the other hand, specific capacitance per weight after about the 8 h milling takes a maximum value of 12 Fg^{-1} , and then gradually decreases with the time evolution. Surprisingly, the specific capacitance per surface area after 4 h milling takes a

maximum value of $3 \mu\text{Fcm}^{-2}$ although a graphitic feature remains in this sample as shown in Fig. 4. Therefore, if the graphitic feature is preserved in the carbon materials and the specific surface area can make large about $1500 \text{ m}^2\text{g}^{-1}$, the specific capacitance per weight would be expected to be 45 Fg^{-1} under the current condition.

4. Conclusions

Electrode properties of nano-structural graphite synthesized by the mechanical ball milling under hydrogen atmosphere as EDLCs in the organic electrolyte were investigated. First, the four samples were prepared from the pure graphite by ball milling for 80h under hydrogen or argon atmosphere using steel or zirconia balls. The Z-H (milling using zirconia balls under hydrogen) sample revealed both the highest values of specific surface area and specific capacitance per weight among all the samples prepared in this work. Next, the optimum conditions of the mechanical milling for the Z-H sample were examined. The result indicated that after the milling for 8h, the sample remained a graphitic feature besides possessing a high specific surface area, and specific capacitance per weight could reach up to 12Fg^{-1} . On the other hand, the S-H sample (milled by steel balls under hydrogen atmosphere) possessed several hundreds times smaller capacitance than the other samples in spite of even having high surface area. The reason is due to the contamination of iron scraps. The negative influence of the iron scraps could be taken off by the heat treatment to change the iron scraps into cementite (Fe_3C). Therefore, it is important for designing the carbon material as the EDLC electrode by mechanically milling to optimize the milling conditions like the ball kind, atmospheres, the milling time and the heat treatments.

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Captions

Table 1: Mechanical milling conditions (balls and atmospheres) and characteristics (BET surface area, and hydrogen content and impurity by OCEA method) of the eight different samples. In the column of specific surface area, calculated data of the surface area per carbon content are also shown in the bracket.

Table 2: Capacitance per weight (Fg^{-1}) and per BET surface area (μFcm^{-2}) for the various electrodes used as EDLC. * There are measured at 0.1mA.

Figure 1: Schematic figure of EDLC cell.

Figure 2: XRD profiles of the nano-structured graphite milled for 80h; S-H (with steel balls under hydrogen), Z-H (zirconia, hydrogen), S-A (steel, argon) and Z-A (zirconia, argon) and corresponding samples after heat treatment at 450 °C. In the S-H-450 profile, the trace of graphite (~ 20 deg.) and Fe_3C (~45 deg.) can be found.

Figure 3: TDS profiles of the nano-structured graphite milled for 80h under hydrogen atmosphere of 1 MPa using steel (S-H) and zirconia balls (Z-H) and those after heat treatment at 450 °C.

Figure 4: XRD profiles of the Z-H samples (with zirconia balls under hydrogen

atmosphere) prepared by milling time for 2, 4, 8, 32, 80 and 112h, respectively.

Figure 5: Specific surface area (m^2g^{-1}), specific capacitance per surface area (μFcm^{-2}) and specific capacitance per mass (Fg^{-1}) as a function of milling time of the sample Z-H (milled with zirconia balls under hydrogen).

Table 1: Mechanical milling conditions (balls and atmospheres) and characteristics (BET surface area, and hydrogen content and impurity by OCEA method) of the eight different samples. In the column of specific surface area, calculated data of the surface area par carbon content are also shown in the bracket.

Sample name	Balls	Milling atmosphere	Heat treatment	Specific surface area [m²g⁻¹]	H content [mass%]	Impurity [mass%]
S-H	Steel	Hydrogen	None	300 (400)	4.3	25
S-H-450			450°C	320 (430)	---	---
Z-H	ZrO₂	Hydrogen	None	530 (570)	2.5	6.6
Z-H-450			450°C	520 (560)	---	---
S-A	Steel	Argon	None	170 (170)	---	0.7
S-A-450			450°C	260 (260)	---	
Z-A	ZrO₂	Argon	None	28 (47)	---	41
Z-A-450			450°C	38 (64)	---	

Table 2: Capacitance per weight (Fg^{-1}) and per BET surface area (μFcm^{-2}) for the various electrodes used as EDLC. * There are measured at 0.1mA.

Sample	S-H	S-H	Z-H	Z-H	S-A	S-A	Z-A	Z-A	
name		-450		-450		-450		-450	<i>Maxsorb</i>
Specific									
Capacitance	0.03*	7.6	8.0	6.2	4.3	4.9	0.4	0.3	15
	[Fg^{-1}]								
Specific									
Capacitance	0.01*	2.4	1.5	1.2	2.5	1.9	1.4	0.8	0.5
	[μFcm^{-2}]								

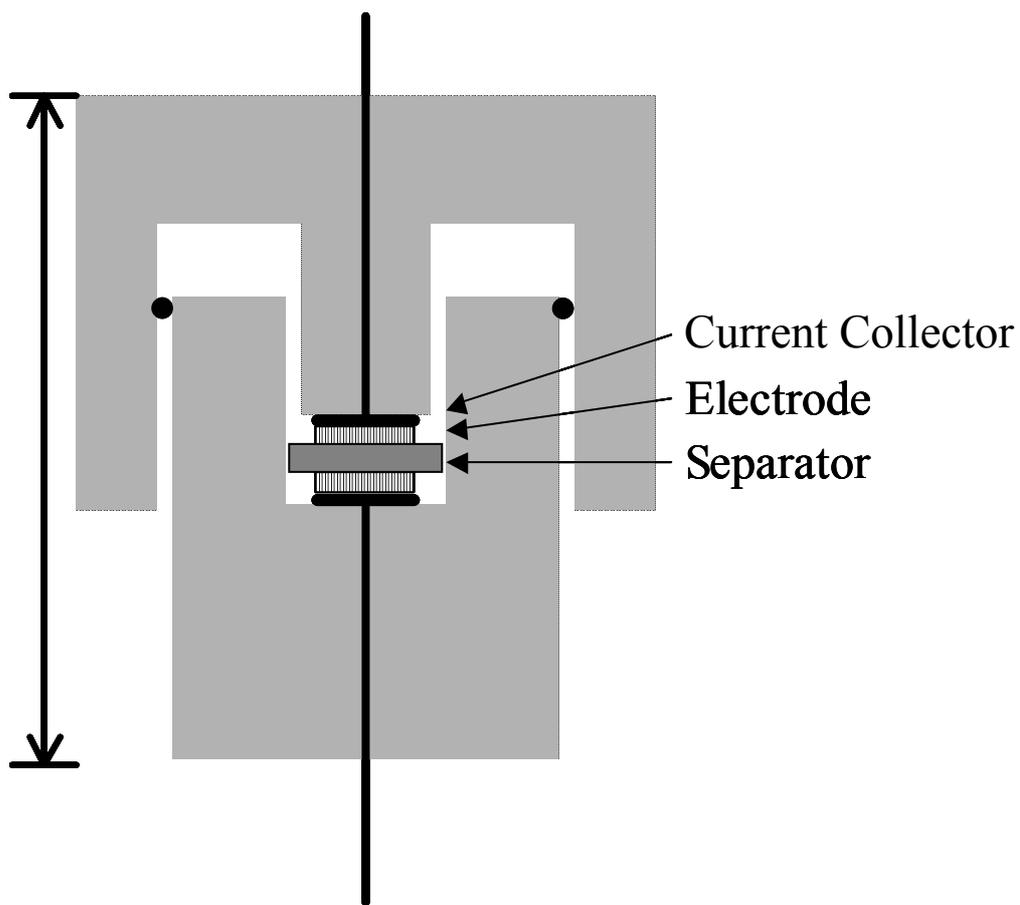


Figure 1: Schematic figure of EDLC cell.

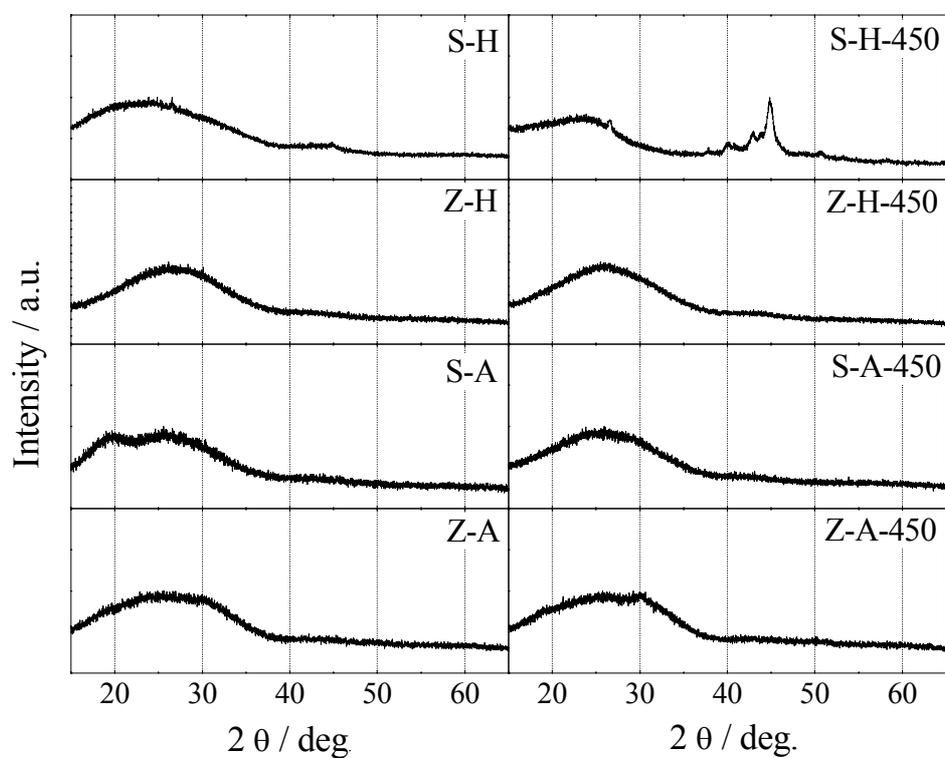


Figure 2: XRD profiles of the nano-structured graphite milled for 80h; S-H (with steel balls under hydrogen), Z-H (zirconia, hydrogen), S-A (steel, argon) and Z-A (zirconia, argon) and corresponding samples after heat treatment at 450 °C. In the S-H-450 profile, the trace of graphite (~ 20 deg.) and Fe_3C (~45 deg.) can be found.

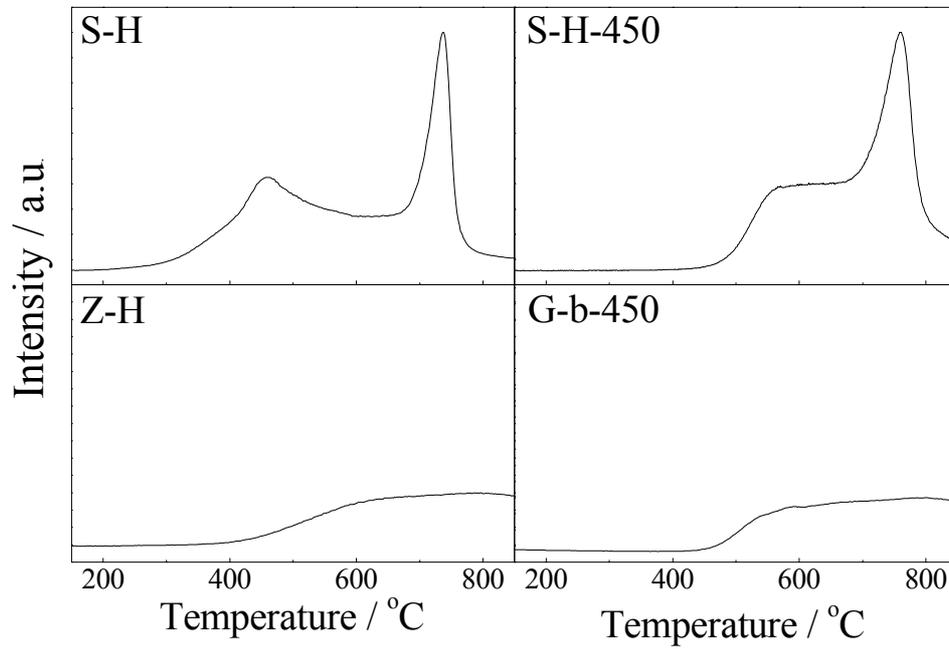


Figure 3: TDS profiles of the nano-structured graphite milled for 80h under hydrogen atmosphere of 1 MPa using steel (S-H) and zirconia balls (Z-H) and those after heat treatment at 450 °C.

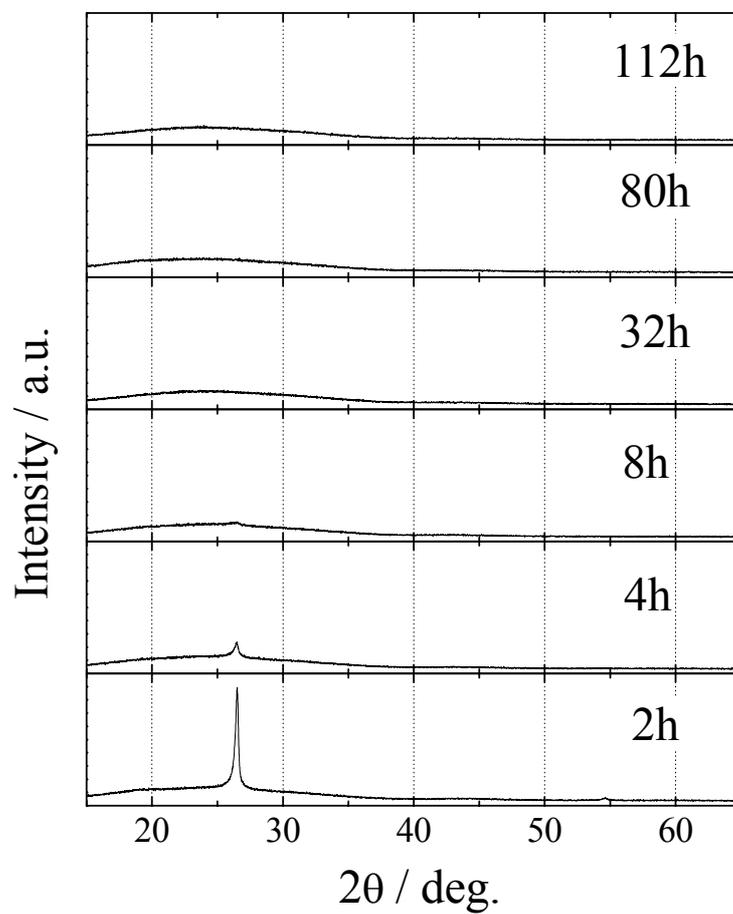


Figure 4: XRD profiles of the Z-H samples (with zirconia balls under hydrogen atmosphere) prepared by milling time for 2, 4, 8, 32, 80 and 112h, respectively.

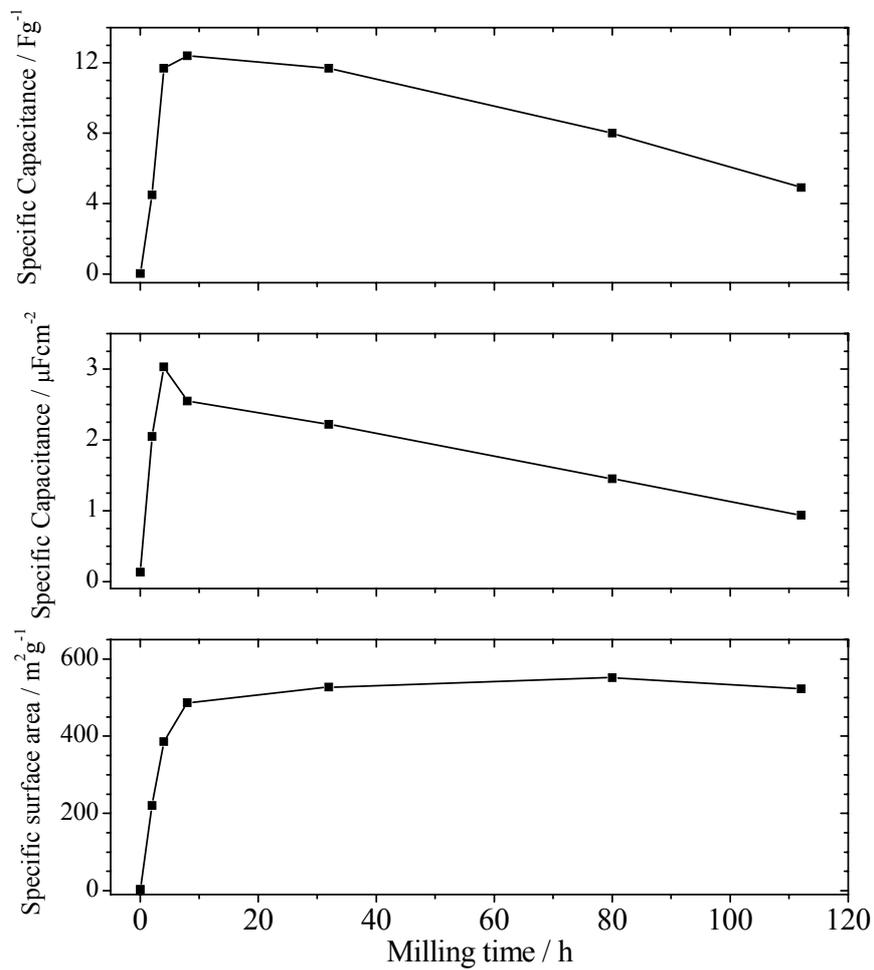


Figure 5: Specific surface area (m^2g^{-1}), specific capacitance per surface area (μFcm^{-2}) and specific capacitance per mass (Fg^{-1}) as a function of milling time of the sample Z-H (milled with zirconia balls under hydrogen).